

QUANTIFICATION OF PARTICLE AGGLOMERATION DURING CHEMICAL
MECHANICAL POLISHING OF METALS AND DIELECTRICS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2010

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To my family and friends

ACKNOWLEDGMENTS

I would like to express sincere gratitude to my advisor Prof. Rajiv K. Singh for his guidance and support throughout my academic pursuit at the University of Florida. His encouragement for improvement in thought process and constant focus on critical thinking made this work more interesting and helped in developing a great thought process. His words have always encouraged me to work harder and enjoy my work. I would like to acknowledge my supervisory committee: Prof. Stephen Pearton, Prof. David Norton, Prof. Timothy Anderson and Prof. Brent Gila.

Special thanks to Thomas (Tom) Gassett for his constant moral support throughout my stay at University of Florida, without which this work would not have been possible. His constant appreciation of my work encouraged me to work harder and strive for excellence and I am grateful to him for everything he did for me. I am also grateful to my parents for their constant support, blessings and giving me complete freedom for pursuing my academic pursuits and personal interests. I am grateful to my sister Hitu who has always motivated me to work harder, stay focused and give my best in whatever I do. I am also grateful to my eldest sister Ritu, brother-in-law Pradeep and my cute nephew Krishang, who always looks up to me, which in turn drove me to do better.

I would like to thank Dr. Purushottam Kumar for his help and numerous intellectually stimulating discussions, academic or otherwise, which helped me extremely in doing this work and am grateful to him for that. A special thanks to Sachin for being a great friend, especially when I needed a friend to discuss all sorts of things here in Gainesville. I have learnt a great deal of things from him and have developed a great thought process from the discussions we had, when it comes to making all kinds

of decisions. I would also like to thank all my friends for all the good times I had in Gainesville and tons of things I learnt from them. I would like to thank all past and present lab mates Dr. Feng-Chi Chang, Dr. Jaeseok Lee, Dr. Karthik Ramani, Dr. Seung – Young, Dr. Sejin Kim, Dr. Taekon Kim and would be doctors Sushant Gupta and Myoung-Hwan for their help and numerous intellectually stimulating discussions, academic or otherwise.

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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AI	Agglomeration index
CMP	Chemical mechanical polishing/planarization
IEP	Iso-electric point
LE	Light extinction
LS	Light scattering
RMS	Root mean square
SEM	Scanning electron microscopy
SPOS	Single particle optical sensor

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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By

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December 2010

Chair: Rajiv K. Singh

Major: Materials Science and Engineering

As we move towards future technologies of 22 nm nodes and beyond, there are stricter requirements on the amount of defects that are allowed during the fabrication process. Chemical mechanical polishing (CMP) forms a critical part of chip manufacturing process and its performance decides the quality of the device been fabricated. For accurate CMP process, material removal rate and surface finish are of utmost importance. These parameters are greatly determined by the slurry characteristics such as particle size, type, shape, mechanical properties and chemistry. The presence of large (agglomerated) particles in CMP slurries has been shown to increase defects during CMP process. The previous work on studying agglomeration behavior in CMP slurries has been qualitative or at best semi-quantitative in nature.

One of the objectives of this work is to study agglomeration behavior of CMP slurries under quantified shear rates. A novel method is developed that uses rheometer as a device to study agglomeration behavior of CMP slurries at different quantified shear rates. The resulting changes in oversize particle distribution of slurries are measured using single particle optical sensing system (SPOS) like Accusizer 780. We measured threshold shear rates, at which each of these slurries starts showing

agglomeration behavior under applied shear rate for any duration up to 2500 s. The threshold value increases from acidic (1000 s^{-1}) to basic (2000 s^{-1}) slurries, as a result of increase in inter-particle repulsive forces between silica particles. De-agglomeration i.e. breaking of oversize particles is observed, when these slurries are subjected to less than threshold shear rates.

Another objective of this work is to characterize the nature of agglomerates that are formed due to shear-induced agglomeration in various CMP slurries. The nature of agglomerates is determined by analyzing oversize particle distribution curves. The agglomerates formed in neutral and acidic pH slurry are relatively harder than the agglomerates formed in basic pH silica slurry. Finally, agglomeration index (AI) is used to calculate stability ratio of CMP slurries with different chemistries. Stability ratio, unlike agglomeration index, is independent of shear rate and is shown to be a better way to define slurry stability.

CHAPTER 1 INTRODUCTION

Chemical Mechanical Planarization

Chemical mechanical planarization (CMP) is the most common planarization technique for both local and global planarization. With the growing miniaturization of electronic devices, there are stricter requirements on the amount of defects that are allowed during the fabrication process. CMP forms a critical part of chip manufacturing process and its performance decides the quality of the device been fabricated. The science of CMP is very different from traditional semiconductor manufacturing technology such as film deposition, ion implantation, lithography, thermal annealing, vapor phase processing [1]. For accurate CMP process, material removal rate and surface finish are of utmost importance. These parameters are greatly determined by the type of slurry used and slurry characteristics, which are largely determined by externally induced forces and slurry chemistry. There are more than 20 input and output variables that need to be optimized to get a desired CMP performance, some of the variables are listed in Table 1-1 [2]. For CMP slurries, the particle characteristics play a big role in determining surface finish and material removal rate. The increase in oversize particle concentration during slurry delivery is one of the major sources of defects during CMP.

Slurry Delivery

The presence of large oversize particles (>0.5 micron) in CMP slurries could be due to slurry blending or slurry distribution system, which uses pumps for slurry delivery. Feng-Chi et al. [4] studied the effect of different pumps like positive displacement, bellows and magnetic levitated centrifugal pump on CMP slurry particle agglomeration

characteristics. They studied the effect of shear induced by these pumps on agglomeration of commonly used CMP slurries. The effect of shear rate on agglomeration becomes severe with changes in slurry chemistry by modifying pH, addition of salt and surfactants. The changes in oversize particle distribution in these slurries were studied using single particle optical sensor (SPOS) system like Accusizer 780.

Outline of Research

Chapter 3 consists of the details regarding the theory of instruments used for characterization of CMP slurries like Accusizer 780, which is a single particle optical sensor (SPOS) system. Rheometer is a device used to study variation in fluid viscosity as a function of shear rate. Zetaplus is a device used to measure zeta potential, the potential that is the closest approximation to the surface potential of particle.

Chapter 4 develops a novel technique to study agglomeration behavior of CMP slurries as a function of quantified shear rate. A method is developed to use rheometer as a device to apply different shear rates to CMP slurry and the change in oversize particle distribution is measured using Accusizer 780. Chapter 5 shows application of novel technique to study agglomeration behavior of CMP slurries with different slurry chemistries under varied shear rates and the change in oversize particle distribution is measured using Accusizer 780.

Chapter 6 focuses on characterizing the nature of agglomerates that are formed when the slurry is subjected to various shear rates. The method developed to determine nature of agglomerates is applied to slurry with different chemistries. The nature of agglomerates is determined by analyzing oversize particle distribution curves. Chapter 7 shows calculation of agglomeration index (AI) for different quantified shear rates using

rheometer and is used to calculate stability ratio of CMP slurry. Stability ratio is measured for slurries with different internal slurry chemistries and calculated at different quantified shear rates. Unlike agglomeration index, stability ratio is independent of shear rate and shown to be a better way to define slurry stability. Chapter 8 gives the conclusions derived from the research work carried out in this dissertation and provides direction for future research.

Table 1-1. Various variables in chemical mechanical polishing (CMP). [2]

Input Variables	Micro-scale Parameters	Nano-scale Interactions
Particle Characteristics	Pad	Chemo-mechanical
Size	Contact angle	Dynamics of surface-layer formation
Size distribution	Pressure on the pad	Thickness
Shape	Particles on the pad	Uniformity
Mechanical properties	Pressure	Rate of formation
Chemistry	Coverage	Layer removal mechanism
Dispersion		
Concentration		
Agglomeration		
Oversize particles		Abrasion frequency
	Chemical concentration and distribution	
Slurry Chemistry		Chemical and mechanical
Oxidizers	Contact mode	Etching
pH stabilizers	Direct	Mechanical removal
Complexing agents	Mixed	
Dispersants	Hydroplaning	
Concentration		
pH and pH drift		
Down pressure and linear velocity		
Pad characteristics		
Mechanical properties		
Topography		
Conditioning		
Substrate characteristics		
Feature size		
Feature density		

CHAPTER 2 LITERATURE REVIEW

Chemical Mechanical Planarization Process

Chemical mechanical planarization (CMP) is a widely used method for planarization of oxide and metal layers in semiconductor industry. CMP has emerged as the fastest-growing operation in the semiconductor manufacturing industry and is expected to show growth in the future. The rapid increase of CMP is due to introduction of copper based interconnects for logic and other devices[5, 6]. The market size of CMP equipment and consumables i.e. slurries, pads is over \$1 billion [7]. CMP is both local and global planarization process where the wafer gets planarized as a result of relative motion between a wafer and a polishing pad in the presence of slurry while applying pressure. It has become the most widely used method for polishing a wafer to a required thickness and planarity. One of the unique aspects of CMP is its ability to polish both metal and dielectric layers in multilevel metallization interconnect structures when a well designed slurry and pad is used.

The following is the mechanism of CMP that explains process of planarization on a wafer surface: [8]

- i. Initially chemical reaction by the slurry forms a soft chemically modified surface layer that can be removed easily
- ii. This soft chemically modified layer is mechanically removed by slurry's abrasive component (generally silica, alumina or ceria particle depending on the substrate to be polished), applied pressure and relative velocity of polishing.

Preston equation (3-1) that gives rate of removal of material is given as: [9-11]

$$R = kPV \quad [2-1]$$

where R = rate of removal

k = constant for given tool and process conditions, including parameters such as oxide hardness, polishing slurry and polishing pad

P = applied pressure

V = relative velocity between the wafer and polishing pad

Smoluchowski Theory for Aggregation of Particles

It is clear that agglomeration of abrasive particles in slurry due to shear stresses induced by pumps is a critical issue in CMP process today especially with stricter requirements on defectivity during CMP. A detailed understanding of agglomeration process due to pumps is the need of the day, which would help in predicting slurry behavior and hence its stability.

Smoluchowski theory [12-14] gives a detail account of aggregation in colloidal suspension due to shear forces. Particle transport brought by fluid motion gives a tremendous increase in the rate of interparticle collisions and aggregation brought about in this way is known as orthokinetic aggregation. The fundamental assumption is that the particle collisions are binary and proportional to the particle concentration. The rate of change of k-fold aggregates where $k = i + j$ is given by

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k}^{l=k-1} k_{ij} N_i N_j - N_k \sum_{k=1}^{\infty} k_{ki} N_i \quad [2-2]$$

where k_{ij} represents second order rate constant for aggregation in absence of any electrostatic interactions. The first term on right hand side of equation represents rate of formation of k-fold aggregates and second term represents loss of k-fold aggregates by collision or aggregation with other aggregates.

Assuming that colloidal particles are subjected to uniform laminar shear, k_{ij} is given as:

$$k_{ij} = 4/3 G (a_i + a_j)^3 \quad [2-3]$$

where G is shear rate and a_i, a_j are particle sizes

The rate of aggregation will be significantly influenced by the electrostatic interactions between particles in the aqueous system. Electrostatic interactions provide a potential barrier, which hinders the particle agglomeration process. The aggregation rate then becomes

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k}^{l=k-1} (k_{ij} / W_{ij}) N_i N_j - N_k \sum_{k=1}^{\infty} (k_{ki} / W_{ki}) N_i \quad [2-4]$$

where 'W' is the stability ratio

The term stability ratio is defined as the ratio of rapid aggregation rate in absence of any electrostatic interactions to the slow aggregation rate in presence of electrostatic interactions. High stability ratio implies more stable colloidal dispersion, which in our case is CMP slurry.

Slurry Stability

In CMP, unstable slurry can lead to significant defects during wafer polishing. The important issues related to slurry performance in CMP are material removal rate, global planarity, surface topography (dishing and erosion), surface defectivity (including roughness, scratches, dents and delamination), and particle contamination. It is critical to understand the mechanism active during CMP for optimally designing slurry formulations. The most important fundamental parameters that need to be optimized for achieving acceptable characteristics in CMP slurry are listed in Table 2-1 [8, 15-21]. These parameters in turn are obtained after extensive measurements that are detailed elsewhere [8, 15-21]. Highly stable CMP slurry is critical to reduce process dependent

defectivity like scratches and particle residue. The slurry handling process should not lead to formation of large particle agglomerates. Commonly used methods for achieving slurry stability are:

- i. Electrostatic interaction between particles
- ii. Polymer stabilization

Electrostatic Stability

When two same charged particles come close to each other in an aqueous system, there is an interaction between diffuse layers that surrounds these particle surfaces. The osmotic pressure causes these particles to move away due to its higher counter ion concentrations (Figure 2-1) [22, 23]. Thickness of these diffuse layers is given by Debye length $1/\kappa$

$$1/k = \sqrt{\frac{\epsilon_r \epsilon_0 RT}{4\pi F^2 \sum_{i=1}^n C_i Z_i^2}} \quad [2-5]$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of vacuum, R is the gas constant, T is temperature, F is Faraday's constant, C_i is the molar concentration of any ion 'i' in solution phase and Z_i is the valence of ion in solution phase. For the case of spherical particles each of size 'a' having Debye length i.e. diffuse layer thickness much greater than particle size i.e. $ka \ll 1$, repulsive potential when these two particles approach close to each other is given by

$$V_R = \frac{\epsilon_r a^2 \psi_0^2}{R} e^{-kH} \quad [2-6]$$

where Ψ_0 is the surface potential, H is the nearest distance between particle surfaces and k is Boltzmann's constant. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the total potential (V_{total}) in colloidal systems is given as

$$V_{total} = V_A + V_R \quad [2-7]$$

where V_A is Van Der Waals potential due to attraction and V_R is repulsive double layer potential. The stability of colloidal particles is determined by the balance between V_A and V_R .

For similar particles of radius 'a' having centers separated by distance 'H', Van Der Waals attraction potential V_A is given as

$$V_A = \frac{-Aa}{12H} \quad [2-8]$$

where H is the nearest distance between particle surfaces and A is Hamaker constant. From this equation it is evident that as particle size increases, attraction force between particles increases. For achieving same degree of colloidal stability as smaller size particles, a thicker stabilizing layer will be required that will give stronger repulsive forces between particles and thereby hindering agglomeration of particles.

Stabilization Using Polymers

Stabilization of colloidal dispersion in aqueous systems could be achieved by addition of surfactants i.e. ionic or non-ionic polymers. The length of polymer chains that are adsorbed on particle surfaces decides the extent of repulsive forces. Work by Basim et al. [24] showed that when cationic surfactant like trimethyl ammonium bromide (C_n TAB) was added to silica slurries, the slurry gets stabilized as a result of additional repulsive forces. When concentration of C_n TAB exceeds critical micelle concentration (CMC), it results in formation of micelles which thereby gets adsorbed on silica

surfaces. These adsorbed micelles gives rise to repulsive forces when particles interact and thereby preventing coagulation of particles. These kind of repulsion between silica particles were observed for surfactants with carbon chains of C_n TAB larger than 8 i.e. $n > 8$.

However, surfactants also provide lubricating effect as observed in case of C_n TAB, which results in lower material removal rate. Thus, stabilization of silica slurry by higher repulsion in this case was observed at the cost of low material removal rate. Steric stabilization is another type of polymer stabilization method for colloidal dispersions in aqueous systems [22, 25]. The most effective steric stabilizers are polymers that have some affinity for the surface and get adsorb in such a way, that segments of polymer chains extend into dispersion medium.

When these particles with adsorbed polymers on their surface, approach each other the adsorbed layers come into contact and on further approach there is interpenetration of hydrophilic chains (Figure 2-2 - 2-3) [12]. These chains being hydrated, on overlapping undergo dehydration which increases free energy resulting in repulsion between particles [12]. The work by Napper et. al. [26] shows that polymer stabilization occurs due to disfavored thermodynamics governed by following equation

$$\Delta G_F = \Delta H_F - T\Delta S_F \quad [2-9]$$

where ΔG_F is the change in free energy of two approaching polymer particles, ΔH_F and ΔS_F are changes in enthalpy and entropy, T is the temperature, subscript F represents flocculation. From thermodynamics, it is known that there should be decrease in free energy ΔG_F for flocculation to occur. Varying the right hand side of above equation in

such a way that ΔG_F never decreases; we can achieve conditions where it is difficult for flocculation to occur. This could be achieved in three different ways:

- i. Enthalpic stabilization: Having positive changes of the enthalpy and entropy in such a way that ΔH_F is larger than ΔS_F and flocculation is disfavored. However, increasing the temperature can cause flocculation to occur.
- ii. Entropic stabilization: Having negative changes of the enthalpy and entropy in such a way that ΔH_F is smaller than ΔS_F and flocculation is disfavored. However, lowering the temperature can cause flocculation to occur.
- iii. Enthalpic - Entropic stabilization: Having positive change of the enthalpy and negative change of entropy so that free energy increases and flocculation is disfavored. Flocculation cannot be achieved in this case even by changing the temperature.

For the adsorbed layer it could be fair to assume that these layers have lower Hamaker constant resulting in smaller Van Der Waals attraction. So the work of adsorbed polymeric layers is to limit the attraction between the particles by keeping them finite distance apart, in the range where V_A is smaller. So, even if particles come into contact with each other, the aggregates formed are weak and can be easily broken by low amount of shear. Thickness of the adsorbed polymer layer relative to the particle size is the critical factor that decides the degree of steric stabilization. Since attraction potential energy V_A is proportional to particle size, larger particles will require thicker stabilizing layers to confer the same degree of stability.

Combination of ionic and non-ionic surfactants is also employed to achieve steric stabilization. In the work by Palla et al.[27] anionic and non-ionic surfactants were used to stabilize alumina particles. The anionic surfactant gets adsorbed on positively charged alumina particles and non-ionic surfactant penetrates into anionic surfactant layers owing to hydrocarbon chain interactions. The surfactant adsorption has three important steps:

- i. Driving force of the adsorption of ionic surfactants depends on length and concentration of hydrocarbon chains.
- ii. Hydrocarbon chains then interact with anionic and nonionic surfactants.
- iii. Extent of polymer-solvent interaction should be greater than polymer-polymer interaction to help prevent coiled polymers and resulting in steric stabilization when non-ionic surfactants are adsorbed onto particle surfaces.

Agglomeration of Particles in Chemical Mechanical Polishing (CMP) Slurries

CMP slurry stability plays a critical part while deciding performance of CMP process.

During slurry storage or delivery, agglomeration of particles can take place forming larger size particles, which results in defectivity during CMP. CMP slurry consists of abrasive particles, chemicals like oxidizers, buffering agents, dispersants, complexing agents and a synergistic combination of all these is required to form stable CMP slurry.

The agglomeration of CMP slurry could result as a consequence of changes in abrasive particles, slurry chemicals, pH and the external forces like shear induced by pumps employed for slurry delivery. There are two ways in which agglomeration of particles in CMP slurry could take place:

- i. Changes in slurry chemistry due to changes interparticle interactions due to addition of salts and surfactants
- ii. External forces acting on CMP slurry during slurry handling

Defectivity Due to Change in Particle Size

In CMP process, the oxides and other chemicals soften the top surface and the abrasive particles provide the mechanical force for removal of these soft layers. Cook et al. [11] proposed indentation model for polishing of glass. According to the model, material removal or indentation depth is directly proportional to particle size, down pressure and inversely to material properties like elastic modulus and hardness. The following equation gives indentation depth R_s as

$$R_s = \frac{3}{4} \phi \left(\frac{P}{2KE} \right)^{2/3} \quad [2-10]$$

where a is particle size, P down pressure, K surface particle fill factor and E is young's modulus. So, as particle size increases, it will lead to formation of large ' R_s ' and thereby causing increase in defectivity in fragile materials, especially low-k substrates. The work by Mahajan and Basim et al. [19] confirm this fact and they observed that the particles greater than 0.5 μm resulted in surface defectivity. There is a shift in CMP mechanism from contact based to indentation based as particle size increases, which results in defectivity and hence deteriorates the CMP polish performances and material removal rate.

Generally, during copper (low-k) CMP there are four different types of particle-induced defectivity like killer scratch, triangle scratch, shallow scratch and embedded particle [28]. The killer scratch effects copper interconnects by either damaging or cutting them, whereas the triangle scratch results in electrical short-circuit by forming metal residual on a subsequent metal layer and scratches could be as deep as 2000 \AA . Shallow trenches and embedded particles influence the dielectric reliability.

As we move to 22, 32 and 45 nm node, low-k material are commonly used in the interlayer dielectrics. These low-k materials show decreasing modulus and hardness as dielectric constant is reduced. Thus, device integration during CMP of copper/low-k dielectric could be challenging, as these materials with poor mechanical properties can easily form surface defects. The tolerance for defects and particle densities on wafer is continuously reduced to ensure device reliability. International Technology Roadmap for Semiconductors (ITRS) has forecasted requirement of reduction of these surface

defects for near term technology nodes, given in Table 2-2 [29]. Thus, it is critical to have robust CMP slurries to reduced defectivity during CMP of metals and dielectrics.

Effect of Stress Induced Particle Agglomeration on Defectivity

In the semiconductor industry, CMP process involves use of pumps for slurry blending and slurry delivery. The work by Feng-Chi et al. [4] demonstrated that type of pump used, has a significant influence on oversize particle (>0.5 micron) distribution of CMP slurry. Different pumps produce different kinds of stress levels and this was shown to be the reason for difference in oversize distribution of slurries pumped using various pumps. In the absence of shear, the particles in the slurry are prevented from undergoing agglomeration by electrostatic interactions that generate repulsive forces between these particles. However, the shear flow causes particle to approach each other and when they are close enough the attractive Van Der Waals force exceeds the inter-particle repulsive force and the particle undergoes agglomeration. With increase in shear rate, more particles are able to come closer to each other and that results in increased particle agglomeration (Figure 2-2, 2-3) [12]. The effect of different pumps on the cumulative concentration of oversize particles, where cumulative concentration is the sum of the number of particles in 0.5 - 10 μm , is shown in Figure 2-4, 2-5 [30]. They also showed that the degree of agglomeration and roughness/defect density are positively correlated as shown in Figure 2-6 [30]. Further, they observed that for low-k wafers, polishing effects were more severe when these circulated slurries were used. As compared to BD1 wafers, ultra low-k wafers exhibit poor mechanical properties (elastic modulus and hardness). Among the different pumps that were used, magnetically levitated (maglev) centrifugal pump caused less shear induced defectivity

(e.g. scratches and embedded particles) during CMP of low-k dielectrics. Maglev pump was qualitatively analyzed to be a low shear device.

Effect of Ionic Strength in Pump-Induced Agglomeration in Slurries

Chemical Mechanical Polishing (CMP) slurry is an important consumable in semiconductor industry. The highly stable CMP slurry is critical for CMP performance and minimizes process dependent defectivity. Stable suspensions in CMP slurry are obtained as a result of repulsive forces between these particles. These repulsive forces result from overlapping of similar surface charges by dissociation of the metal oxide groups (M^+OH^-). Feng-Chi et al. [30] demonstrated that if salts are added to these slurries, the repulsive forces get diminished between abrasive particles, which results in agglomeration of particles. The introduction of salt increases the polishing rate due to screening the surface charge between abrasive particles and substrate, which leads to increase in friction force during polishing. Basim et al. [31] studied effect of salt addition on silica slurry and considered the agglomerates that were formed to be soft but still lead to poor surface quality after CMP. The cumulative concentration and normalized mean value of large size agglomerate concentration was observed to increase by a significant amount. When the slurries with salt were circulated using these pumps, the effect of shear rate on degree of agglomeration was more severe in case of slurry with salt then the one without it.

The inter-particle and zeta potential measurements confirmed that the repulsive forces in case of salt added slurry was relatively less than the slurry with no salt (Figure 2-7 - 2-11) [30]. This explains the fact that for the same pump, degree of agglomeration will be more in case of slurry with salt then the slurry without salt, as due to screening, repulsive forces are reduced and so same amount of shear rate causes more particle to

approach close enough and then Van Der Waals attraction overcomes repulsive forces and agglomeration takes place.

Effect of Surfactants in Slurry on Stress Induced Agglomeration

Electrostatic stabilization is one of the methods to achieve stability in colloidal suspensions. Polymer stabilization is another method used to achieve stable colloidal suspension by employing surfactants either ionic or non-ionic. Feng-Chi et al. [30] studied the effect of surfactant addition to unformulated ceria and silica slurry. For silica slurry, both cationic (CTAB) and anionic surfactants (SDS) at pH 9 were used. The cationic surfactant neutralizes the negatively charged silica surface causing screening effect that reduces the magnitude of repulsive forces between silica particles. As a result, agglomeration was seen during slurry formulation and handling process. The shear rate had a profound effect on agglomeration and degree of agglomeration was severe in this case as compared to silica slurry without any cationic surfactant. Whereas, when anionic surfactants (SDS) was added to silica slurry, stronger electrostatic interaction between silica particles was observed which reduced the degree of agglomeration due to shear stress during slurry handling. The shear induced particle agglomeration is determined from the normalized tail distribution of oversize particles and the curves for cationic, anionic and as-received silica slurry are as shown in Figure 2-12 [30]. The variation in magnitude of surface charges due to surfactants in silica slurry was confirmed by zeta potential measurements as shown in Figure 2-13 [30].

Effect of addition of surfactants on stability of ceria slurry was also studied using cationic surfactant like tetramethyl ammonium bromide, dicyclotrimethyl ammonium bromide ($C_{10}TAB$), anionic surfactants like sodium dodecyl sulfate and polymer

dispersant like polyacrylic acid separately. For ceria slurry, addition of ionic surfactant shifts the isoelectric point (IEP) of ceria to more acidic pH as a result of more negative charges adsorbed on surface. On other hand, addition of anionic surfactant to ceria shifts IEP to more alkaline pH due to the positive charges of hydrophilic heads. These effects were confirmed by zeta potential measurements given in Figure 2-14-2-16 [30]. The effect of shear during slurry handling on particle agglomeration in ceria slurries was significantly reduced in formulated ceria slurries as adsorption of cationic surfactant provides increased repulsive forces between ceria particles as compared to unformulated one. Thus, addition of cationic surfactant to ceria slurry could increase its stability and in contrast could deteriorate the stability of silica slurries resulting in formation of more agglomerates due to shear during slurry handling for the latter and less agglomerates for the former slurry. CMP performance deteriorated when unformulated ceria and silica slurries containing cationic surfactants were used, as evident from increased roughness values (Figure 2-17) [30] whereas for CMP process performed using unformulated silica and formulated ceria slurry, there was significant decrease in roughness values after CMP.

Agglomeration Index for Quantifying Stability of Slurries

As we move beyond 45 nm to 32 and 22 nm nodes, it is critical to have controllability over agglomeration of abrasive particles to minimize defectivity during chemical mechanical polishing (CMP). A method for quantifying slurry stability is needed to prevent particle-induced defectivity. For slurry stability analysis, inter-particle force and/or zeta potential measurements are done. However, these measurements do not fully describe agglomeration process in CMP as a function of different surfactants or other chemicals / additives. Besides, various light scattering techniques that measure

particle size distribution are insufficient for determining the degree of agglomeration in CMP slurries as they are unable to detect changes in slurry characteristics.

Feng-Chi et al. [32] developed a novel method for determining the degree of agglomeration in CMP slurry due to shear induced during slurry handling. They introduced the term agglomeration index (AI), defined as a logarithm of the ratio of external shear rate (G) to the stability ratio (W) i.e. $\log(G/W)$. A slurry with lower AI at a given shear rate will be a more stable colloidal suspension, as lower AI implies higher stability ratio 'W'. Now, 'W' is defined as the ratio of rapid coagulation rate to slow coagulation rate where slow coagulation rate is the rate of growth of aggregates in the presence of electrostatic interactions. Higher 'W' value means lower value of slow coagulation rate and hence more stable slurry due to stronger electrostatic interactions.

Determination of Agglomeration Index (AI)

Feng-Chi et al. [30] determined AI of CMP slurries in three steps:

- i. Subject CMP slurries to high shear pumping device like positive displacement pumps
- ii. Measure oversize particle tail distribution using SPOS Accusizer 780 system
- iii. Model changes in tail distribution using Smoluchowski's theory; Figure 2-18 – 2-20 [30] shows how AI is determined for CMP slurries.

They calculated AI of various types of slurries with different surfactants, particle sizes, different kinds of abrasive particles, salts and pH values using positive displacement pumps and are detailed in Table 2-3 [30].

According to Smoluchowski slow coagulation theory [12, 14], the total change in the rate of agglomerate concentrations such as singlet (dN_1/dt), doublets (dN_2/dt), triplets (dN_3/dt) and so on is expressed as

$$\frac{dN_1}{dt} = -(k_{11} / W_{11})N_1^2 - (k_{12} / W_{12})N_1N_2 - (k_{13} / W_{13})N_1N_3 \quad [2-10]$$

$$\frac{dN_2}{dt} = (k_{11} / W_{11})N_1^2 / 2 - (k_{12} / W_{12})N_1N_2 - (k_{23} / W_{23})N_2N_3 \quad [2-11]$$

$$\frac{dN_3}{dt} = (k_{12} / W_{12})N_1N_2 - (k_{13} / W_{13})N_1N_3 - (k_{23} / W_{23})N_2N_3 \quad [2-12]$$

Where aggregation constant ' k_{ij} ' is given as

$$k_{ij} = 4/3 G (a_i + a_j)^3$$

Individual agglomerate concentration can be derived by integrating above equations and is given as

$$N_k = \frac{N_0 (t / \tau)^{k-1}}{(1 + t / \tau)^{k+1}} \quad [2-13]$$

$$\tau = \frac{W_{ij}}{k_{ij} N_0} \quad [2-14]$$

where ' N_0 ' is total initial particle concentration, ' t ' is aggregation time and ' W ' is stability ratio.

To understand the relation between AI and CMP performance, low-k copper wafers were polished using slurries with different AI values. After detail analysis it was found that slurries with AI value greater than 1.8 would form large number of agglomerate particles during slurry handling thereby causing defectivity [32]. Thus, AI was used to predict degree of agglomeration in various CMP slurries and lower AI values (< 1.8) were recommended for slurries, in order to achieve surface with minimum defectivity during CMP. It is important to note that these AI values were determined using positive displacement pump and AI will decrease if a low shear rate pump like

magnetic levitated centrifugal pump is used for determining AI, as it is directly proportional to logarithmic value of shear rate 'G'.

Table 2-1. Important principles for designing CMP slurries [8, 15-21]

Global Planarization:
 Formation of a thin surface layer which is passivated
 Reduction of chemical etching
 Reduction of mechanical polishing

Removal (Polishing Rate):
 Rapid formation of a thin surface layer
 Control over mechanical/interfacial properties of thin surface layer
 Stress induction by abrasive to remove the surface layer
 Indentation-based wear
 Fracture/delamination-based removal

Slurry Handling:
 Formulation of stable slurries
 Control of inter-particle and particle-surface interactions
 Steric-force based repulsion in ionic systems

Surface Defectivity:
 Rapid formation of a thin surface layer
 Reduction of mechanical polishing
 Control of particle size distribution
 Control of particle size and hardness

Selectivity:
 Top-layer chemo-mechanical polishing
 Bottom-layer mechanical polishing
 Minimization of mechanical component in slurry

Table 2-2. Interconnect surface requirements at near term technology nodes [29]

Technology node	59	45	36	28
Number of metal levels	12	12	12	13
Average dielectric constant	2.7-3.1	2.4-2.8	2.2-2.6	2.2-2.6
Dishing planarity (nm)	20	16	14	11
Minimum defect particle size (nm)	28.5	22.5	17.5	14

Table 2-3. Agglomeration index of various chemical mechanical polishing (CMP) slurries. Table adapted from reference [30]

Type of Slurry	Particle Size (nm)	Agglomeration Index (AI)
Silica: pH 11	30	1.36
Silica: pH 11 + salt	30	1.96
Silica: pH 7	30	3.92
Silica: pH 7 + salt	30	4.26
Silica: pH 2	30	4.36
Silica: pH 2 + salt	30	4.96
Silica: pH 9	80	1.76
Silica: pH 9 + anionic	80	0.66
Silica: pH 3	80	2.46
Silica: pH 10	150	4.48
Ceria: pH 5 + cationic 1	70	2.36
Ceria: pH 5 + cationic 2	70	1.96

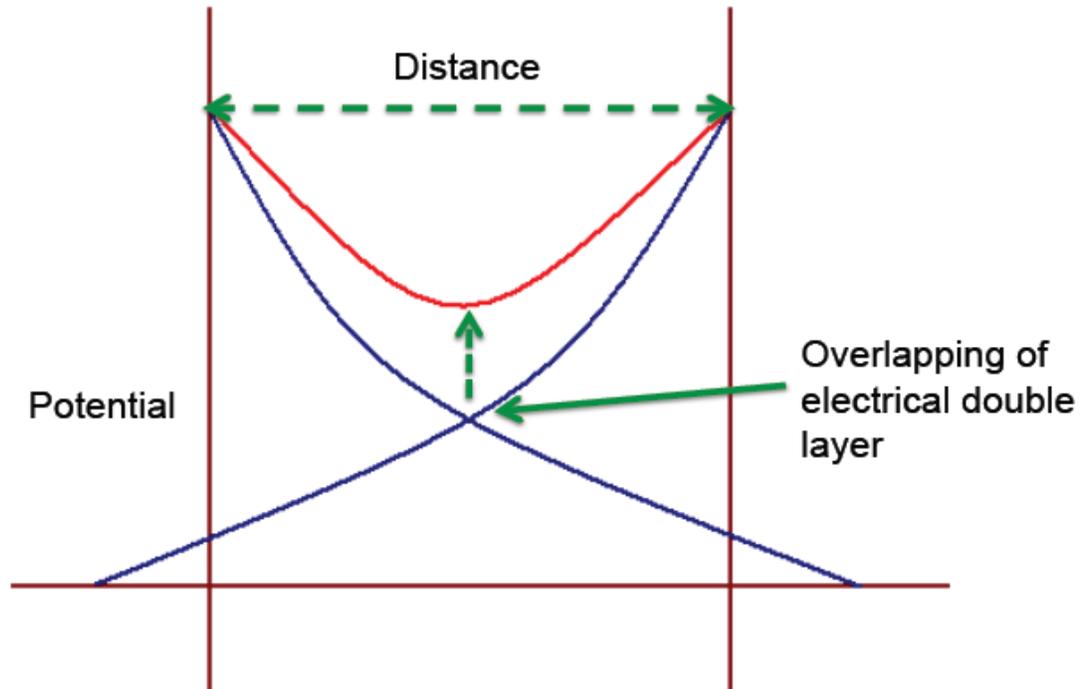


Figure 2-1. Interaction of electrical double layer [22, 23]

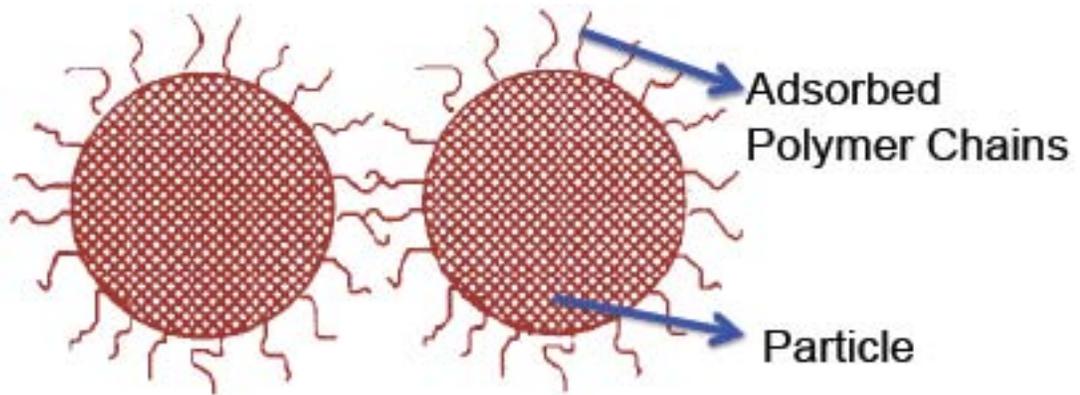


Figure 2-2. Steric stabilization provided by terminally adsorbed polymer chains [12]

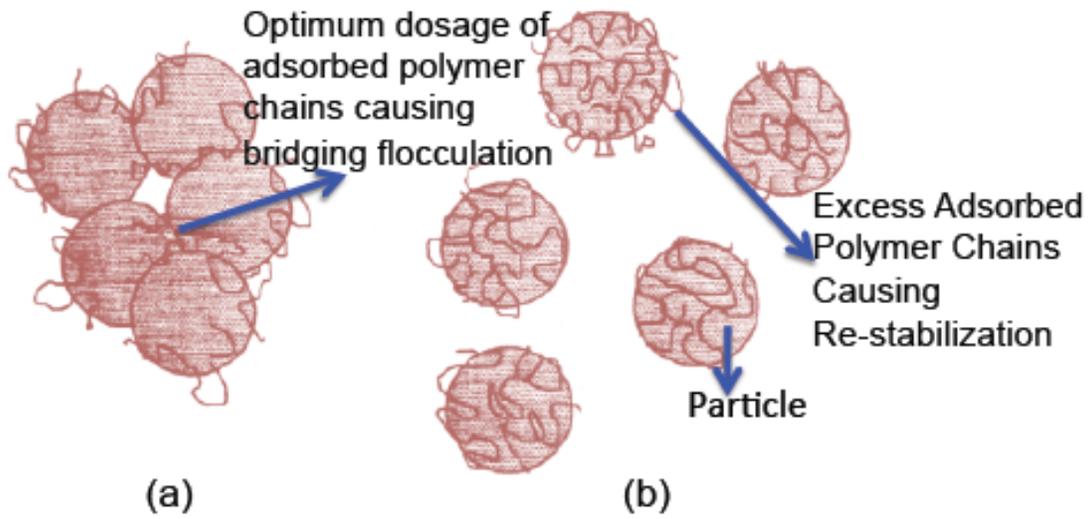


Figure 2-3. Schematic showing (a) bridging flocculation and (b) re-stabilization by adsorbed polymer chains [12]

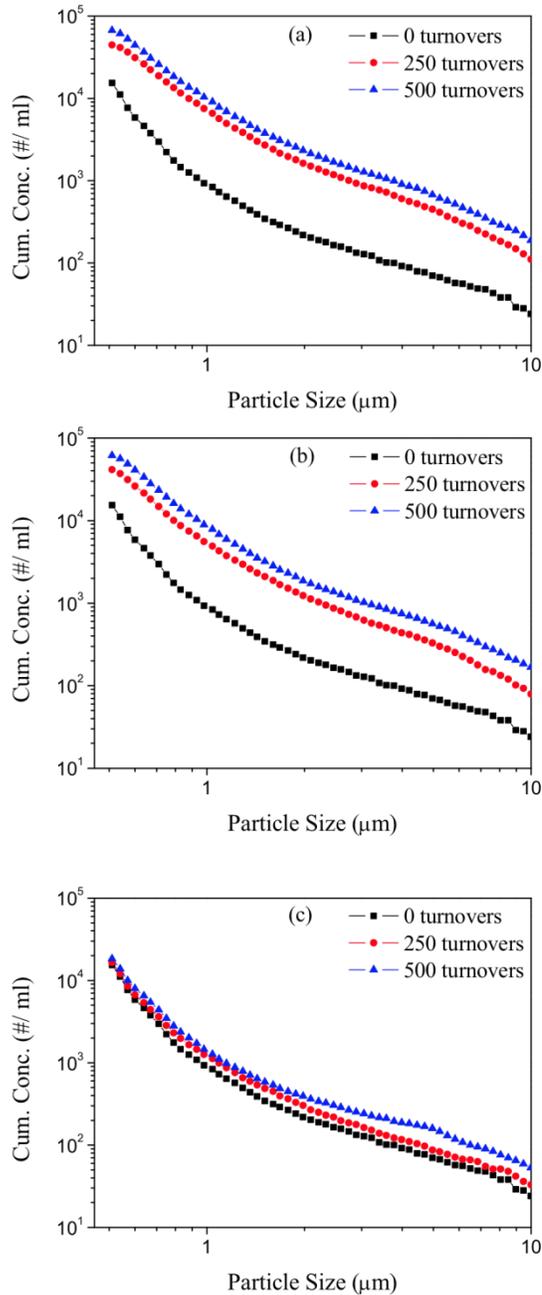


Figure 2-4. Cumulative concentration vs. particle size for various turnovers for (a) bellows, (b) diaphragm and (c) magnetically levitated (maglev) centrifugal pump. (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

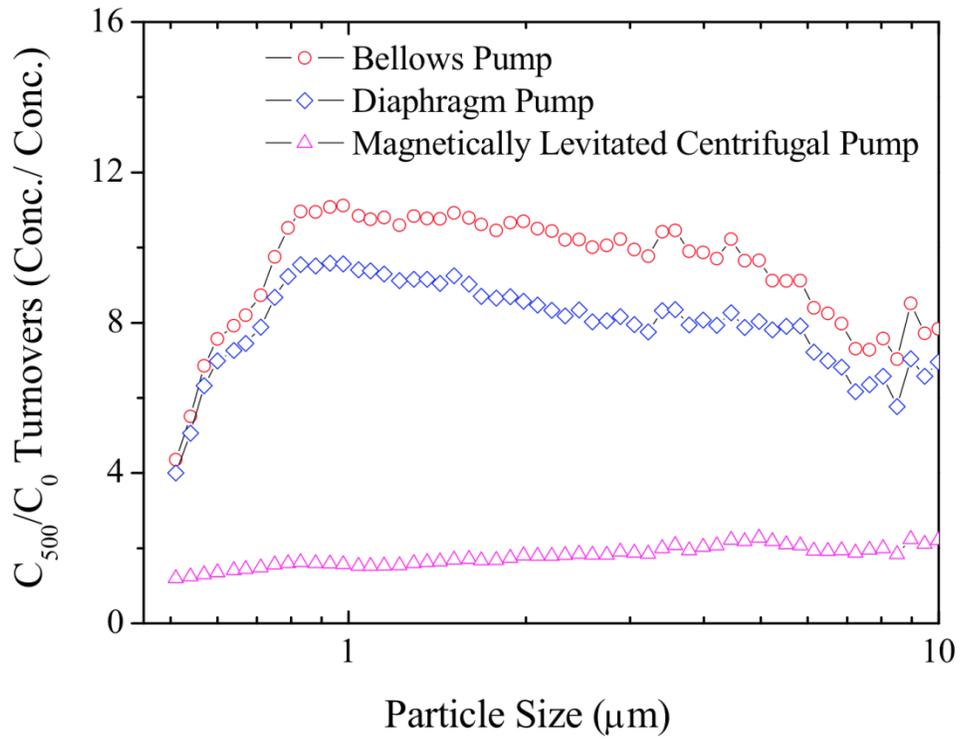


Figure 2-5. Normalized oversize particle distribution for bellows, diaphragm and magnetically levitated centrifugal pumps (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

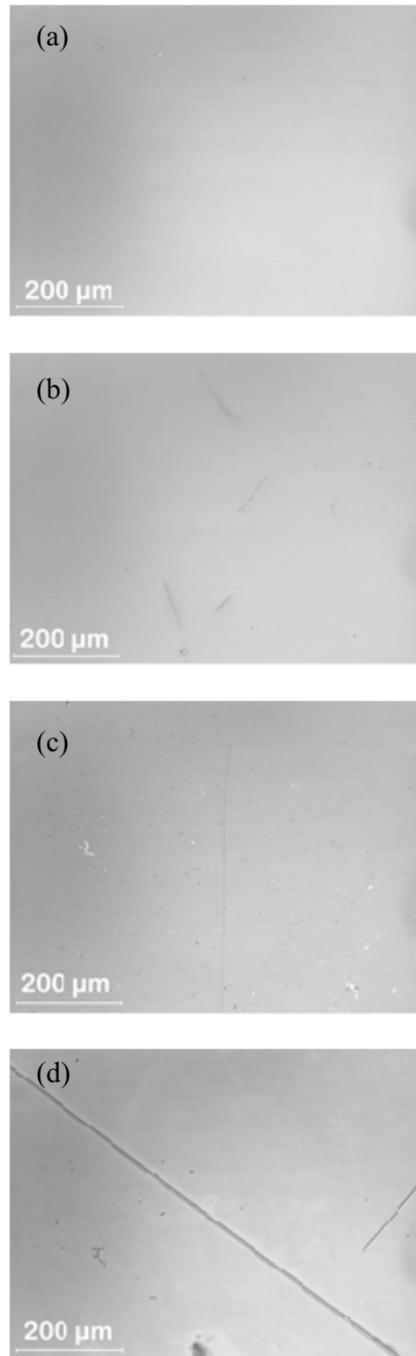


Figure 2-6. Optical images of: (a) BD1 and (c) ultra low-k wafers polished by maglev pump circulated slurries, and (b) BD1 and (d) ultra low k wafers polished by positive displacement pump circulated slurries (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

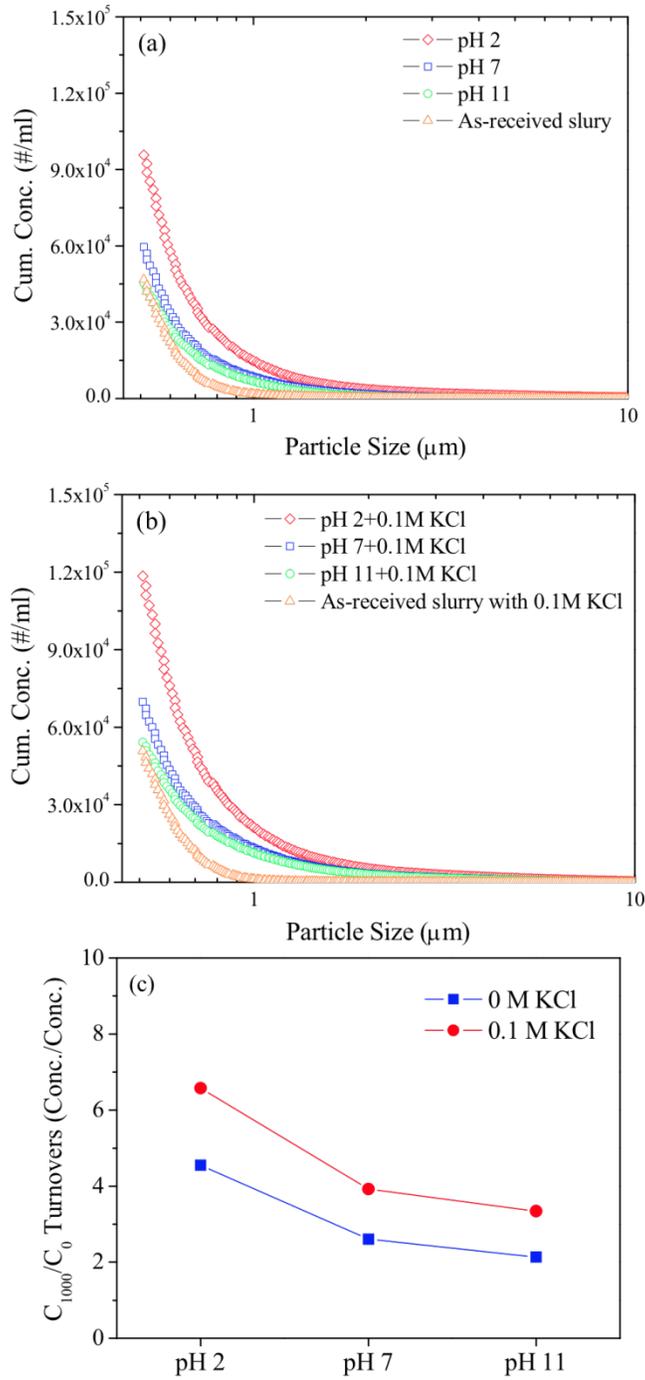


Figure 2-7. Circulated silica slurries for 1000 turnovers at pH 2, 7 and 11: (a) cumulative concentration without salt, (b) cumulative concentration with 0.1M KCl, and (c) mean value of normalized oversize particles in 0.50 to 1 μm (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

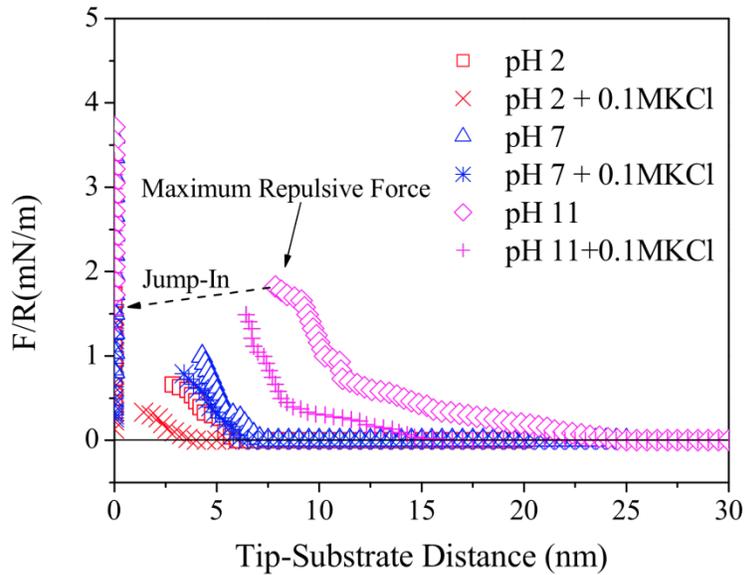


Figure 2-8. Force vs. tip-substrate distance between a silica substrate and silica probe in supernatant slurries at pH 2, 7, and 11, with and without 0.1M KCl (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

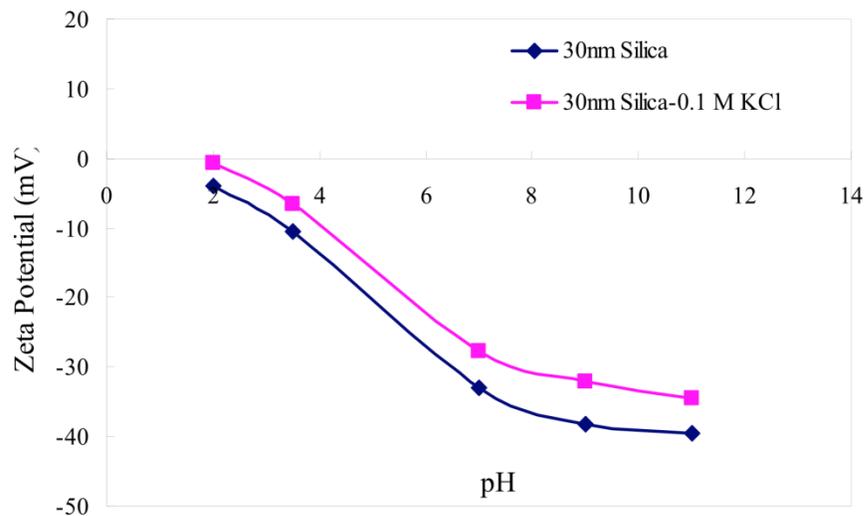


Figure 2-9. Zeta potential of 30 nm silica slurries for different pH, with and without 0.1M KCl (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

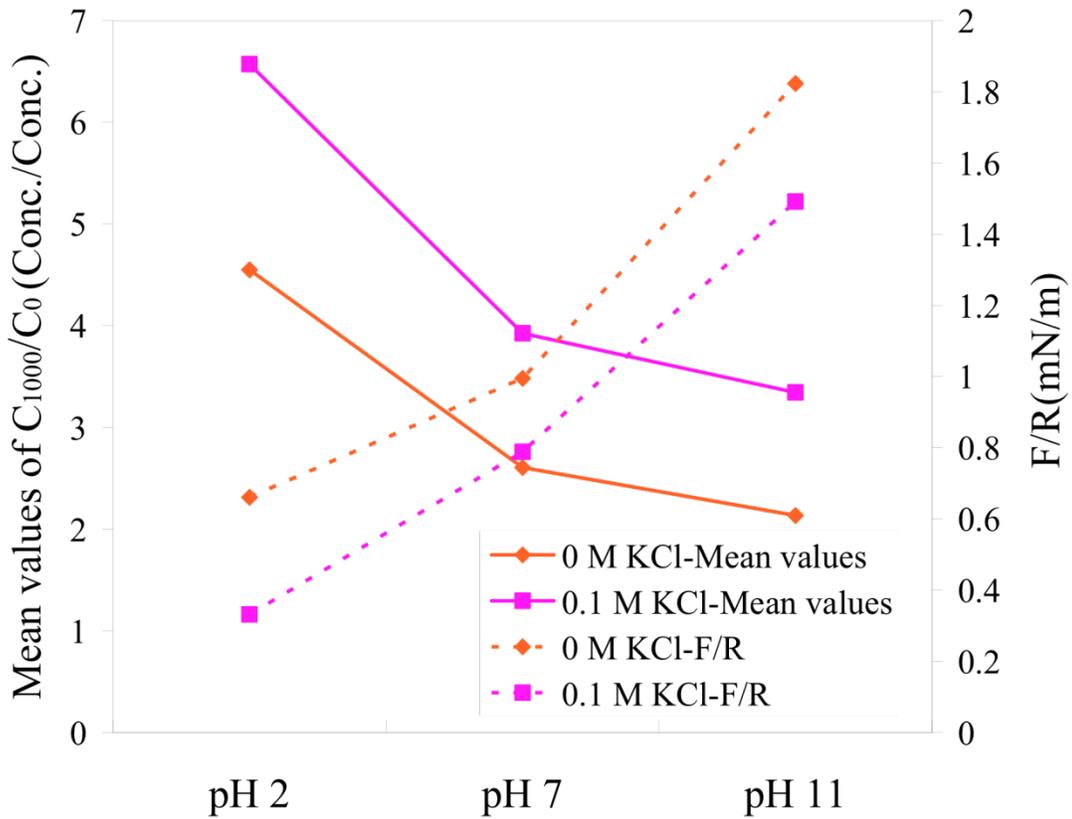


Figure 2-10. Correlation between repulsive inter-particle forces and mean values of normalized oversize particles for different pH, with and without 0.1M KCl (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

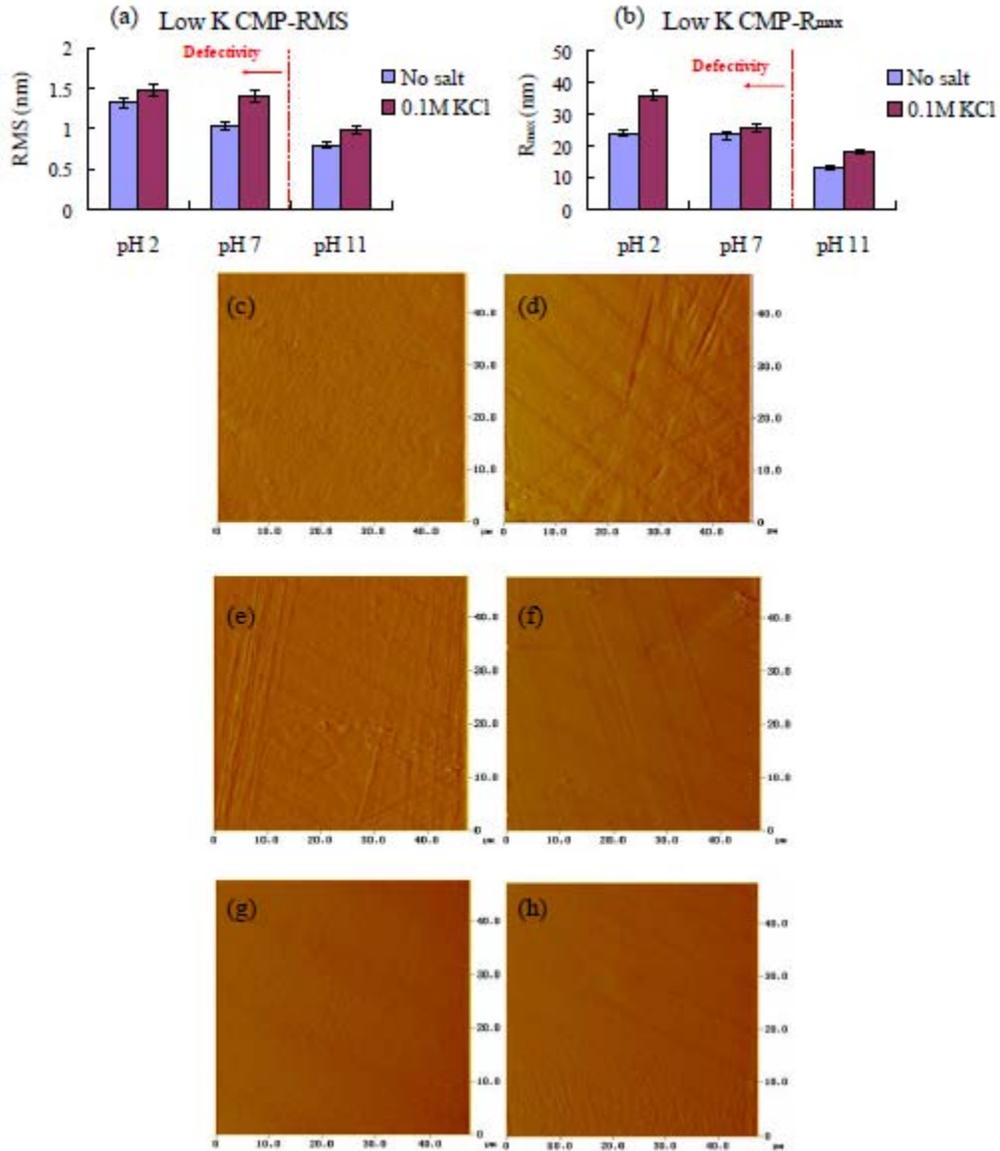


Figure 2-11. Surface roughness for different pH: (a) RMS and (b) R_{\max} , and AFM images of low-k wafers polished by circulated silica slurries at (c) pH 2, (d) pH 2 with 0.1M KCl, (e) pH 7, (f) pH 7 with 0.1M KCl, (g) pH 11, and (h) pH 11 with 0.1M KCl (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

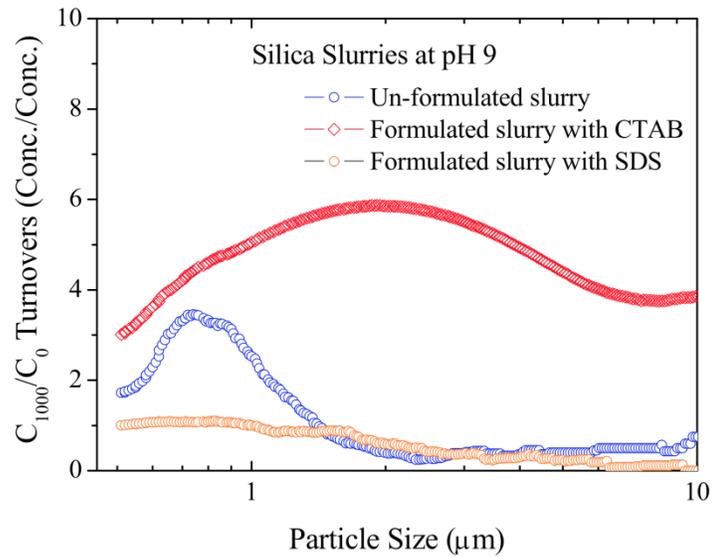


Figure 2-12. Comparison of particle agglomeration in un-formulated and formulated silica slurries (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

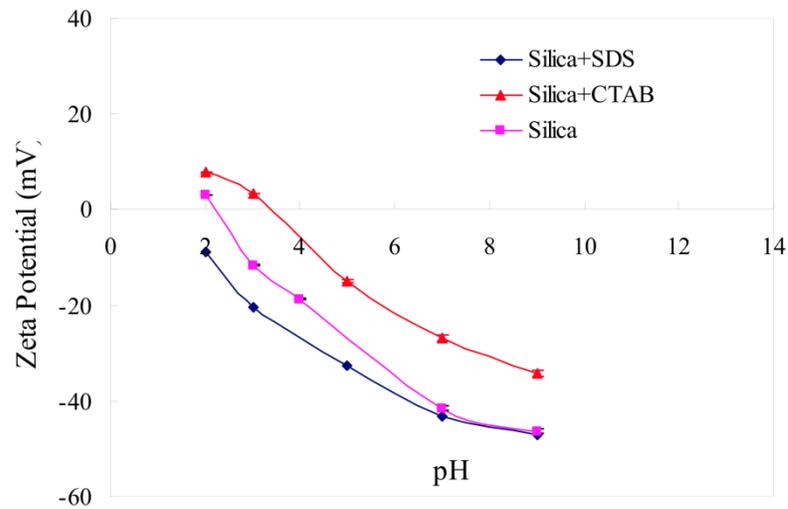


Figure 2-13. Plot of zeta potential vs. pH in silica slurry with surfactants (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

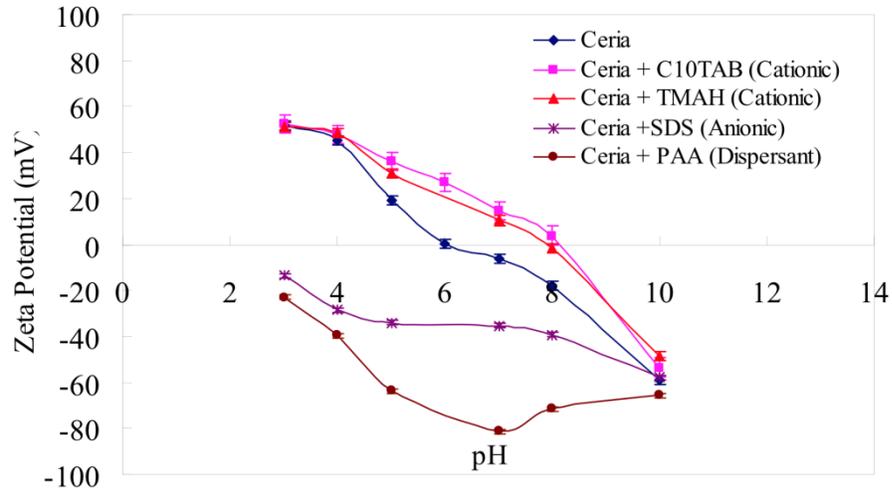


Figure 2-14. Plot of zeta potential vs. pH: potential curves of formulated ceria slurries with varying surfactants (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

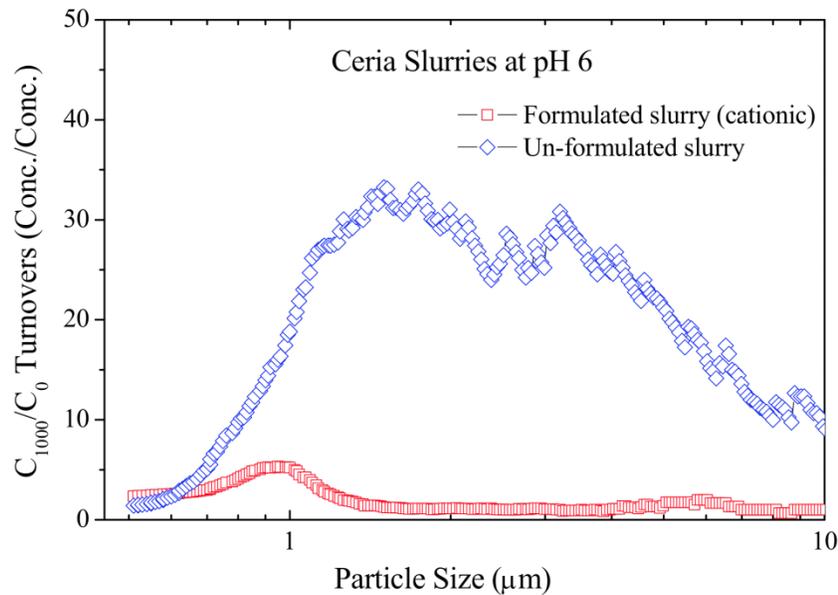


Figure 2-15. Comparison of shear induced particle agglomeration in un-formulated and formulated ceria slurries (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

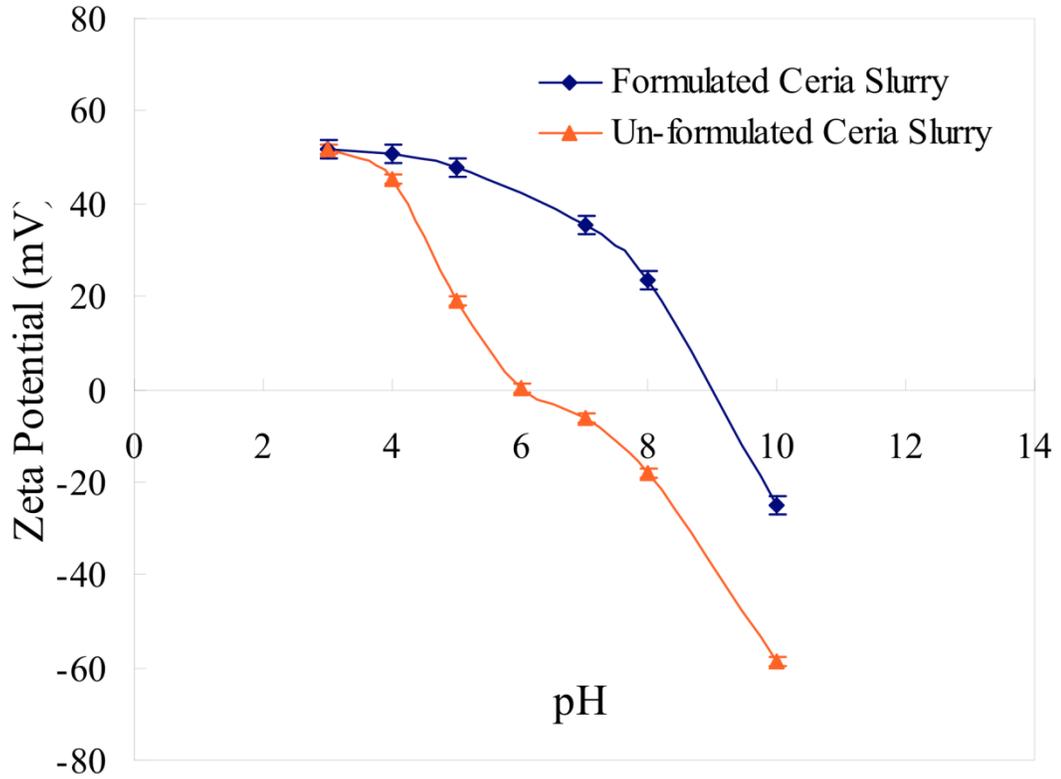


Figure 2-16. Plot of zeta potential vs. pH in ceria slurry with cationic surfactant (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

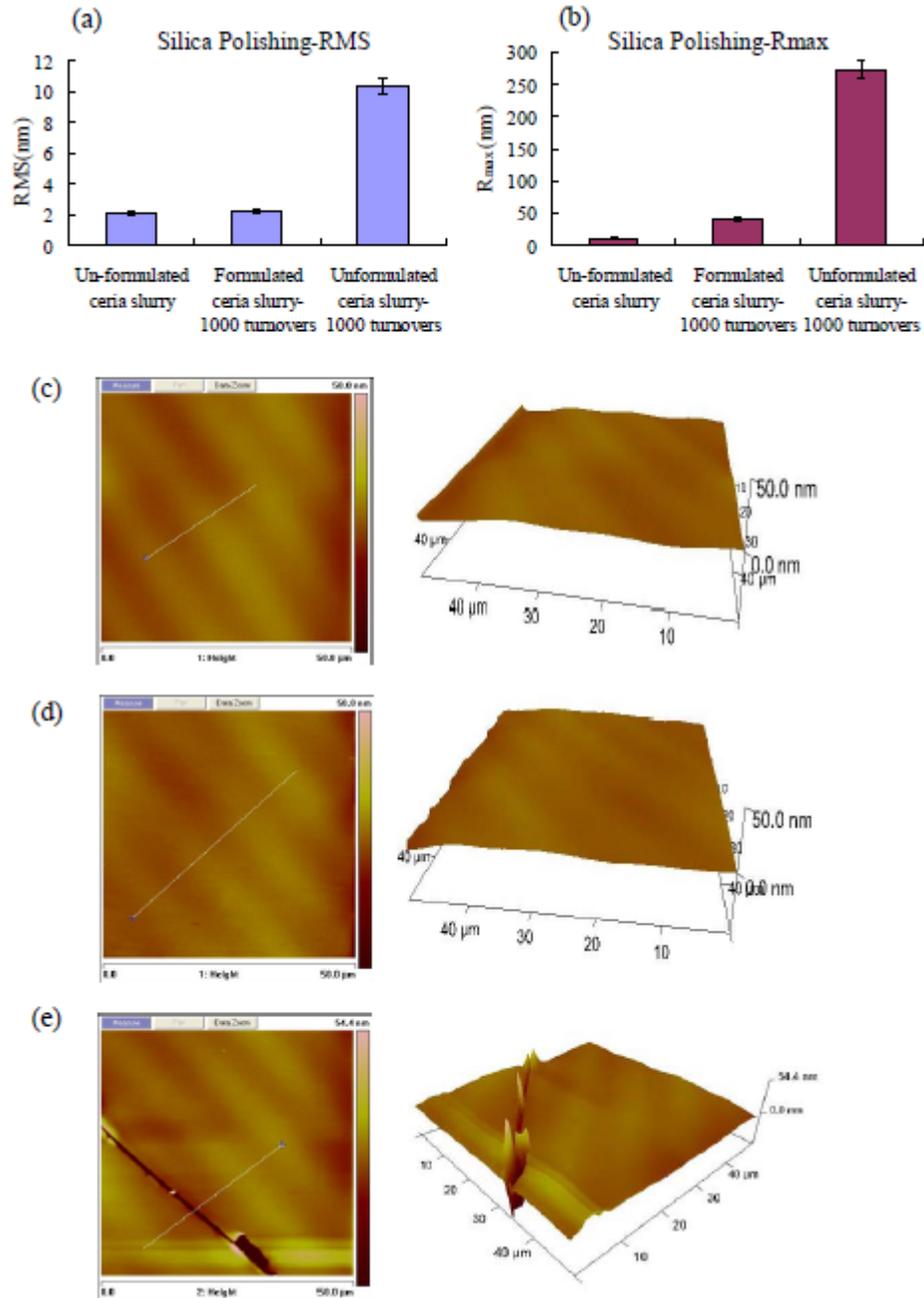


Figure 2-17. CMP of silica: (a) surface roughness (RMS), (b) R_{max} , (c) AFM images of silica wafers polished by un-formulated ceria slurry at pH 6, (d) formulated ceria slurry (cationic surfactant) at pH 6 (1000 turnovers), and (d) un-formulated ceria slurry at pH 6 (1000 turnovers) (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

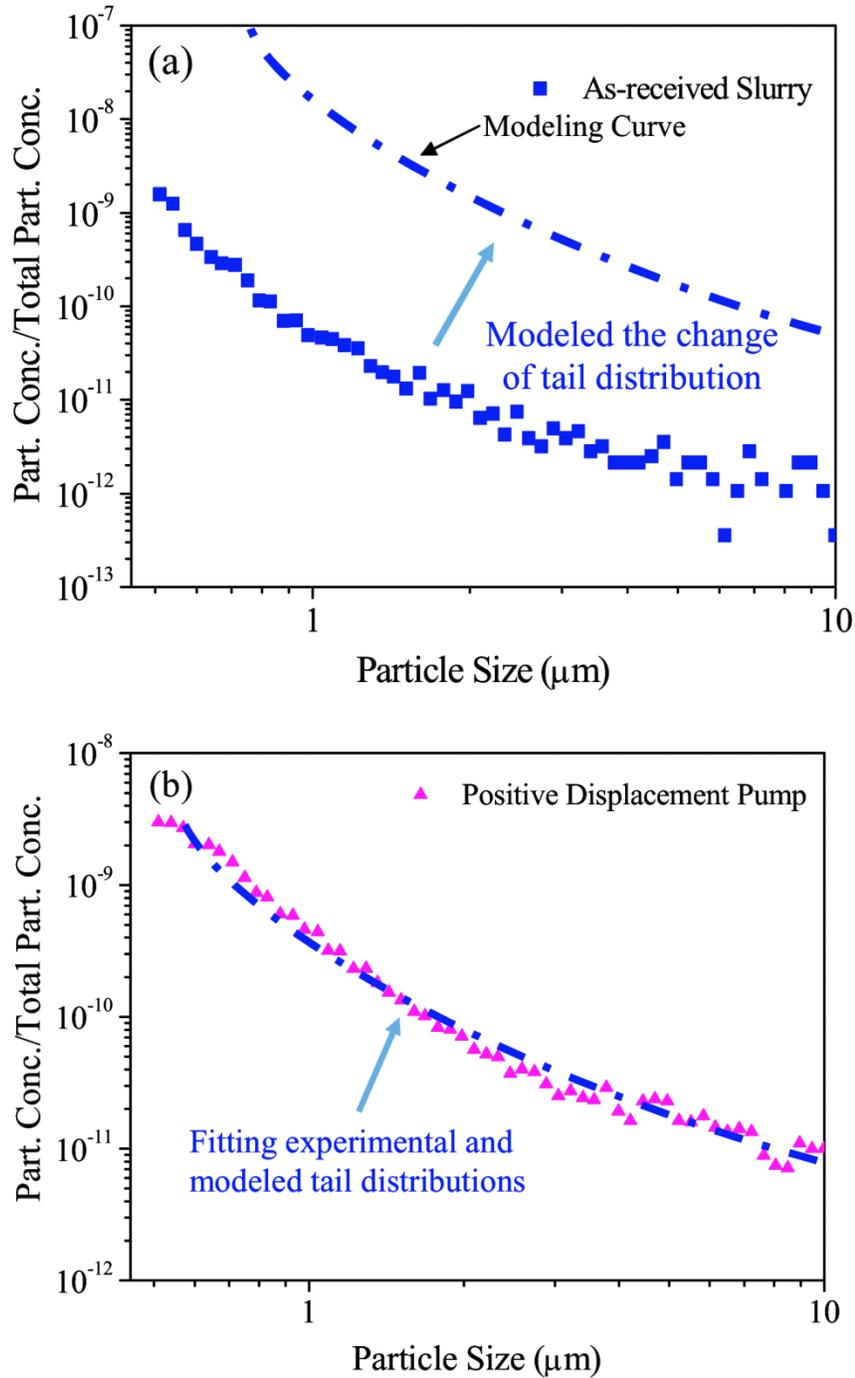


Figure 2-18. Schematics for determination of agglomeration index (AI): (a) modeling change in tail distribution of oversize particles; and (b) fitting experimental and modeled tail distributions to obtain AI (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

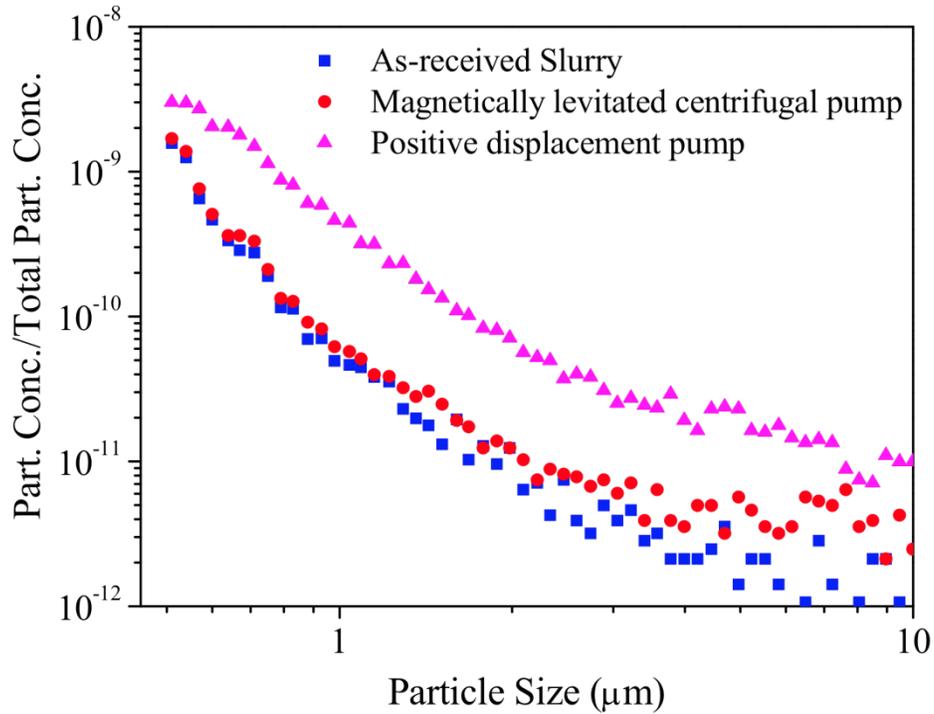


Figure 2-19. Tail distributions of as-received slurry and circulated slurries by positive displacement and magnetically levitated centrifugal pumps (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

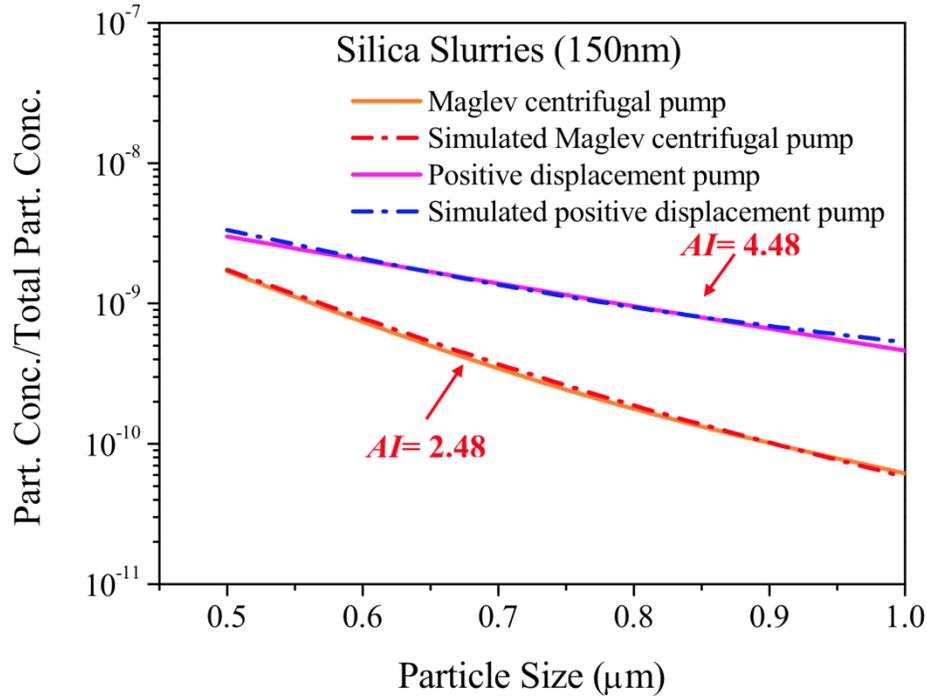


Figure 2-20. Effect of external shear stress on agglomeration index (AI): experimental and modeled tail distributions in positive displacement and maglev centrifugal pumps (Reprinted with permission from Feng-Chi Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123 [30])

CHAPTER 3 MEASUREMENTS FOR CHEMICAL MECHANICAL POLISHING SLURRIES

Introduction

Chemical mechanical polishing (CMP) slurry is one of the most critical consumable in semiconductor industry. CMP slurry is an optimum combination of abrasives like silica, alumina or ceria particles, oxidizers, additives, corrosion inhibitors and other chemicals and their synergistic effects results in optimal removal rates and surface smoothness. The particle size distribution in slurry decides CMP performance. Particles could undergo agglomeration due to shear forces induced during slurry formulation and handling. There are measurement techniques to detect changes in particle size distribution as listed in Table 3-1 [33]. Each of the measurement techniques is based on different principles like light scattering, refraction, microscopy, sedimentation, sieving, and particle counter. These methods have their limitations in terms of determining particles in certain size range from few nanometers to thousand microns.

Oversize Particle Distribution Measurements

Accusizer 7880 manufactured by PSS Nicomp is a single particle optical sensor system ("SPOS") that measures particle size distribution in the range 0.5-200 μm [34]. SPOS detects individual particles in a certain size range as each particle passes through a very thin "optical-sensing zone". The concentrated suspensions are diluted sufficiently so that particle passes one at a time through detection zone. Two physical methods are traditionally used to implement SPOS technique namely Light Extinction ("LE") and Light Scattering ("LS").

Light Extinction (LE) Method [35]

When individual particle suspended in a fluid passes through the light beam in a flow channel, there is a decrease in intensity of light that transmits across the flow channel. Measurement of the resulting decrease in intensity of light forms the basis of the LE method. The “optical-sensing zone” or “view volume” of an LE sensor consists of the walls of the channel and the thickness of the flat ribbon of light that defines the illuminating beam (Figure 3-1) [35].

Light refraction is the physical effect that underlies the LE method. Refractive index of most of the particles is different from the fluid they are surrounded by and in most cases it is water. The particles behave like lenses, either causing the light rays that are incident upon them to be refracted or deflected away from the detector on the opposite side of the flow channel. As a result, the particle causes removal of a small fraction of the incident light rays that otherwise would have illuminated the detector. For LE method the useful particle range is 1.3 to 400 μm and below 1.3 μm , due to prevailing noise, the signal due to particle cannot be reliably detected. Below 1.3 μm , scattering is the physical effect that is mainly responsible for the decrease in light intensity reaching the forward detector. In any case, the reduction of the incident light signal at the detector is the net result and hence the name light “extinction”.

A plot of a typical simplified time dependent signal output V_{LE} , of the detector in an LE type sensor is shown in Figure 3-2 [35]. The detected light level is at its maximum level, given by V_0 and when V_{LE} is reduced due to particles passing through view volume, it results in a negative going pulse superimposed on the d.c. “background” level. The pulse height, ΔV_{LE} being dependent on the size of the particle, increases

monotonically with the particle size. ΔV_{LE} becomes larger as particle size becomes larger (Figure 3-2). The pulse width depends on view volume thickness 'w', velocity 'v' of the fluid/particle mixture passing through the sensor (Figure 3-3) [35].

$$\Delta t = w/v = abw/F$$

Now, 'v' depends on fluid flow rate 'F', 'a' and 'b' are dimensions of the flow channel.

Typically, $\Delta t = 14 \mu\text{sec}$, $F = 1 \text{ ml/sec}$ (60 ml/min)

The area of illumination of the LE detector A_0 is equal to 'a' times 'w' when there is no particle in view volume as shown in Figure 3-3. As particle enters view volume, it reduces area ΔA effectively equal to cross-sectional area of the particle. For an ideal case, for a spherical diameter 'd', ΔA equals area of circle of same diameter given by $\Pi d^2/4$. For particles larger than 3 - 5 μm and smaller than beam thickness 'w', light refractions dominates LE. LE type sensor has a quadratic response i.e. signal depends on the square of the particle diameter. Below 1.3 μm , where light scattering dominates sensor response, the pulse height decreases faster with decreasing diameter (approximately as 4th power of d).

Light Scattering (LS) Method [35]

Light Scattering (LS) method is complementary to LE method. When particles less than 1.3 μm pass through view volume, they cause scattering of light that results in increase in intensity of light incident on LS detector. As in LE method, "view volume" acts as a source of the scattered light, however, in absence of particle there is little or no light detected from the zone in the absence of a particle. The detector that is utilized for the LS method captures the light that is scattered over a particular, optimized range of solid angles. A plot of a typical time-dependent signal output V_{LS} of the detector in an

LS type sensor is shown in Figure 3-4 [35]. Initially with no particle in flow channel output is ideally zero but when a particle passes through the sensing zone, a positive going pulse appears at the output of the detector. The pulse height (ΔV_{LS}) depends on size and composition of the particle with assumption that solid angle of scattering detections is appropriately chosen, ΔV_{LS} increases monotonically with particle diameter and pulse height becomes larger as particle size becomes larger. Sensitivity is the major advantage of LS method over LE method.

Accusizer 780 by PSS Nicomp uses a new patented hybrid design developed by PSS, which combines the advantages of the LE like large particle size range and relative insensitivity to particle composition and LS method like high sensitivity and lower diameter limit. Electronically LE and LS signal responses are combined resulting in a single “summation” signal pulse. Accusizer 780 could be used for particle size analysis of highly concentrated sample as well. The dilution system dilutes the sample in two stages till acceptable particle concentration is obtained for SPOS sensor. In the auto-dilution system, the total extent of initial sample suspension is equal to the product of dilution factors, where DF1 and DF2 are dilution factors for first and second stage respectively, as given by

$$C_i / C_2 = (C_i / C_1) \times (C_1 / C_2) = DF1 \times DF2 \quad [3-1]$$

where C_i , C_1 , C_2 are initial, first and second stage concentrations respectively.

In the present work, 1ml of sample was introduced in the solution chamber and diluted with de-ionized water. Particles in the slurry are diluted through a two-stage dilution system and then flow through sensor zone, a laser diode, which causes a drop or increase in voltage depending upon physical method, extinction or scattering

respectively. Accusizer gives number of particles of different sizes present in the sample and their number are be added up to give cumulative concentration of oversize particles. The cumulative concentration tail has been qualitatively used in the past for determining effect of shear induced during slurry handling on agglomeration behavior of particles.

Rheometer

Rheometers have been traditionally used to measure the response of a liquid, suspension or slurry when subjected to applied forces. It is mainly used for fluids whose viscosity values are not constant but rather changes depending on the amount of applied forces e.g. Newtonian and Non-Newtonian fluids. Physica UDS 200 can be used as rotational, shear stress, creep and oscillatory rheometer [36]. It uses concentric cylinders, cones and plates as measuring systems. The sample is contained in the measuring gap between fixed plate and the rotating cone. The angle between the surface of the cone and the plate is of the order of one degree, thereby making it a shallow cone. The measuring drive is based on a highly dynamical motor-driven system without gears and without mechanical force transducer, with torque measurement and optical actuator. The measuring drive is suited to run rotational, strain, and relaxation tests with simultaneous control of the shear rate i.e. pre-selected number of revolutions and measurement of the torque (shear stress) acting on the measuring bob. Physics UDS 200 allows user to run controlled stress tests to determine the flow behavior of highly viscous substances, along with measuring the viscosity of fluids. By using Physica UDS 200 rheometer, we are able to apply quantified shear rates to the CMP slurry, which is introduced on the plate. The volume of sample is 3 ml that is subjected to quantified shear rates for by using cone of diameter 75 mm, air gap of 0.05 mm.

Using values of shear rate and viscosity, this rheometer also gives values of shear stress.

Zeta Potential Measurements

Stabilization of colloidal suspension through electrostatic or polymeric stabilization methods are possible due to the presence of electrical double layer closed to the charged particle surface. However, so far there is no experimental measurement technique that allows measurement of the surface potential. The potential of the shear plane, called as zeta potential, could be measured for an aqueous system by electrokinetic experiments.

Brookhaven Zetaplus is used to measure zeta potential of abrasive particles in CMP slurries. Smoluchowski equation can be applied to measure zeta potential (ζ) when thickness of the electric double layer given by Debye length ($1/\kappa$)

$$\zeta = \frac{\eta v_E}{\varepsilon E_0} \quad [3-2]$$

where η and ε are viscosity and dielectric constants in the solution and E_0 is electric field. v_E is the electrophoretic velocity [13, 22] of colloidal particles which could be measured by electrophoresis method, employed by Brookhaven Zetaplus. For the case where double layer thickness $1/\kappa$ is much greater than particle size, Huckel equation (eqn. 3-3) could be used to find zeta potential.

$$\zeta = \frac{3 \eta v_E}{2 \varepsilon E_0} \quad [3-3]$$

Table 3-1. Various particle size analysis measurements [33]

Method	Medium	Size Range (micron)
Microscopy		
Optical	Liquid/Gas	0.5-400
Electron	Vacuum	0.0001-400
Sieving	Air	37-8000
	Liquid	May-00
Sedimentation		
Gravity	Liquid	0.5-100
Centrifuge	Liquid	0.01-300
Ultra-centrifuge	Liquid	0.001-300
Single particle counters		
Electrical sensing		
Zone	Liquid	0.3-1200
Time of light	Gas	0.2-700
Light scattering		
Diffraction (LALLS)	Liquid/Gas	(0.1) 0.5-1800
Dynamic (PCS)	Liquid	0.002-0.5(1)
Gas adsorption	Gas/Vacuum	0.005-5

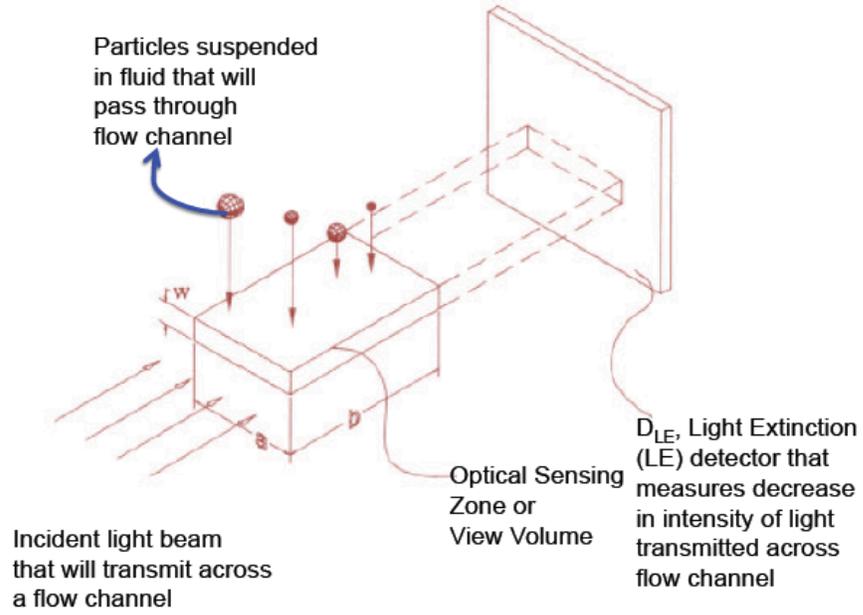


Figure 3-1. Schematics for optical scheme of a light extinction (LE) type sensor [35]

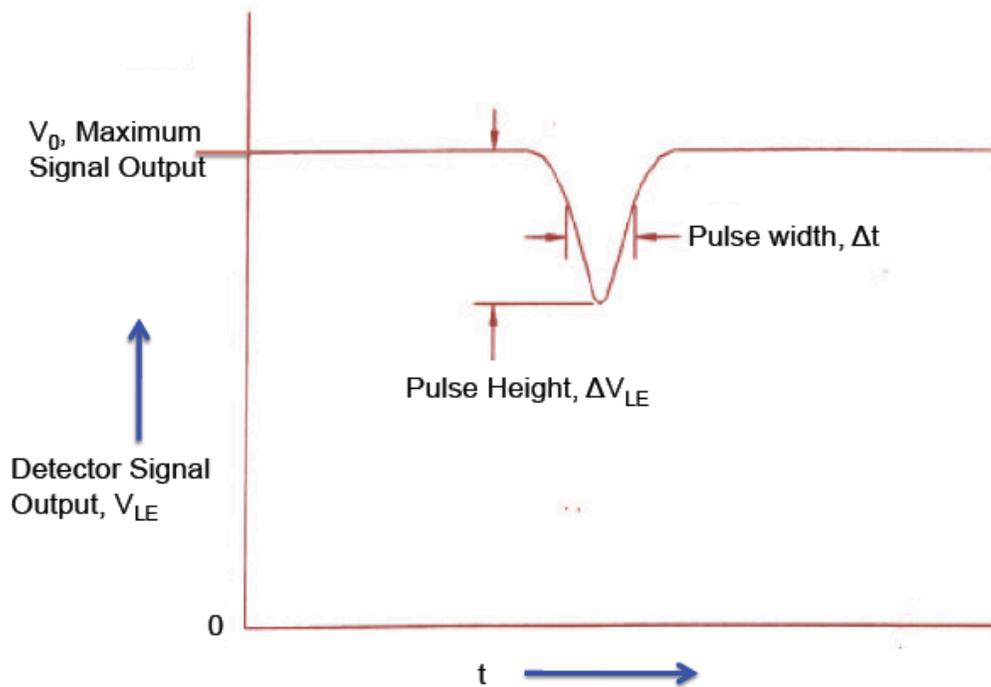


Figure 3-2. Detector signal output in LE type sensor, resulting from momentary passage of particle through view volume (in Figure 3-1) [35]

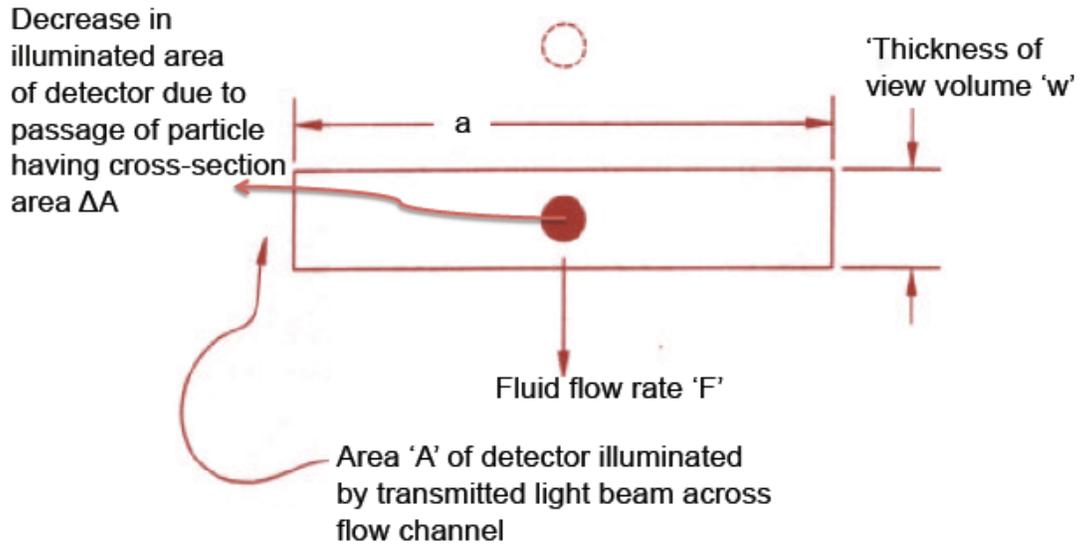


Figure 3-3. Area of illumination at LE detector, decreased by passage of particle of area ΔA through view volume [35]

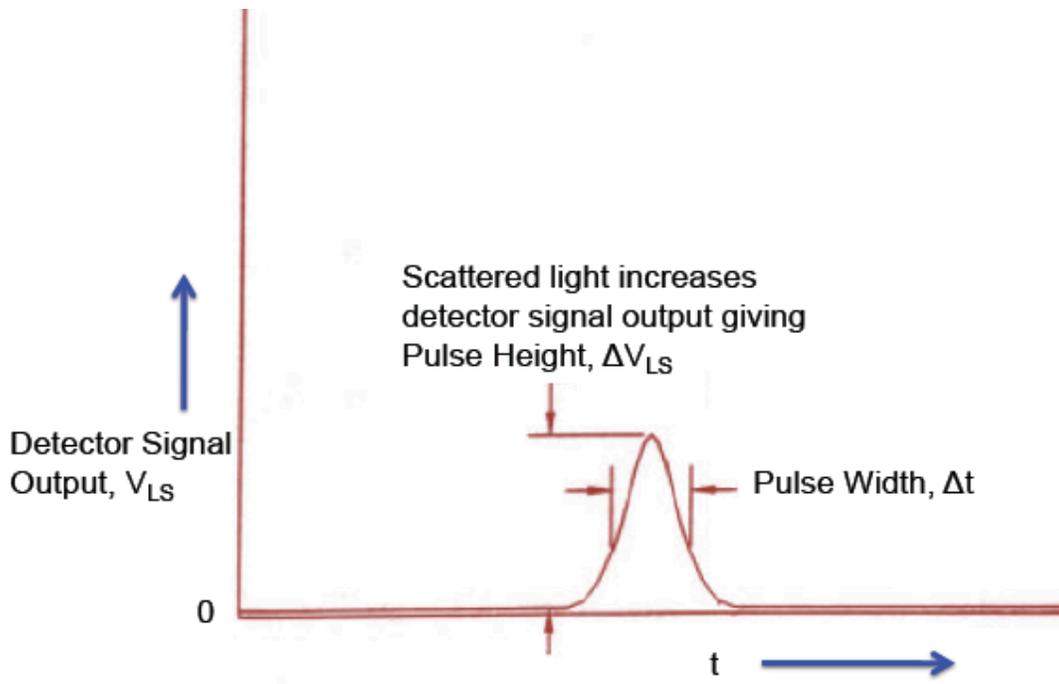


Figure 3-4. Detector signal output in light scattering (LS) type sensor, resulting from passage of particle through view volume [35]

CHAPTER 4
STUDY OF AGGLOMERATION BEHAVIOR OF CHEMICAL MECHANICAL
POLISHING SLURRY BY RHEOLOGICAL MEASUREMENTS UNDER VARIED
SHEAR ENVIRONMENT

Introduction

Chemical mechanical planarization (CMP) is commonly used for both local and global planarization of metals and dielectrics in the semiconductor industry. Due to its unique capability of eliminating topographic variations and simultaneously achieve wafer level global planarization, it has become the most sought after method for planarization of wafers. Highly stable slurry is critical for CMP performance. During polishing process, one of the main reasons for defectivity is the presence of large agglomerates in the slurry. With increased exacting requirements expected for future generation of devices, it is very important to develop highly stable performance slurries for CMP [37]. It is critical to reduce and control formation of agglomerates during slurry handling.

Feng-Chi et al. [4] showed that high shear inducing pumps used for slurry delivery cause a significant increase in concentration of agglomerates. The effect of shear rate is aggravated when salts and surfactants are added to the slurry, which changes the slurry chemistry, resulting in increased rate of formation of agglomerates in the slurry [30]. So far all the studies on understanding agglomeration behavior of CMP slurry have been qualitative or at best semi-quantitative in nature. A detailed understanding of agglomeration behavior of CMP slurries at quantified shear rates is critical to complete understanding of how shear rates affect agglomeration behavior of CMP slurries. To control agglomeration in slurry it is essential to know the shear rate range in which agglomeration of particles takes place and effect of duration of shear rates on these particles.

Rheometer is a device that is essentially used to study change in behavior of fluids as a result of applied forces like change in viscosity of Newtonian and Non-Newtonian fluids as a function of shear rates. Moinpour et al. [38] showed that when CMP slurries were subjected to different shear rates for a prolonged period of times the viscosity changes and drops with time. They believed that these drop in viscosity was due to agglomeration of particles, as larger particles make the fluids less viscous. However, change in normalized particle size distribution, which shows whether it is net agglomeration or de-agglomeration taking place as function of shear rates is the key to understand agglomeration behavior of CMP slurries. Physica UDS 200 rheometer uses concentric cylinders, cones and plates as measuring systems [36]. The measurement based on highly dynamical motor driven system, allows control of the shear rates acting on the measuring bob, which allows running controlled shear stress tests to determine the flow behavior of viscous substances. This rheometer allows user to apply shear rates up to 5000 s^{-1} and simultaneously maintain desired temperature control.

Experimental

EM3530K is a silica slurry with 30-wt%, 35 nm silica particles loading at pH~10. 10 wt% silica slurry, termed as-received slurry, was prepared using EM3530K slurry, keeping the pH~10. The initial oversize particle distribution of this slurry was measured using Accusizer 780, a single particle optical sensor (SPOS) system. Accusizer has two-stage dilution system that allows one to use samples with any concentration, as the dilution system is capable of diluting slurry sample to acceptable concentration to allow its photo-zone sensor to detect single particles in $0.51 - 200 \mu\text{m}$. 3 ml of 10wt% silica slurry was subjected to different shear rates $100 - 3000 \text{ s}^{-1}$ for various times 100 - 2500

s (Table 4-1) using rheometer UDS 200. After the slurry is subjected to shear rate, the oversize particle distribution is again measured using Accusizer 780 to observe the resulting change in oversize particle distribution. The primary particle size measurements by Feng Chi et al. [30] have shown that shear stress does not cause a significant change in primary particle sizes of the abrasives in CMP slurry.

Results and Discussions

With increase use of chemical mechanical polishing (CMP) in multilevel interconnect fabrication; it is critical to have highly stable slurries for acceptable CMP performance. To understand the effect of shear on agglomeration behavior of silica slurries, rheometer is used to subject slurries to different shear rates in $100 - 3000 \text{ s}^{-1}$ (Table 4-1) and the change in oversize particle distribution is measured using Accusizer 780. Normalized concentration is then calculated from these particle size distribution measurements. The normalized concentration is defined as the ratio of cumulative concentration ($C_{s,G-t}$) of the slurry that is subjected to shear rate 'G' for time 't' seconds to cumulative concentration (C_{ar}) of as-received slurry, which is in this case is 10wt% 35 nm silica slurry at pH~10. The slurry that is subjected to shear rate 'G' for any time 't' seconds is termed as stressed slurry.

$$\text{Normalized concentration} = \frac{\text{Cumulative concentration of stressed slurry } (C_{s,G-t})}{\text{Cumulative concentration of as-received slurry } (C_{ar})} \quad [4-1]$$

The normalized concentration shows whether agglomeration or de-agglomeration takes place. If the value of normalized concentration is less than 1, it indicates that the oversize particles i.e. agglomerates are breaking due to shear stress, which results in

decrease in cumulative concentration of the stressed slurry. Alternatively, if the value of normalized concentration is greater than 1, it indicates the oversize particles i.e. agglomerates are forming due to shear stress, which results in increase in cumulative concentration of the stressed slurry.

The response of slurry changes with shear rates (Figure 4-1 – 4-5). For shear rates of $100 - 1000 \text{ s}^{-1}$ for 100 s, 1000 s and 2500 s each, the normalized concentration curves show that net de-agglomeration takes place, implying breaking down of oversize particles i.e. agglomerates that are present in the slurry. The fact that these agglomerates breakdown under low shear rates implies that they are weakly held. When the slurry is subjected to these low shear rates for higher duration, net de-agglomeration increases, indicating increased breakage of weakly held agglomerates.

When the slurry sample was subjected to 1500 s^{-1} (Figure 4-3), de-agglomeration was observed only for the first 100 second. However, for 1000 and 2500 s, normalized concentration became greater than 1 i.e. silica slurry started showing agglomeration. Camp[39] explained that for a fixed solids concentration, same aggregation could be obtained either by a short period of high shear or a long period of low shear. This explains the agglomeration observed at 1500 s^{-1} for time 1000 s and 2500 s. The product of shear rate 1500 s^{-1} and time (1000 and 2500 s) is just sufficient enough to cause agglomeration in the slurry, but small enough to cause agglomeration at lower time 100 seconds.

Further, for shear rates of $2000 - 3000 \text{ s}^{-1}$ the normalized concentration was greater than 1 for any duration up to 2500 s that indicates occurrence of shear induced agglomeration. The shear rate at which slurry shows agglomeration for any duration is

termed as threshold shear rate. For basic silica slurry, value of threshold shear rate is 2000 s^{-1} as we observed agglomeration for any duration from 100 s up to 2500 s. The value of normalized concentration increases as shear rate is increased from 2000 - 3000 s^{-1} . Also as duration is increased, net agglomeration increases in the slurries, which drives up the values of normalized concentration. This kind of behavior is consistent with that predicted by Smoluchowski's theory of agglomeration. The rate of formation of agglomerates is given as: [12]

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k}^{l=k-1} k_{ij} N_i N_j - N_k \sum_{k=1}^{\infty} k_{ki} N_i \quad [4-2]$$

and agglomeration growth rate is given as

$$k_{ij} = 4/3 G (a_i + a_j)^3 \quad [4-3]$$

where G is shear rate. As per equation [4-3], increase in shear rate will lead to increase in agglomeration rate and thus, for same duration higher shear rates would give larger concentration of oversize particles (Figure 4-4 – 4-5). Also the theory considers continuous buildup of agglomerates with time, which explains increase in normalized concentration for 2000 s^{-1} - 3000 s^{-1} from 100 to 2500 s.

Summary

There is a need to understand changes in behavior of CMP slurries when subjected to various quantified shear rates. In this work, novel method of using rheometer to understand agglomeration behavior of CMP slurries under varied quantified shear rates was demonstrated. The response of CMP slurries to different shear rates has two regimes, one in which it shows de-agglomeration and other it shows agglomeration. For shear rates $100 - 1000 \text{ s}^{-1}$, net de-agglomeration is observed

due to break down of agglomerates present in the slurry. For shear rate of 1500 s^{-1} de-agglomeration was observed for duration of 100 s, however, agglomeration was observed for higher duration of 1000 s and 2500 s. As CMP slurry was subjected to higher shear rates of $2000 - 3000 \text{ s}^{-1}$, we observed net agglomeration effect. Increase in shear rates and times lead to increase in concentration of agglomerates. For silica slurry with $\text{pH} \sim 10$, the threshold shear rate i.e. shear rate at which slurry shows agglomeration for any duration, is measured to be 2000 s^{-1} . By using this novel method it is possible to quantify shear rates for which CMP slurry will show de-agglomeration or agglomeration behavior.

Table 4-1. Various shear rates and times for silica slurry

Shear Rate (s^{-1})	Time (s)
100	100, 1000, 2500
1000	100, 1000, 2500
1500	100, 1000, 2500
2000	100, 1000, 2500
3000	100, 1000, 2500

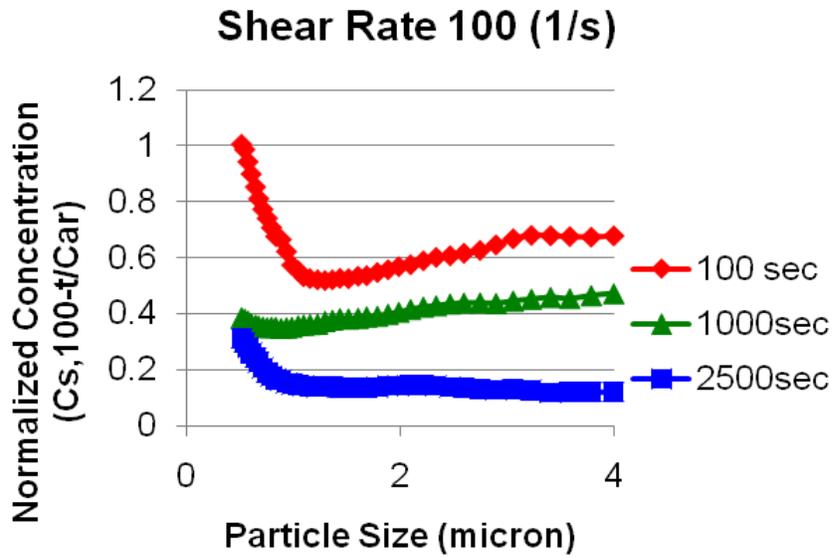


Figure 4-1. Normalized oversize particle distribution for 100 s^{-1} and various times

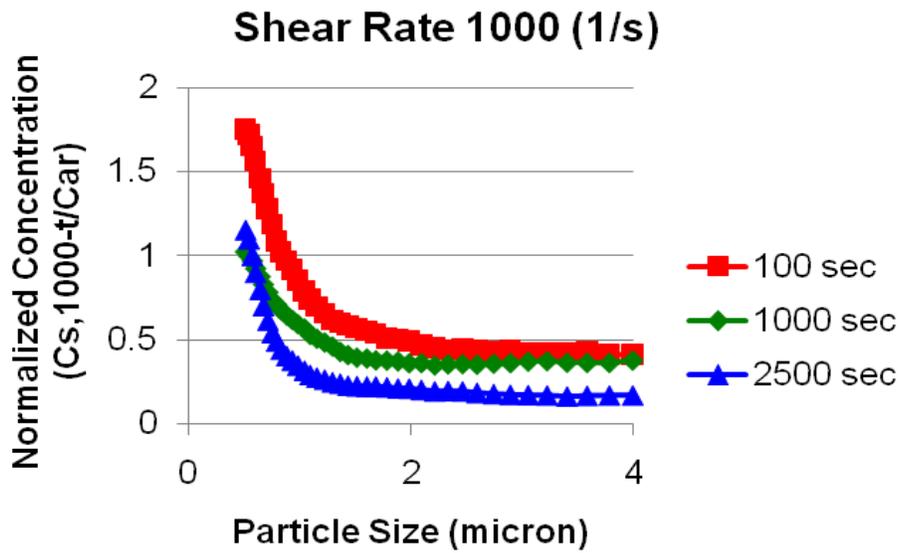


Figure 4-2. Normalized oversize particle distribution for 1000 s^{-1} and various times

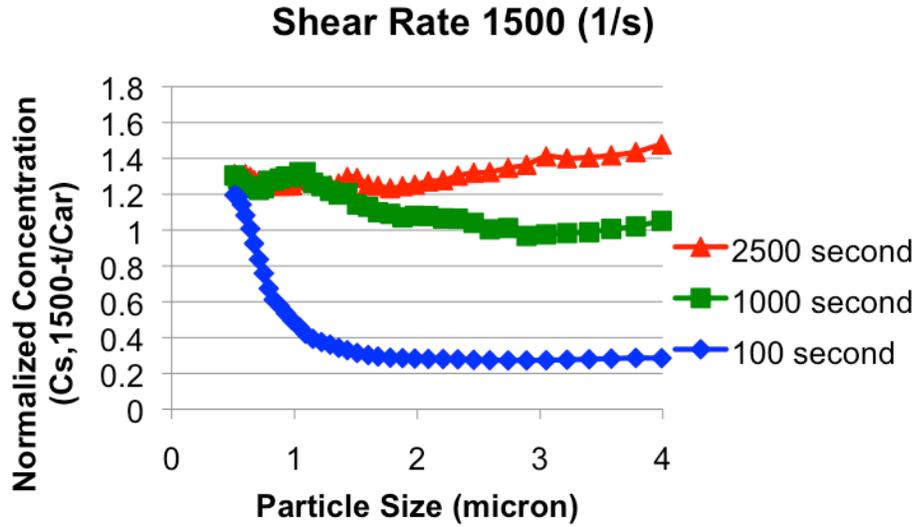


Figure 4-3. Normalized oversize particle distribution for 1500 s^{-1} and various times

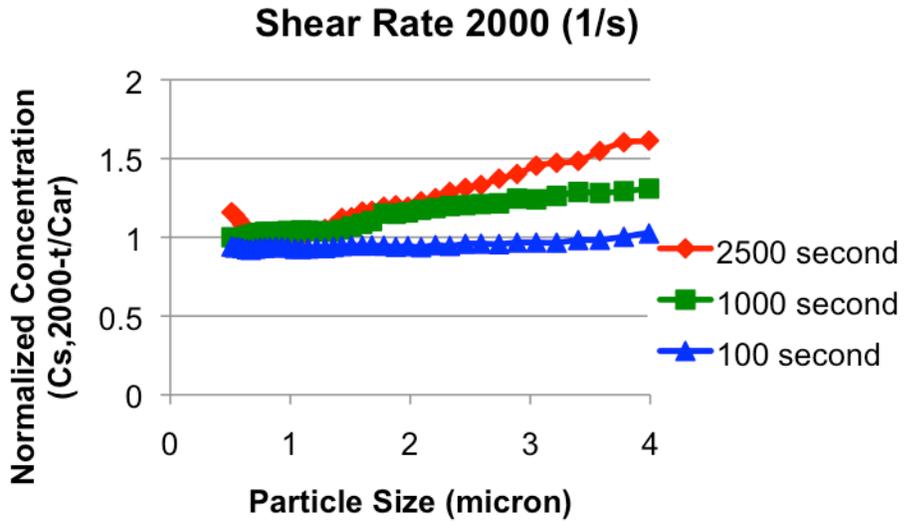


Figure 4-4. Normalized oversize particle distribution for 2000 s^{-1} and various times

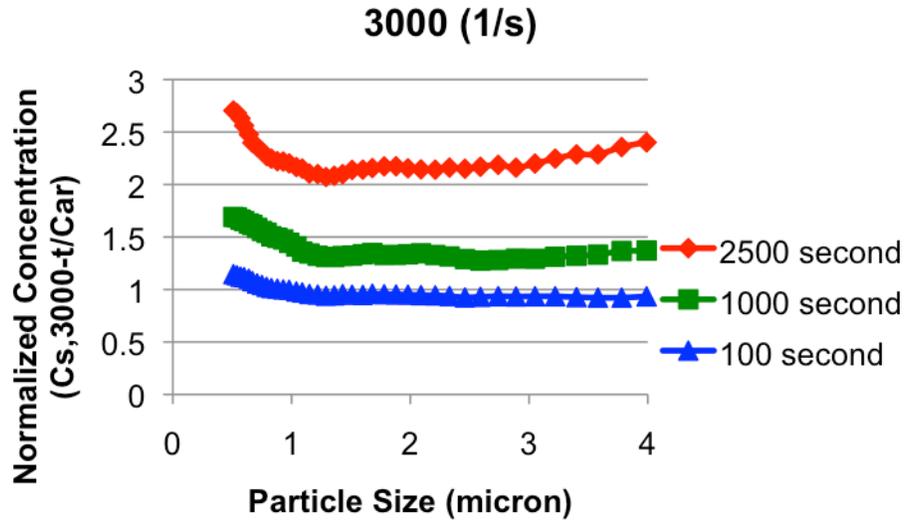


Figure 4-5. Normalized oversize particle distribution for 3000 s^{-1} and various times

CHAPTER 5 SILICA SLURRY STABILITY UNDER DIFFERENT CHEMICAL AND SHEAR ENVIRONMENT

Introduction

Chemical mechanical planarization (CMP) is most commonly used for eliminating topographic variations and achieving global planarization at wafer level in ultra large-scale integration (ULSI) circuit [3, 17, 40, 41]. In the last decade there has been significant advancements in CMP technology which includes development of more sophisticated processing tools and formulation of novel slurries to further enhance CMP process performance.[42] Slurries with different types of abrasives like silica, alumina, ceria particles and different slurry chemistries like pH, ionic concentration, surfactants are commonly used for controlling material removal rate, defectivity, corrosion and surface finish. In case of silica slurry, silica particles is negatively charged under basic pH conditions and with changes in slurry chemistry like reduction of pH, it is seen that there is a reduction in inter-particle repulsive forces between silica particles. This leads to increase in agglomeration of abrasive particles that causes a rise in defectivity during CMP process.

One of the main causes of the increase in agglomeration is due to the shear stress induced by pumps used for slurry delivery. Chang et al. [4] qualitatively showed that using higher shear rate pump leads to significant increase in agglomeration as compared to low shear rate pump. The agglomeration is aggravated as the slurry pH is reduced or ionic concentration increased for silica slurries [30]. The isoelectric point (IEP) of silica is 2 and as the pH is increased there is an increase in repulsive forces as confirmed by zeta potential measurements. They also measured repulsive forces near the silica surface by AFM force measurements. The repulsive forces around silica

surface tend to decrease as the pH is reduced or ionic concentration is increased, as a result of screening of surface charges. A detailed understanding of changes in agglomeration behavior as slurry chemistry is changed at different quantified shear rates, is essential for attaining control over slurry agglomeration due to different amount of shear stress induced by pumps.

Rheometer is a device commonly used to study viscosity of fluids as a function of shear rates. In our work we employ Paar Physica UDS 200 Rheometer for applying different quantified shear rates to slurries. The oversize particle distribution of these slurries are measured using Accusizer 780, a single particle optical sensing (SPOS) system.

Experimental

EM3530K is a silica slurry with 30-wt%, 35 nm silica particles loading at pH~10. Two types of 10-wt% silica slurry were prepared using EM3530K slurry, one with pH~7 and other with pH~2. The pH of the silica slurry was altered using 1N nitric acid. Initial oversize particle distribution of these slurries was measured using Accusizer 780, a single particle optical sensor (SPOS) system. Accusizer has two-stage dilution system that allows one to use samples with any concentration, as the dilution system is capable of diluting slurry sample to acceptable concentration to allow its photo-zone sensor to detect single particles in 0.51 – 200 μm . 3 ml of 10wt% silica slurry was subjected to different shear rates 100 – 3000 s^{-1} for various times 100 - 2500 s (Table 5-1) using rheometer UDS 200. After the slurry is subjected to shear rate, the oversize particle distribution is again measured using Accusizer 780 to observe the resulting change in oversize particle distribution. The primary particle size measurements by Feng Chi et al.

[30] have shown that shear stress does not cause a significant change in primary particle sizes of the abrasives in CMP slurries.

Results and Discussion

CMP slurry performance is determined to a large extent by the amount of agglomerates in the slurry. The repulsive inter-particle forces in the slurry results in stabilization of slurry and if these forces are reduced as a result of changes in slurry chemistry, it leads to agglomeration. The isoelectric point (IEP) of silica slurry is around 2 and as the slurry pH is lowered from basic to acidic and approaches IEP, the repulsive inter-particle forces decreases [30]. Furthermore, the agglomeration problem gets severe once the slurry is subjected to shear stress from pumping devices. In the present work, objective is to study agglomeration and de-agglomeration in silica slurries when it is subjected to different shear rates.

Neutral pH

Neutral pH silica slurry samples are subjected to different shear rates 100 – 3000 s^{-1} using rheometer UDS 200 for various times 100 -2500 s (Table 5-1) and the change in oversize particle distribution is measured using Accusizer 780. Normalized concentrations are then calculated from these particle size distribution measurements and that gives the response of slurry for different shear rates (Figure 5-1 – 5-5). For shear rates of 100 s^{-1} (Figure 5-1) for 100 - 2500 s, the normalized concentration curves show that net de-agglomeration takes place, implying breaking down of oversize particles i.e. agglomerates that are present in the slurry. The fact that these agglomerates breakdown under low shear rates implies that they are weakly held. When the slurry is subjected to these low shear rates for higher duration, net de-agglomeration increases, indicating increased breakage of weakly held agglomerates.

When the slurry sample was subjected to 1000 s^{-1} (Figure 5-2), de-agglomeration is observed only for the first 100 second. However, for 1000 s and 2500 s, normalized concentration became greater than 1 i.e. silica slurry started showing agglomeration. Camp [39] explained that for a fixed solids concentration, same aggregation could be obtained either by a short period of high shear or a long period of low shear. This explains the agglomeration observed at 1000 s^{-1} for time 1000 s and 2500 s. The product of shear rate 1000 s^{-1} and time (1000 and 2500 s) is just sufficient enough to cause agglomeration in the slurry, but small enough to cause agglomeration at lesser time 100 seconds.

Further, for shear rates of $1500 - 3000 \text{ s}^{-1}$ the normalized concentration was greater than 1 for any duration up to 2500 s, which indicates occurrence of shear induced agglomeration. The shear rate at which slurry shows agglomeration for any duration is termed as threshold shear rate. For neutral silica slurry, value of threshold shear rate is 1500 s^{-1} as we observed agglomeration for any duration from 100 s up to 2500 s. The value of normalized concentration increases as shear rate is increased from 1500 s^{-1} - 3000 s^{-1} . Also as duration is increased, net agglomeration increases in the slurries, which drives up the values of normalized concentration.

Acidic pH

Acidic pH silica slurries are subjected to different shear rates $100 - 3000 \text{ s}^{-1}$ using rheometer UDS 200 for various times 100 -2500 s (Table 5-1) and the change in oversize particle distribution is measured using Accusizer 780. Normalized concentrations are then calculated from these particle size distribution measurements and that gives the response of slurry for different shear rates (Figure 5-6 – 5-10). For shear rates of 100 s^{-1} (Figure 5-1) for 100 - 2500 s, the normalized concentration curves

show that net de-agglomeration takes place, implying breaking down of oversize particles i.e. agglomerates that are present in the slurry. The fact that these agglomerates breakdown under low shear rates implies that they are weakly held. When the slurry is subjected to these low shear rates for higher duration, net de-agglomeration increases, indicating increased breakage of weakly held agglomerates.

Further, for shear rates of 1000 s^{-1} – 3000 s^{-1} the normalized concentration was greater than 1 for any duration up to 2500 s that indicates occurrence of shear induced agglomeration. The shear rate at which slurry shows agglomeration for any duration is termed as threshold shear rate. For acidic silica slurry, value of threshold shear rate is 1000 s^{-1} as we observed agglomeration for any duration from 100 s up to 2500 s. The value of normalized concentration increases as shear rate is increased from 1000 s^{-1} - 3000 s^{-1} . Also as duration is increased, net agglomeration increases in the slurries, which drives up the values of normalized concentration.

Comparison of Normalized Concentration of Silica Slurries with Different pH

The comparison of de-agglomeration in three different pH (10, 7 and 2) silica slurries is shown in Figure 5-11 – 5-13 for 100 s^{-1} and 100 – 2500 s. From the three curves, it is seen that extent of de-agglomeration is the most for basic pH slurry and decreases with from basic to neutral to acidic pH slurries. The extent of de-agglomeration indicates that the agglomerates present in basic silica slurry break much easily as compared to neutral and acidic slurry. In other words, the strength of agglomerates increases from basic to acidic pH slurry. The isoelectric point for silica particle is around pH~2, so the surface charge on silica particle decreases as the pH of silica slurry is lowered from basic to acidic due to screening of surface charges. The reduction in surface charge results in reduced inter-particle repulsive forces, which

disturbs the silica slurry stability and in the process making it more susceptible to agglomeration. The reduction of repulsive forces increases the inter-particle attractive forces between silica particles and thus, increasing the strength of agglomerates. The relative increase in strength of agglomerates in acidic and neutral pH slurry explains the reduced de-agglomeration in these slurries as compared to the basic slurry.

The threshold shear rates i.e. shear rate for which agglomeration occurs for any duration increases from acidic (1000 s^{-1}) to neutral (1500 s^{-1}) to basic (2000 s^{-1}) pH slurries, as the inter-particle repulsive forces increases with increase in pH, thus requiring more shear stress to induce agglomeration. From the normalized concentration curves of the three slurries it is evident that concentration of larger particles in 1-5 micron range is much higher in neutral and acidic slurry as compared to basic slurry. The increase in concentration of larger particles is again due to increased attraction between silica particles, which causes severe agglomeration when subjected to high shear rates. The higher concentration of oversize particles in turn increases the roughness and defect density of the surface being polished.

Summary

With increase in applications of CMP for planarization of various surfaces, there are stricter requirements to have controllability over the defects created during the CMP process. The formation of large agglomerates due to shear induced by pumps during slurry delivery is a known problem and an understanding of the nature of agglomerates formed due to shear will be instrumental in finding a way to reduce the formation of these agglomerates. From the extent of de-agglomeration it is evident that the agglomerates in neutral and acidic pH silica slurries are relatively harder than the agglomerates present in the basic pH slurry. The threshold shear rate for silica slurries

increases from acidic (1000 s^{-1}) to neutral (1500 s^{-1}) to basic (2000 s^{-1}) pH slurries, as the inter-particle repulsive forces increases with increase in pH. The concentration of larger particles in 1 - 5 micron range is much higher in neutral and acidic slurry as compared to basic slurry, which is due to increased attraction between silica particles. Also, it was seen for basic and neutral pH slurries, that application of lesser shear rate (1500 s^{-1} for basic and 1000 s^{-1} for neutral pH slurry) for prolonged period (1000 to 2500 s) could also result in agglomeration.

Table 5-1. Various shear rates and times for silica slurry

Shear Rate (s^{-1})	Time (s)
100	100, 1000, 2500
1000	100, 1000, 2500
1500	100, 1000, 2500
2000	100, 1000, 2500
3000	100, 1000, 2500

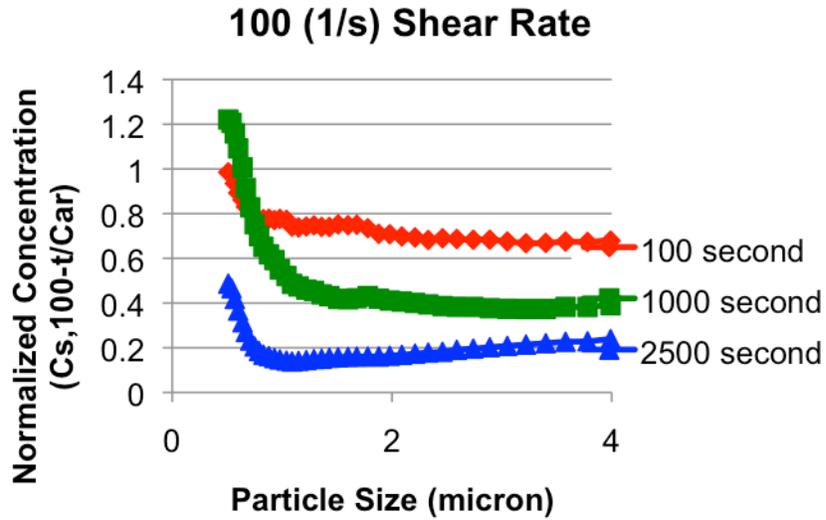


Figure 5-1. Normalized concentration for 100 s^{-1} and various times at pH-7

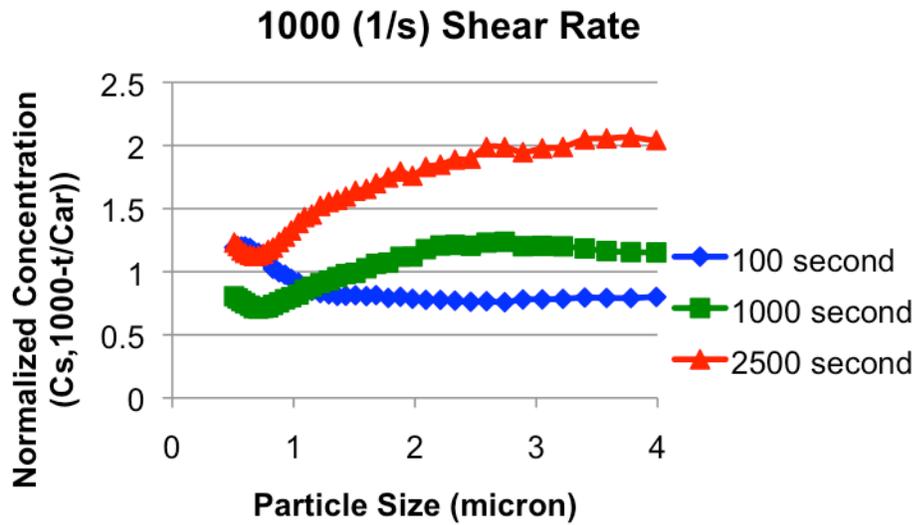


Figure 5-2. Normalized concentration for 1000 s^{-1} and various times at pH-7

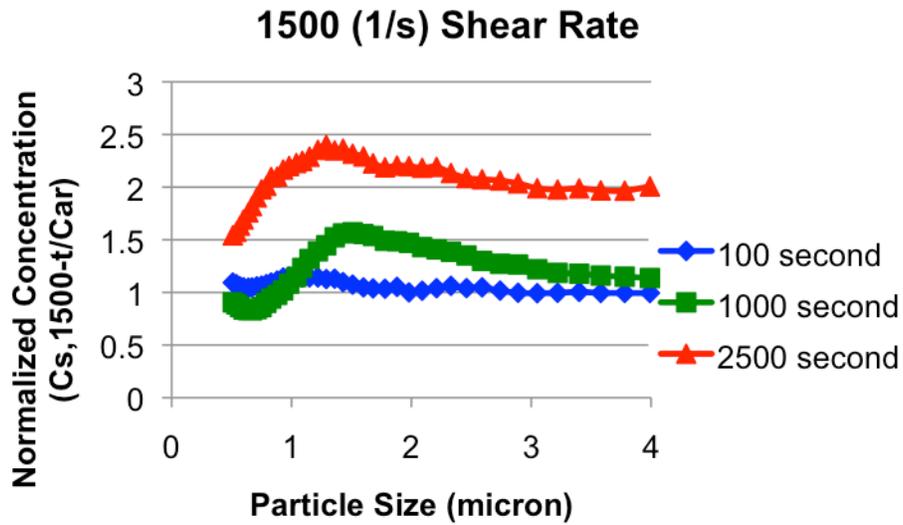


Figure 5-3. Normalized concentration for 1500 s⁻¹ and various times at pH~7

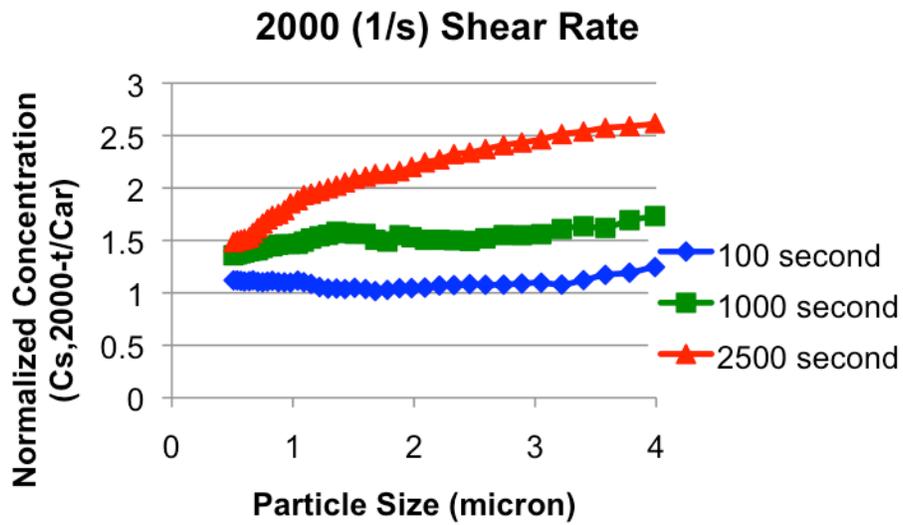


Figure 5-4. Normalized concentration for 2000 s⁻¹ and various times at pH~7

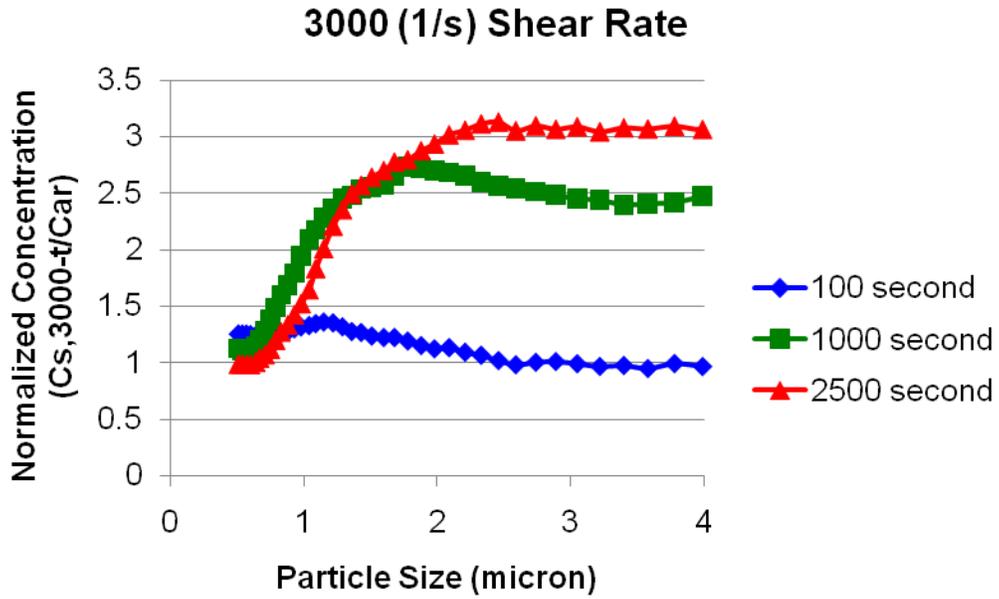


Figure 5-5. Normalized concentration for 3000 s^{-1} and various times at pH~7

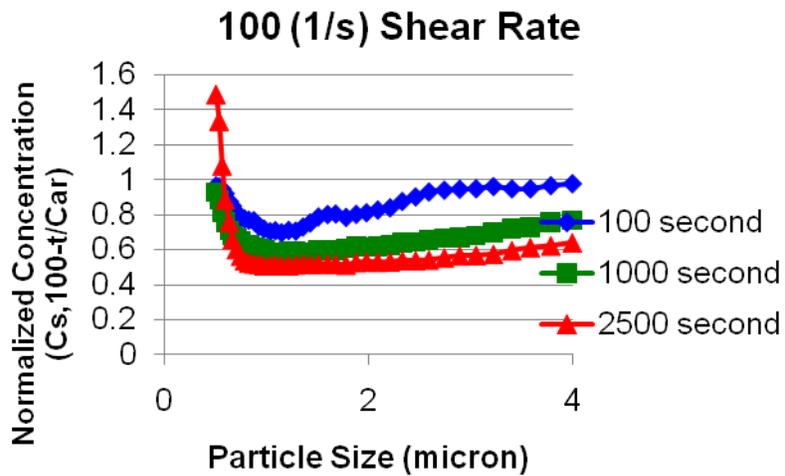


Figure 5-6. Normalized concentration for 100 s^{-1} and various times at pH~2

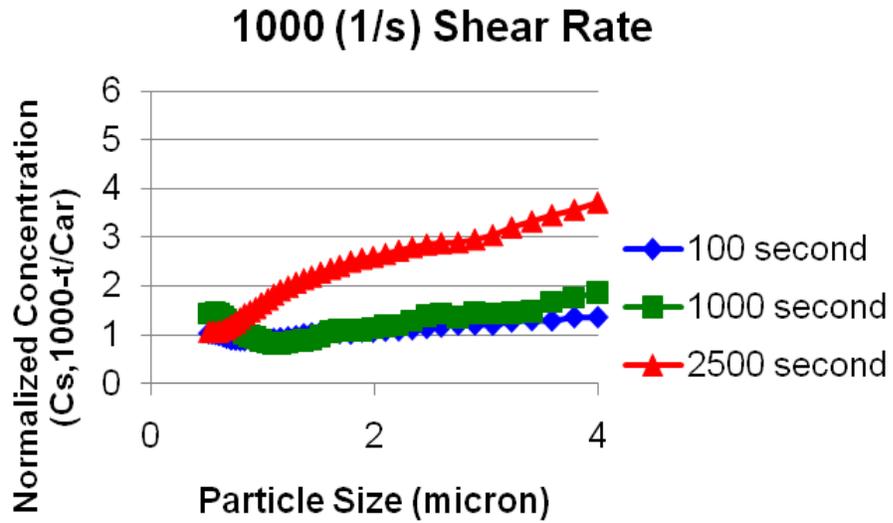


Figure 5-7. Normalized concentration for 1000 s⁻¹ and various times at pH~2

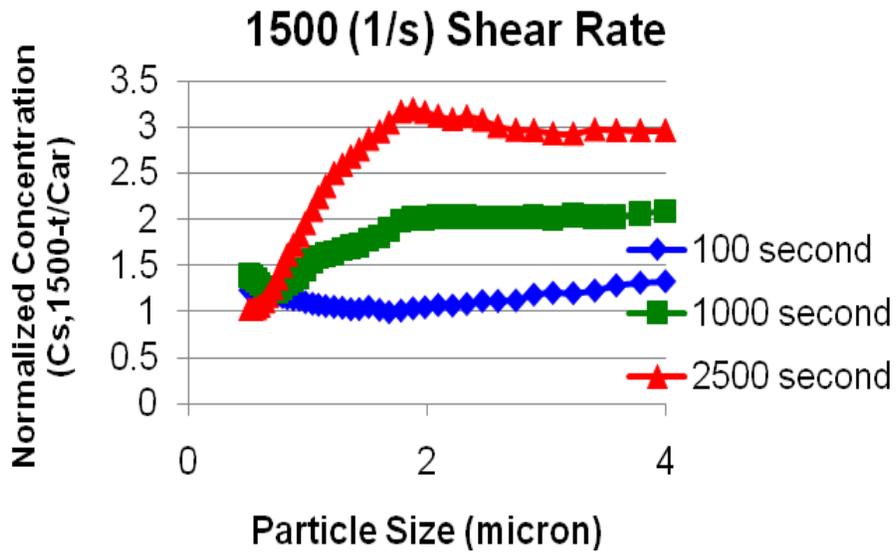


Figure 5-8. Normalized concentration for 1500 s⁻¹ and various times at pH~2

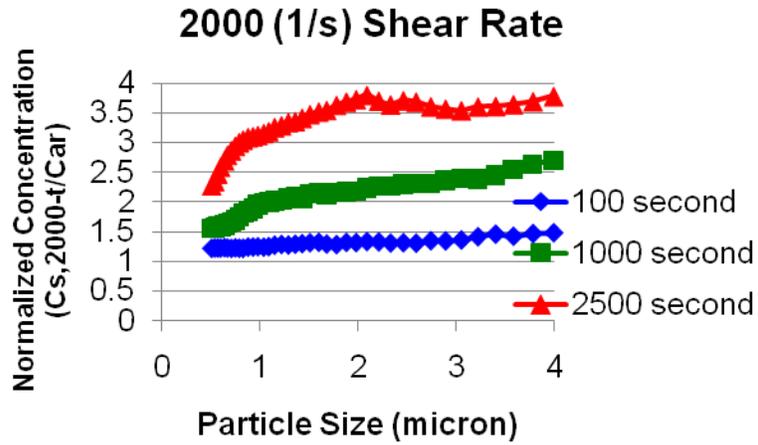


Figure 5-9. Normalized concentration for 2000 s^{-1} and various times at pH~2

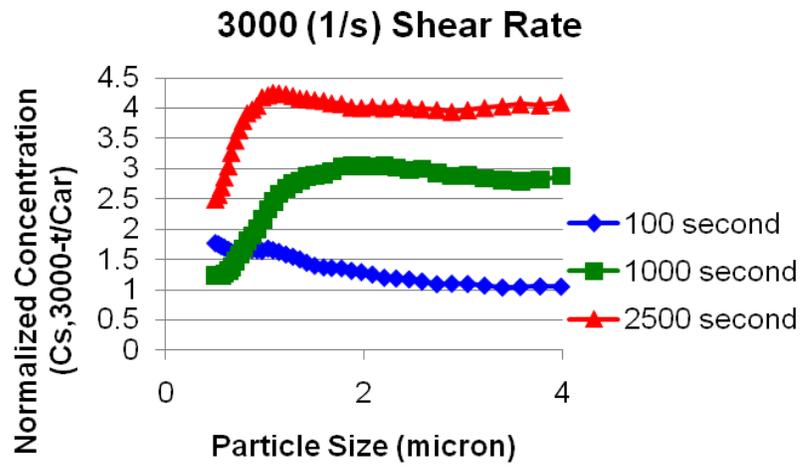


Figure 5-10. Normalized concentration for 3000 s^{-1} and various times at pH~2

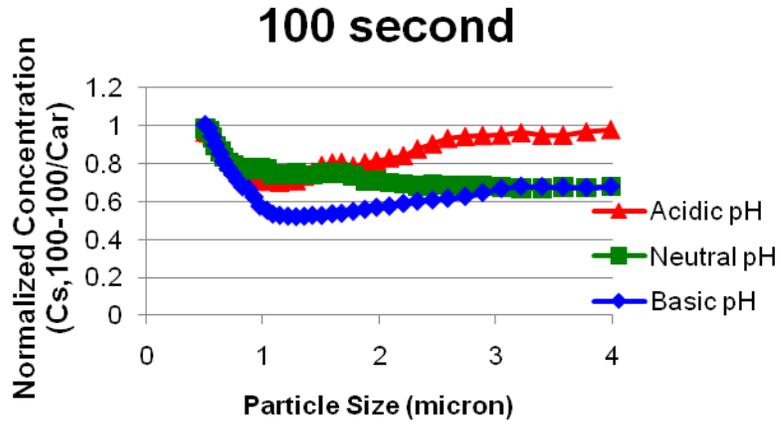


Figure 5-11. Comparison of de-agglomeration of different pH silica slurries for 100 s^{-1} and 100 s

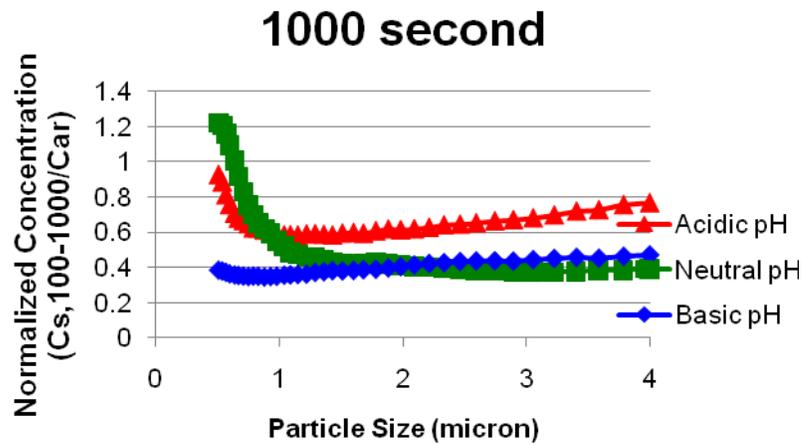


Figure 5-12. Comparison of de-agglomeration of different pH silica slurries for 100 s^{-1} and 1000 s

2500 second

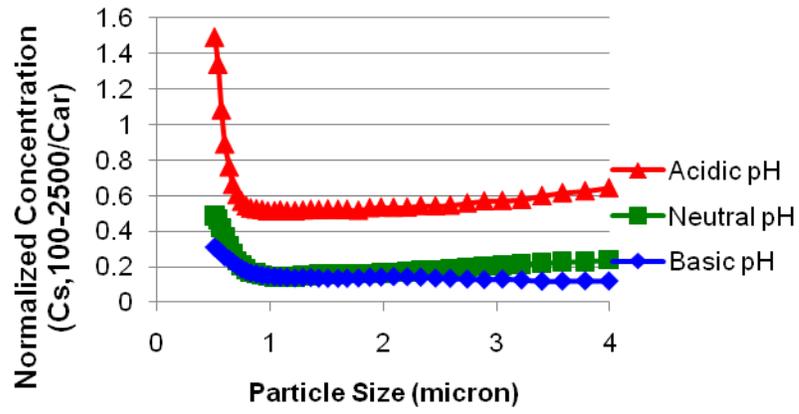


Figure 5-13. Comparison of de-agglomeration of different pH silica slurries for 100 s^{-1} and 2500 s

CHAPTER 6
CHARACTERIZATION OF THE NATURE OF AGGLOMERATES: HARD VS. SOFT
USING RHEOLOGICAL MEASUREMENTS

Introduction

Since its inception, over the past two decades chemical mechanical planarization (CMP) has become a dominant technique for achieving both local and global planarization during manufacturing of integrated circuit (IC). CMP slurries are complex mixtures of oxidizers, abrasives, corrosion inhibitors, buffers and surfactants. The stability of slurry is critical for CMP performance. Changes in slurry chemistry or application of external forces can significantly affect the stability of these slurries.

It has been shown that shear-induced agglomeration due to pumps leads to formation of large particles (agglomerates) that results in significant defects like micro-scratches and other defects on CMP polished wafer surfaces [4, 43-45]. It has emerged that pumps used for slurry delivery results in increase in concentration of oversize ($>0.5 \mu\text{m}$) particles with few studies focusing on the effects of various distribution systems such as different pumps and vacuum-pressure dispense technologies [46-52]. Silica based CMP slurries are colloidal suspensions that are stabilized by repellent electrostatic forces existing between silica particles. However, application of strong external forces can help these particles overcome opposing electrostatic forces and once these particles are close enough, attractive Van Der Waals forces become large enough to overcome inter-particle repulsive forces, thereby leading to agglomeration of silica particles [53, 54]. Feng-Chi et al. showed that effect of shear stress on agglomeration in slurry gets severe with changes in internal slurry chemistry like pH, salt addition and surfactants. Isoelectric point (IEP) of silica slurry is 2.0, so an increase in pH gives increase in stabilization of silica slurry by increasing repulsive forces

between particles. However, the nature of agglomerates formed due to shear induced by pumps needs to be characterized in order to understand type of agglomerates formed i.e. hard or soft and the resulting defects.

Even a small fraction of hard agglomerates result in deformation on the wafer surfaces, resulting in defective microprocessors [55]. Basim et al. [56] showed that presence of hard agglomerates tend to create critical defects on the oxide film and also changes the polishing mechanism. However, some of the agglomerates can be removed by filtration of CMP slurries; nevertheless, there are still defects that are created due to the presence of transient i.e. soft agglomerates that are formed either during the polishing process [57] or during slurry handling. It is critical to characterize the nature of agglomerates formed due to shear-induced agglomeration during slurry handling, in order to determine further course of action to reduce defectivity.

Experimental

EM3530K is a silica slurry with 30-wt%, 35 nm silica particles loading at pH~10. Three types of 10-wt% silica slurries were prepared using EM3530K slurry with pH~10, 7, 2 and these slurries are termed as-received slurries. The pH of the silica slurry was altered using 1N nitric acid. Initial oversize particle distribution of these as-received slurries were measured using Accusizer 780, a single particle optical sensor (SPOS) system. 3 ml of 10wt% silica slurries were subjected to different shear rates 3000 s^{-1} for 1000 s using rheometer UDS 200 and these slurries are termed stressed slurries. After the slurries are subjected to 3000 s^{-1} for 1000 s, the oversize particle distribution of stressed slurries are measured using Accusizer 780 to observe the resulting change in oversize particle distribution. The stressed slurries are then subjected to low shear rates of $100 - 1000 \text{ s}^{-1}$ for 100 s and 1000 s (Table 6-1) and oversize particle distribution is

then measured and the normalized concentration is calculated. The entire experimental process is summarized in flow chart given in Figure 6-1.

Results and Discussion

The formation of agglomerates due to shear induced by pumps is a common problem in CMP industry. The coarser/hard agglomerates present in the slurry during slurry preparation can be filtered out; however, transient agglomerates formed during slurry delivery resulting from shear induced by pumps could result in creation of defects during CMP. The nature of agglomerates formed due to shear-induced agglomeration needs to be characterized to understand the type of defects resulting from the use of the stressed slurry. For forming agglomerates, slurry was subjected to shear rates of 3000 s^{-1} for 1000 s, as agglomeration were observed for the slurries with pH ranging from basic to acidic. The stressed slurries are then subjected to low shear rates for $100 - 1000 \text{ s}^{-1}$ for 100 s and 1000 s to see if we observed de-agglomeration behavior as observed for as-received slurries in previous chapters.

The comparison of de-agglomeration for same shear rate and time in as-received slurry and stressed slurry gives an insight on the nature of agglomerates in stressed slurry. If the extent of de-agglomeration of stressed slurry is more than that of as-received slurry, it indicates that agglomerates in stressed slurry are weaker than those in as-received slurries and hence for same low shear rate and time gives increased break down of agglomerates and these agglomerates can be termed as soft agglomerates. Alternatively, if the extent of de-agglomeration in stressed slurries is less than that in as-received slurries, it indicates agglomerates are stronger in stressed slurry, so the extent of break down is reduced and the agglomerates are termed as hard agglomerates.

Basic pH

The normalized concentration of stressed slurries that are subjected to 100, 500 and 1000 s^{-1} for 100 s and 1000 s are shown in figure 6-2 and 6-3. In previous chapters it was observed that when as-received basic pH slurry is subjected to 100 s^{-1} and 1000 s^{-1} for 100 s and 1000 s they undergo de-agglomeration. Hence, we subjected stressed basic pH slurries to these low shear rates of 100 s^{-1} , 500 s^{-1} and 1000 s^{-1} for 100 s and 1000 s and calculated normalized concentration from their oversize distribution. The de-agglomeration was observed for these stressed slurries as well. However, to characterize the nature of agglomerates in stressed slurries, it is critical to compare the extent of de-agglomeration in stressed slurries with that in as-received slurries. Figure 6-4 shows the comparison of de-agglomeration in stressed slurry with that in as-received slurry under 100 s^{-1} for 100 s and 1000 s. It is observed that extent of de-agglomeration is more in stressed than as-received slurry. This indicates that the agglomerates formed due to shear-induced agglomeration in basic pH slurries are much weaker than that in as-received slurries and hence can be termed as soft agglomerates.

Neutral pH

The normalized concentration of stressed slurries that are subjected to 100, 300 and 500 s^{-1} for 100 s and 1000 s are shown in figure 6-5 and 6-6. In previous chapters it was observed that when as-received neutral pH slurry is subjected to low shear rate for 100 s and 1000 s they undergo de-agglomeration. Hence, we subjected stressed neutral pH slurries to these low shear rates of 100 s^{-1} , 300 s^{-1} and 500 s^{-1} for 100 s and 1000 s and calculated normalized concentration from their oversize distribution. The de-agglomeration was observed for these stressed slurries as well. However, to characterize the nature of agglomerates in stressed slurries, it is critical to compare the

extent of de-agglomeration in stressed slurries with that in as-received slurries. Figure 6-7 shows the comparison of de-agglomeration in stressed slurry with that in as-received slurry under 100 s^{-1} for 100 s and 1000 s. It is observed that extent of de-agglomeration is less in stressed than as-received slurry. This indicates that the agglomerates formed due to shear-induced agglomeration in neutral pH slurries are much stronger than that in as-received slurries making it difficult to break them at low shear rates. Hence, these agglomerates can be termed as hard agglomerates.

Acidic pH

The normalized concentration of stressed slurries that are subjected to 100, 300 and 500 s^{-1} for 100 s and 1000 s are shown in figure 6-8 and 6-9. In previous chapters it was observed that when as-received acidic pH slurry is subjected to low shear rate for 100 s and 1000 s they undergo de-agglomeration. Hence, we subjected stressed acidic pH slurries to these low shear rates of 100 s^{-1} , 300 s^{-1} and 500 s^{-1} for 100 s and 1000 s and calculated normalized concentration from their oversize distribution. The de-agglomeration was observed for these stressed slurries as well. However, to characterize the nature of agglomerates in stressed slurries, it is critical to compare the extent of de-agglomeration in stressed slurries with that in as-received slurries. Figure 6-10 shows the comparison of de-agglomeration in stressed slurry with that in as-received slurry under 100 s^{-1} for 100 s and 1000 s. It is observed that extent of de-agglomeration is less in stressed than as-received slurry. This indicates that the agglomerates formed due to shear-induced agglomeration in acidic pH slurries are much stronger than that in as-received slurries making it difficult to break them at low shear rates. Hence, these agglomerates can be termed as hard agglomerates.

Comparison of Nature of Agglomerates Formed in Slurries with Different pH

From above discussion it is clear that shear-induced agglomerates in basic pH slurries are soft and can be broken easily by subjecting to low shear. However, shear-induced agglomerates in neutral and acidic pH silica slurries are relatively harder. To characterize the strength of shear-induced agglomerates we compare the de-agglomeration of the stressed slurries for three different pH for 100 s^{-1} and time 100 s, 1000 s. The normalized concentration at these shear rates and times are given in Figure 6-11 and 6-12. It is observed that extent of de-agglomeration for basic pH stressed slurry is more than that for neutral and acidic pH slurry. Also extent of de-agglomeration for neutral pH slurry is more than that for acidic pH slurry. These indicate that strength of agglomerates increases from basic to acidic pH slurry and it can be explained based on increased attraction or decrease in repulsive forces between silica particles at acidic pH. Thus, agglomerates in acidic pH stressed slurries are harder, followed by agglomerates in neutral pH stressed slurries that are hard too but relatively less hard than those present in acidic pH stressed slurries. The agglomerates in basic pH stressed slurries are the weakest of all and are termed as soft agglomerates. So in acidic and neutral pH slurries not only is the concentration of oversize particles more than that in basic pH slurry but also the oversize particles are harder in acidic and neutral pH slurries. This explains the observed relative increase in the number of defects when acidic and neutral pH slurries are used instead of basic pH slurry.

Summary

With increase in application of CMP for planarization of various surfaces, there are stricter requirements to have controllability over the defects created during CMP. The

formation of large agglomerates due to shear induced by pumps during slurry delivery is a known problem and an understanding of the nature of agglomerates formed due to shear will be instrumental in finding a way to reduce the formation of these agglomerates. A method was developed to characterize the type of agglomerates formed due to shear-induced agglomeration. The method involves subjecting as-received slurries to high shear rate and time i.e. a condition in which shear-induced agglomeration occurs and then subjected this stressed slurry to low shear rates and time to cause de-agglomeration. The comparison of percentage de-agglomeration in stressed slurries with that in as-received slurries gives an insight into the nature of agglomerates. It was observed that for basic pH silica slurry agglomerates formed due to shear-induced agglomeration are softer. The agglomerates formed in acidic and neutral pH slurries due to shear-induced agglomeration are hard agglomerates, with the ones in acidic pH being the hardest. Thus, in addition to increase in concentration of oversize particles in acidic and neutral pH slurries, presence of hard agglomerates further aggravates formation of defects during CMP when these slurries are used.

Table 6-1. Various low shear rates and times for silica slurry with pH 10 after being subjected to 3000 s^{-1} and 1000 s

Shear Rate (s^{-1})	Time (s)
100	100, 1000
300	100, 1000
500 (for pH 2 and 7) / 1000 (for pH 10)	100, 1000

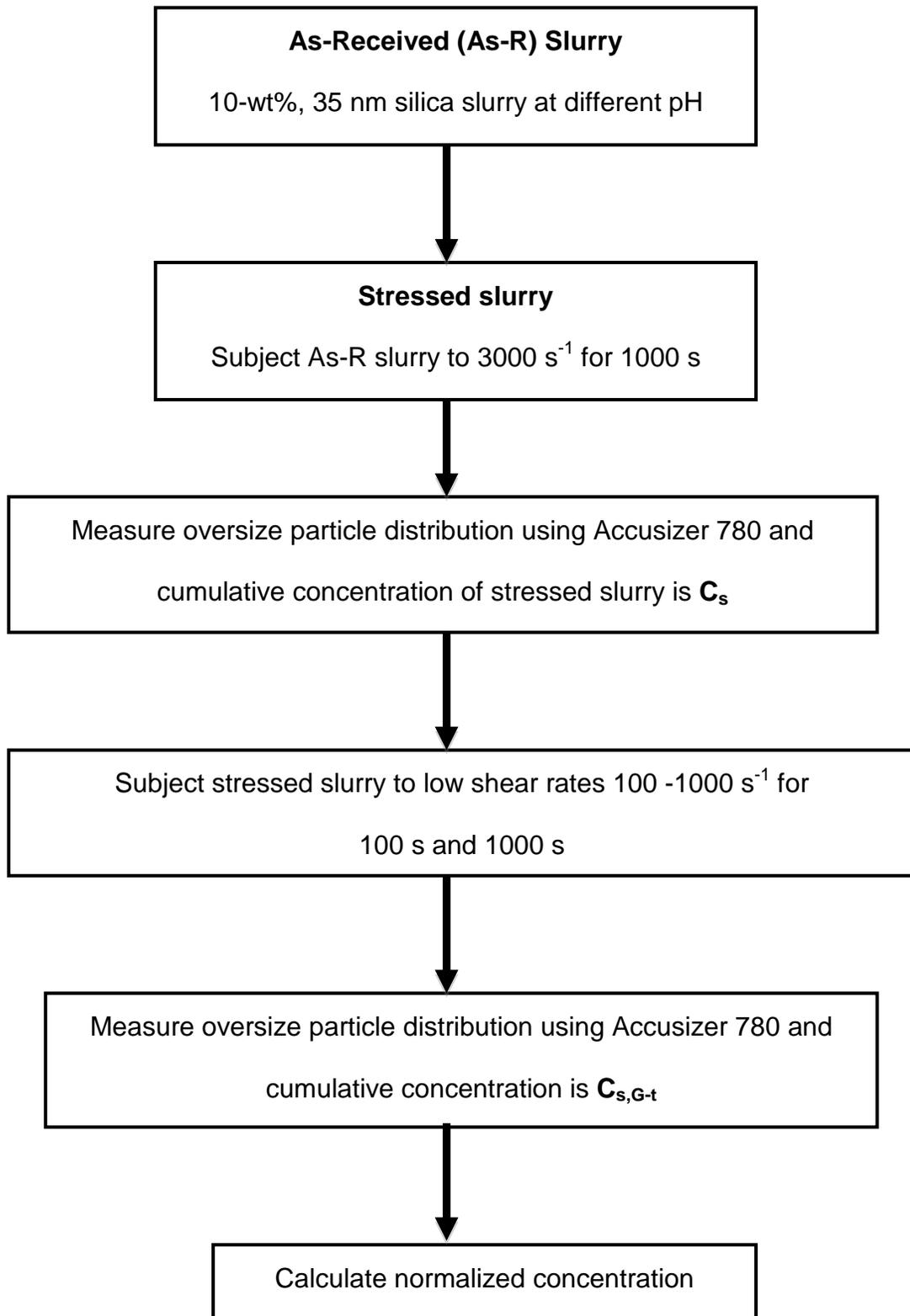


Figure 6-1. Flow chart of experimental procedure

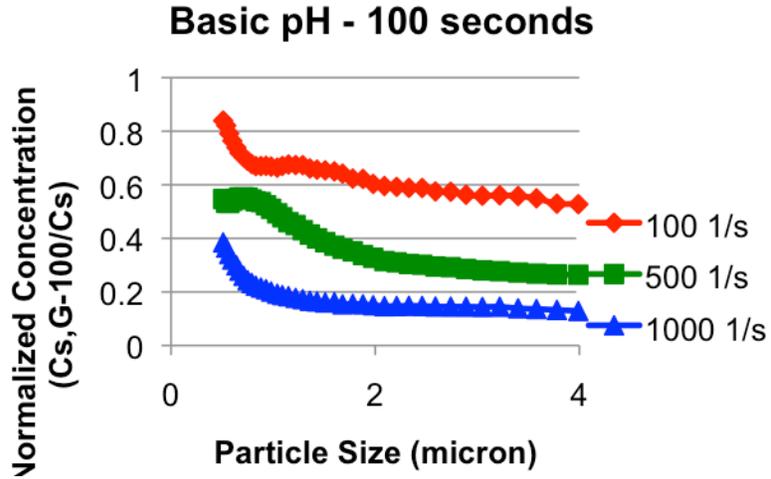


Figure 6-2. Normalized oversize particle distribution for 100 s for various shear rates at pH~10

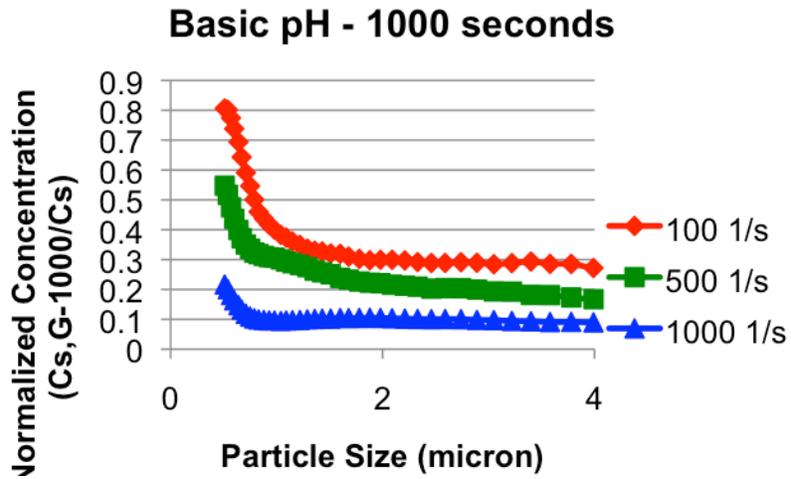


Figure 6-3. Normalized oversize particle distribution for 1000 s for various shear rates at pH~10

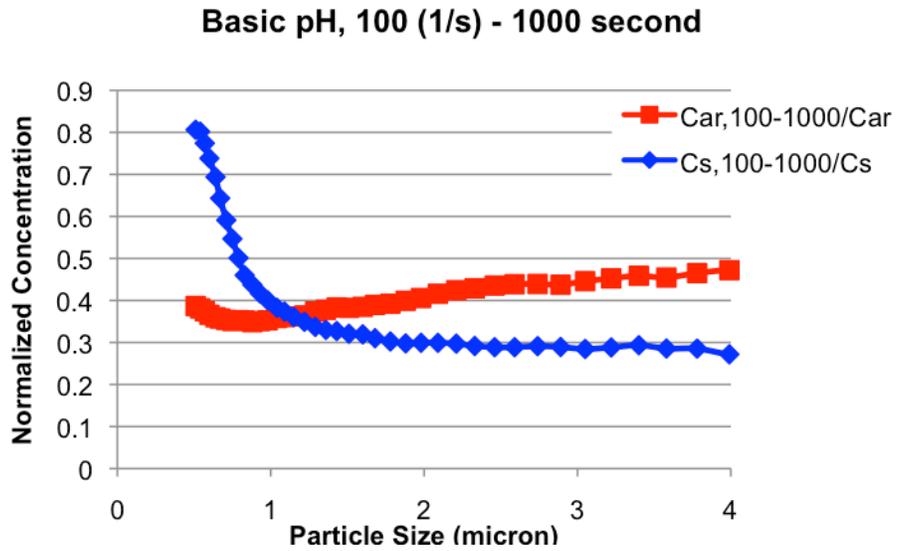


Figure 6-4. Comparison of de-agglomeration in as-received and stressed basic pH silica slurries for 100 s^{-1} and 1000 s

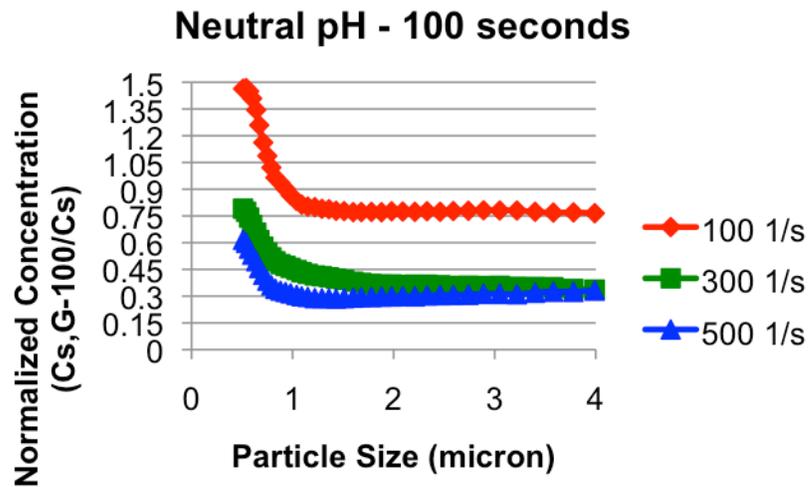


Figure 6-5. Normalized oversize particle distribution for 100 s for various shear rates at $\text{pH} \sim 7$

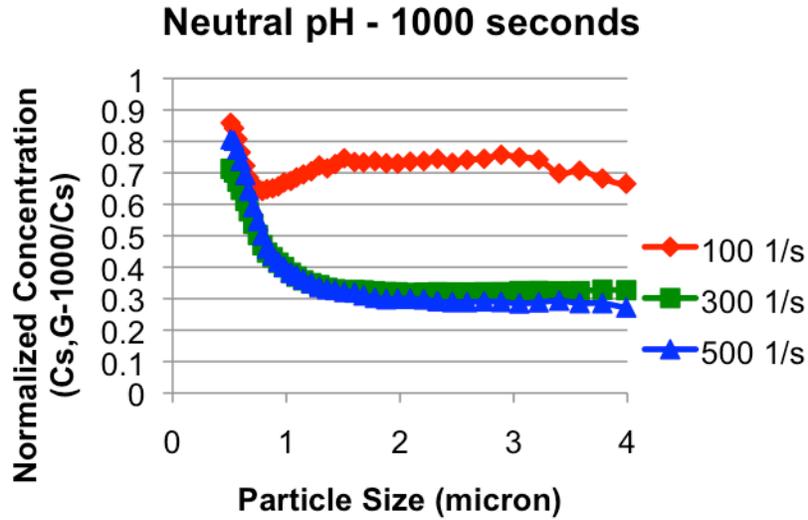


Figure 6-6. Normalized oversize particle distribution for 1000 s for various shear rates at pH~7

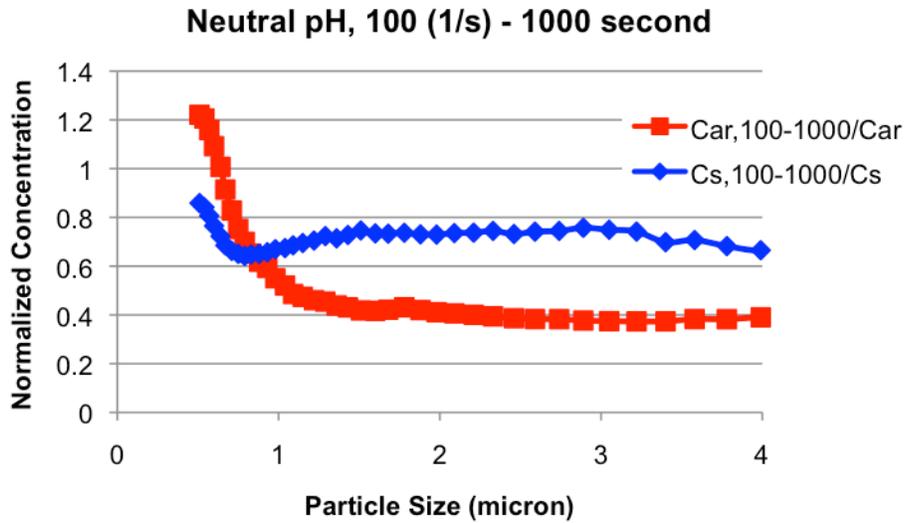


Figure 6-7. Comparison of de-agglomeration in as-received and stressed neutral pH silica slurries for 100 s^{-1} and 1000 s

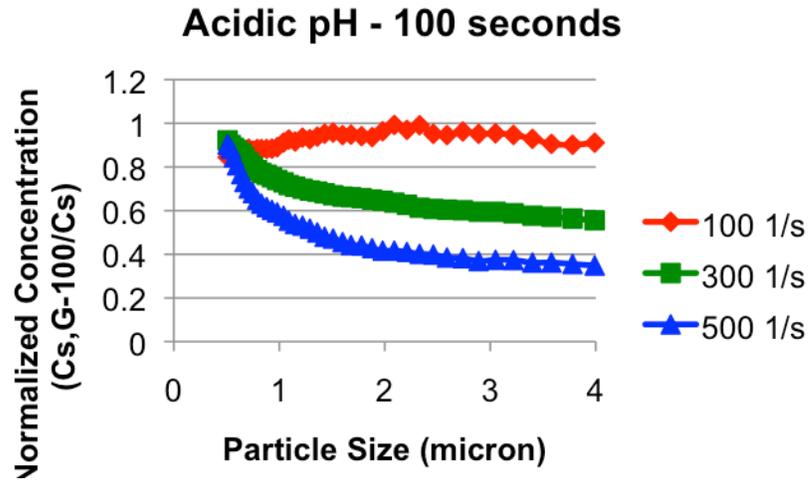


Figure 6-8. Normalized oversize particle distribution for 100 s for various shear rates at pH~2

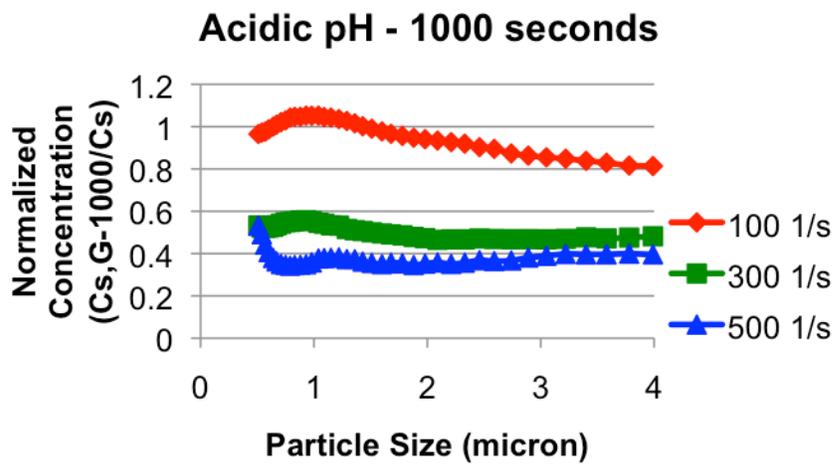


Figure 6-9. Normalized oversize particle distribution for 1000 s for various shear rates at pH~2

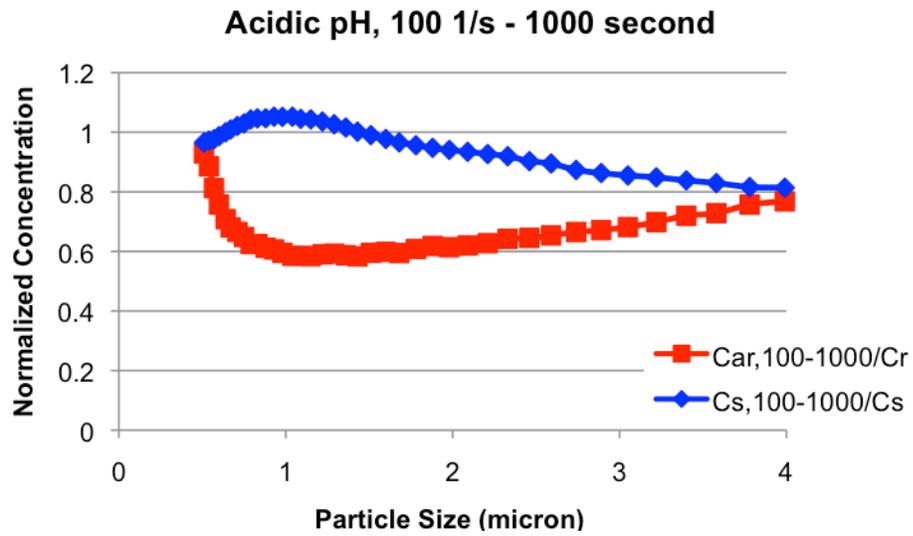


Figure 6-10. Comparison of de-agglomeration in as-received and stressed acidic pH silica slurries for 100 s⁻¹ and 1000 s

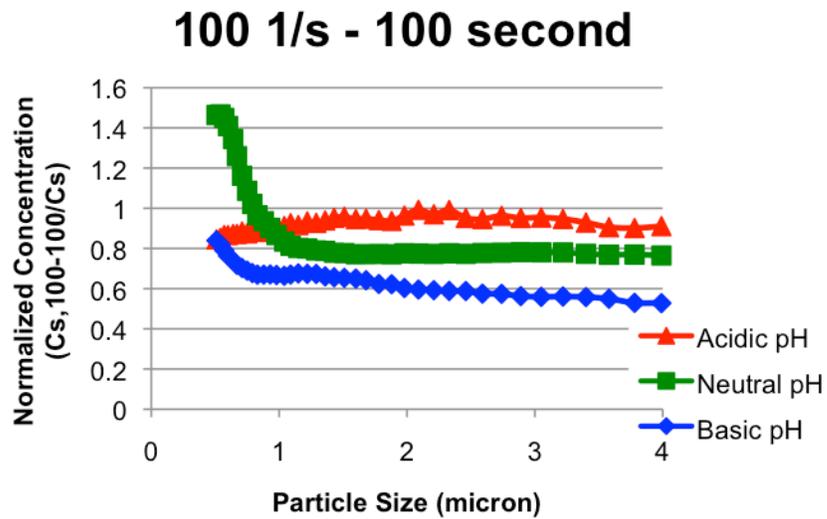


Figure 6-11. Comparison of de-agglomeration in different pH silica slurries for 100 s⁻¹ and 100 s

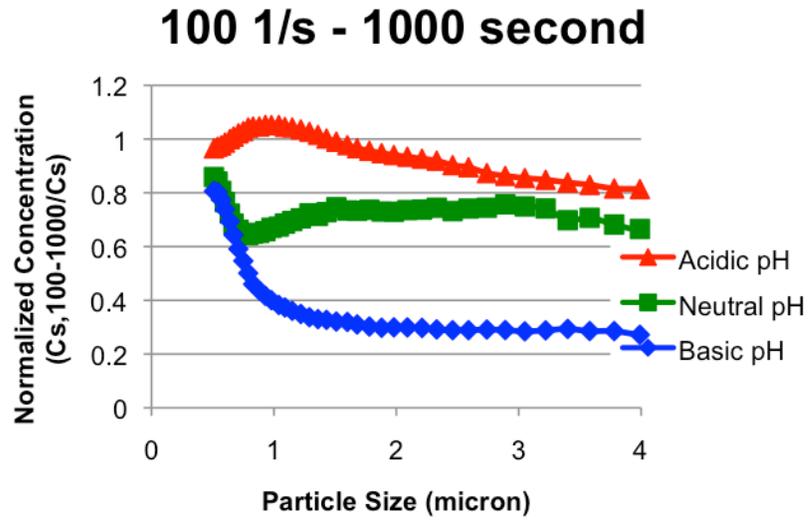


Figure 6-12. Comparison of de-agglomeration in different pH silica slurries for 100 s^{-1} and 1000 s

CHAPTER 7 MEASUREMENT OF STABILITY RATIO: A PARAMETER FOR DEFINING SLURRY STABILITY INDEPENDENT OF SHEAR RATES

Introduction

Chemical mechanical planarization (CMP) process has led to a growth of multi-million dollar industry of CMP consumable especially slurry and nano particles used for CMP slurry formulation. CMP consumables have attracted lot of attraction of researchers in the semiconductor industry especially slurry formulation. Large amount of work in being carried out to formulate various kinds of specialties slurries for different substrates. Initial application of CMP was found in the fabrication of circuit interconnect wiring, so-called back-end processes[8, 58]. Also, the synergistic application of dry etching and CMP was used for fabrication of advanced tungsten plug in addition to copper damascene interconnect structures[59, 60]. With expansion of copper, gallium nitride and other low-k advance applications, it is seen that each of these technologies requires multiple planarization steps and there is a need for creating a well-controlled CMP process. Low-k dielectric films have much lower mechanical properties, which poses new challenges in developing integration schemes like achieving sufficient polishing while maintaining very low down forces during CMP process [17, 61-69]. Especially lot of efforts are directed towards stabilization of slurry and formulating highly stable slurries that involves minimum large size ($> 0.5 \mu\text{m}$) agglomerates. These slurries have slow agglomerate growth rate in response to shear rates that these slurries are subjected to, during slurry delivery as a result of circulation using pumps.[30, 56]

Feng-Chi et al. [32] proposed a term agglomeration index (AI), which is defined as logarithm of the ratio of shear rate to stability ratio, where stability ratio is defined as ratio of number of collisions between particles to the number of collisions leading to

agglomeration. So the inverse of stability ratio defines collision efficiency, so higher the value of stability ratio, lower is the collision efficiency and hence lower are the number of collisions that lead to agglomeration thereby forming large particles in the slurry. Slurry with a lower AI value will be more stable as a result of higher value of stability ratio. Higher value of stability ratio implies lower value of slow coagulation rate, which means that electrostatic interactions are strong enough to keep particles apart due to repulsive forces between them and thereby reduce the rate of formation of agglomerates. They were able to relate AI values to CMP performance in an excellent way by polishing wafers using various slurries and then characterized those wafers by atomic force microscopy (AFM). They concluded that slurries having $AI < 1.8$ were stable ones and did not cause defectivity due to presence of large size agglomerates formed due to shear induced by pumps during slurry circulation. For silica slurry, 35 nm slurry at pH ~10 with AI of 1.36 was the most stable one and caused the least defectivity whereas 35 nm slurry at pH~2 with AI of 4.96 and 135 nm slurry at pH ~10 with Ai of 4.48 were the most unstable slurries and caused large number of defects.

AI values were determined using a high shearing positive displacement pump. If we make use of any other pump with causes different amount of shear stress, we would obtain different AI values, as AI is a function of shear rate applied to the slurry. Now, if an unstable slurry having AI value > 1.8 (AI value obtained using same positive displacement pump that was used by Feng-Chi et al.) is subjected to a low shear stress causing pump, we could obtain an AI value less than 1.8 indicating that it is a stable slurry [32]. So unstable slurry could have AI value less than 1.8 if a low shear pump is used and AI value greater than 1.8 if a positive displacement pump is used. Hence,

there is an urgent need to find a parameter that is independent of shear rate in order to define slurry stability. Generally, zeta potential, particle size measurements are used to monitor stability of slurries qualitatively. However, these measurements are unable to quantify the degree of agglomeration and/or slurry stability as and when the slurries are formulated. In a modification to the novel method developed by Feng-Chi et al. [32], we subject CMP slurries to quantified shear rates using a rheometer, in contrast to a positive displacement pump used in their work. After slurries are subjected to shear by rheometer, we measure their oversize particle distribution using Accusizer 780, which is a single particle optical sensing (SPOS) system. In order to determine AI, Smoluchowski theory of agglomeration was used to model changes in oversize distribution and from AI we can easily calculate stability ratio 'W'.

Experimental

Agglomeration Index (AI) Measurement: AI of CMP slurries is determined using a rheometer Physica Paar UDS 200. AI of slurry was calculated in the following three steps:

- i. Subject CMP slurries to various shear rates $1500 - 3000 \text{ s}^{-1}$ (Table 7-1) using rheometer UDS 200
- ii. Measure oversize particle distribution using SPOS system Accusizer 780
- iii. Model changes in oversize particle distribution using Smoluchowski theory of agglomeration

We selected shear rate of $1500 - 3000 \text{ s}^{-1}$ and 1000 s condition as we were able to obtain agglomeration for all kinds of slurries for these shear rates and time, which is required for modeling the changes in oversize particle distribution. We used various types of slurry for our experimental work with different pH (2, 7 and 10), ionic concentration, particle sizes all with 10-weight percent particle loading. The oversize

particle distribution was then measured using Accusizer 780 (SPOS). This instrument has a two-stage auto dilution system which allows one to use sample of any concentration, as it can dilute the sample to the acceptable concentration for single particle size analysis and can give particle size distribution in 0.51 - 200 μm .

Results and Discussion

Smoluchowski's theory of agglomeration was used to model growth of agglomerates in order to obtain particle size distribution [12, 70]. The theory assumes all particle collisions are binary in nature, proportional to the particle concentration and there is no breaking of agglomerates taking place. Rate of growth of agglomerates singlet, doublets and triplets can be expressed as

$$\frac{dN_1}{dt} = -(k_{11}/W_{11})N_1^2 - (k_{12}/W_{12})N_1N_2 - (k_{13}/W_{13})N_1N_3 \quad [7-1]$$

$$\frac{dN_2}{dt} = (k_{11}/W_{11})N_1^2/2 - (k_{12}/W_{12})N_1N_2 - (k_{23}/W_{23})N_2N_3 \quad [7-2]$$

$$\frac{dN_3}{dt} = (k_{12}/W_{12})N_1N_2 - (k_{13}/W_{13})N_1N_3 - (k_{23}/W_{23})N_2N_3 \quad [7-3]$$

where aggregation constant, $k_{ij} = 4/3 G (a_i+a_j)^3$ is a function of particle size (a) aggregates, i and j -folds and the shear rate (G). From the above equations individual particle concentrations of aggregates can be obtained as follows:

$$N_k = \frac{N_0(t/\tau)^{k-1}}{(1+t/\tau)^{k+1}} \quad [7-4]$$

$$\tau = \frac{W_{ij}}{k_{ij}N_0} \quad [7-5]$$

where N_0 is the initial total particle concentration, t is the aggregation time and W is the stability ratio, which is defined as the ratio of rapid coagulation rate to slow coagulation rate in presence of electrostatic interactions between abrasive particles [13]. Figure 7-1 shows fitting of experimental and simulated curves. Simulation of growth of aggregates is done using initial oversize particle distribution and then by curve fitting experimental and modeling curves we determine AI value.

CMP slurry stability is determined to a large extent by the amount of agglomerates in the slurry. Agglomeration index for different slurries at various shear rates were calculated by following the steps described above and is given in Table 7-2, 7-3 and 7-4. Now, AI is defined as logarithm of the ratio of shear rate to stability ratio of slurry and since we subject the slurry to quantified shear rate using rheometer, we can easily calculate value of stability ratio.

$$AI = \log (G/W) \quad [7-6]$$

Simplifying further and solving for W , we get

$$W = G / 10^{(AI)} \quad [7-7]$$

where G is shear rate. The values of stability ratio are calculated for the slurries at different shear rates. From Figure 7-2 it is seen that stability ratio of a slurry is constant for a given slurry condition and independent of shear rate that is applied to the slurry. The values of stability ratio for various slurries are detailed in Table 7-5. It is seen that silica slurry of 35 nm primary particle size at pH ~10 and no salt has the highest stability ratio which makes it the most stable of all the slurries tested and silica slurry of 35 nm particle size at pH ~2 with 0.1M KCl is the most unstable form of slurry and susceptible to severe shear induced agglomeration. Also changing the primary particle size

significantly influences slurry stability and the values of stability ratio shows that 135 nm silica slurry at pH~10 is significantly more unstable than 35 nm silica slurry at pH ~10. These conclusions regarding stability of various silica slurries is in agreement with the conclusions derived in previous work by Feng-Chi et al., however, the stability ratio which is used to define slurry stability here is independent of shear rate and hence a better way to define slurry stability.

From equation [7-6] it is evident that AI value is a function of shear rate and one will obtain different AI values when different shearing device is used. Hence, it undermines the effort of finding AI values for measuring slurry stability if a different shearing device is used. However, stability ratio being independent of shear rate is a better way to define slurry stability. The stability ratio is also defined as ratio of the number of collisions between the particles to the number of collisions leading to agglomeration. The inverse of stability ratio gives collision efficiency, so lower is the value of stability ratio, higher is the value of collision efficiency, which implies more collisions between particles leading to agglomeration.

Summary

Chemical mechanical planarization (CMP) is the widely used method for surface planarization. CMP slurry is a critical component of CMP process and presence of large particles significantly affects the amount of defects, surface finish and material removal rate. There is an urgent need for a parameter that defines slurry stability independent of shear rate. In the present work, agglomeration index (AI) was computed for various slurries at different shear rates. AI was used to calculate stability ratio for various slurries at different shear rates. However, stability ratio was found to be constant for a given slurry condition, independent of shear rate applied to the slurry. Comparison of

the values of stability ratio shows that silica slurry of 35 nm primary particle size at pH ~10 and no salt, is the most stable and the silica slurry of 35 nm particle size at pH ~2 with salt is the most unstable form of slurry and susceptible to severe shear induced agglomeration. Also, 35 nm silica slurry at pH ~10 is significantly more stable than 135 nm silica slurry at pH ~10.

Table 7-1. Different shear rates and times for various silica slurries

Shear Rates (s^{-1})	Time (s)
1500	1000
2000	1000
3000	1000

Table 7-2. Assigned name for various slurries

Slurry Type	Assigned Name
Silica: pH 10, 35 nm	A
Silica: pH 7, 35 nm	B
Silica: pH 2, 35 nm	C
Silica: pH 2 + 0.1M KCl, 35 nm	D

Table 7-3. Agglomeration index (AI) for different slurries at various shear rates (s^{-1})

Shear Rate (s^{-1})	A	B	C	D
1500	1.97	2.30	2.61	3.07
2000	2.09	2.42	2.74	3.17
3000	2.27	2.60	2.91	3.39

Table 7-4. Agglomeration indexes (AI) for different slurries at shear rate of $3000 s^{-1}$

Slurry Type	AI
Silica: pH 10 + 0.1M KCl, 35 nm	2.44
Silica: pH 7 + 0.1M KCl, 35 nm	2.81
Silica: pH 10, 135 nm	3.28

Table 7-5. Stability ratio for various slurries

Slurry Type	Stability Ratio
Silica: pH 10, 35nm (A)	16.53
Silica: pH 10 + 0.1M KCl, 35nm	10.8
Silica: pH 7, 35nm (B)	7.61
Silica: pH 7 + 0.1M KCl, 35nm	4.65
Silica: pH 2, 35nm (C)	3.64
Silica: pH 2 + 0.1M KCl, 35nm (D)	1.28
Silica: pH 10, 135nm	1.56

Curve Fitting to obtain A.I.

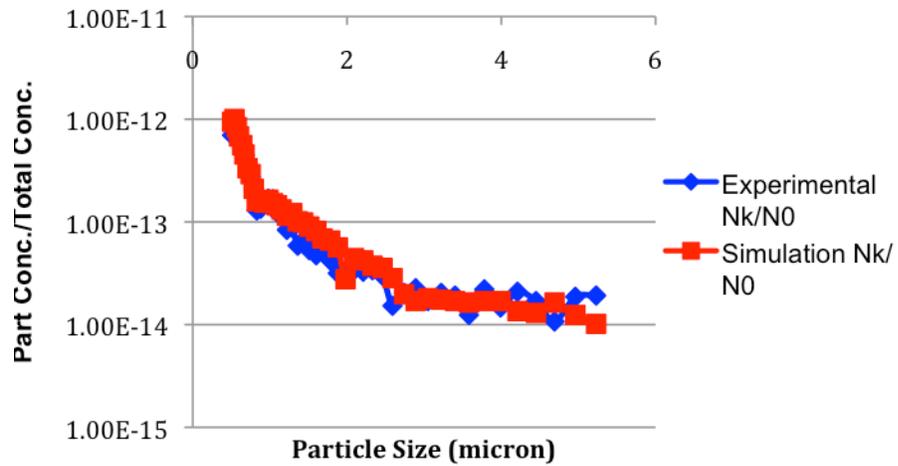


Figure 7-1. Schematic illustration of fitting experimental and modeled tail distributions to obtain the agglomeration index

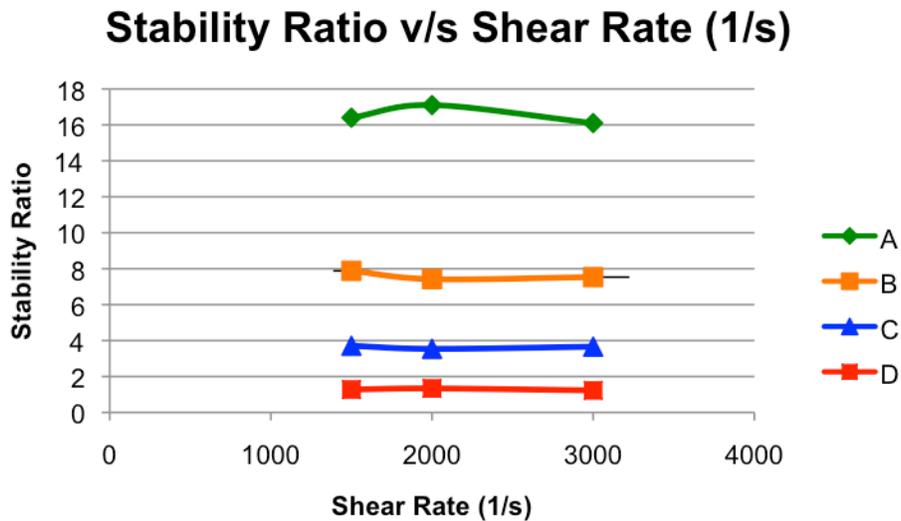


Figure 7-2. Stability ratio v/s different shear rates (s^{-1})

CHAPTER 8 CONCLUSIONS

Chemical mechanical planarization (CMP) is the most commonly used method used to achieve local as well as global planarization of metals and dielectrics. With increasing miniaturization of devices there are more exacting requirements on the performance of CMP process where material removal rate and surface finish decides CMP performance to a large extent. Presence of large oversize particles (>0.5 micron) in the slurry is one of the main reasons for resulting defects during CMP process. One of the main reasons for presence of large particles in the slurry is due to usage of pumps during slurry delivery. The shear rate of pumps is known to cause agglomeration problem in CMP slurries, with increasing shear rate leading to increase in agglomeration in the slurries. However, so far all the work on shear-induced agglomeration has been qualitative or at best semi-quantitative in nature.

In the present work, a novel technique to study agglomeration behavior as a function of quantified shear rates is developed. Rheometer was used as a means to subject slurry to quantified shear rates for different times. The resulting change in oversize particle distribution was measured using Accusizer 780, a single particle optical sensing (SPOS) system. The behavior of silica slurry when subjected to different shear rates falls into two regimes, one de-agglomeration and other agglomeration. There is a threshold shear rate for each slurry condition, above which agglomeration is observed and below which de-agglomeration is observed. The de-agglomeration increased as the slurry pH was increased and away from its isoelectric point at pH \sim 2. Based on percentage de-agglomeration the strength of the agglomerates present in the as-received basic pH slurry is seen to be less than that for neutral and acidic pH

slurries. The increase in attractive forces between silica particles as the pH is lowered towards isoelectric point leads to formation of stronger agglomerates in acidic and neutral pH slurries, with agglomerates in acidic pH slurry being stronger than that in neutral pH slurries. The threshold shear rate to initiate agglomeration in basic pH silica slurry is 2000 s^{-1} , for neutral pH is 1500 s^{-1} and for acidic pH is 1000 s^{-1} . The decrease in threshold shear rate was seen to be due to decrease in repulsive forces between the interacting silica particles as the slurry pH is reduced.

The nature of agglomerates hard or soft could determine the kind of defects created during the CMP process. The large particles that are present in the slurry could be filtered out, however, the transient agglomerates are generated due to shear induced by pump, which create defects on CMP polished wafer surfaces. To understand the nature of agglomerates, the slurry is subjected to high shear rates and times such as 3000 s^{-1} and 1000 s , corresponding to the conditions for which agglomeration was observed for all slurries. Subsequently, the stressed slurry is subjected to lower shear rates and times such as $100 - 1000 \text{ s}^{-1}$, 100 s and 1000 s , corresponding to the conditions for which de-agglomeration is observed for as-received slurries. Based on comparison of percentage de-agglomeration in stressed and as-received slurries, it is qualitatively showed that all the agglomerates formed due to shear-induced agglomeration in basic pH slurries are soft agglomerates, whereas as those formed in neutral and acidic pH stressed slurries are hard agglomerates, with agglomerates in acidic pH slurry being stronger than that in neutral pH slurries. In this way a unique method is developed to characterize the nature of shear-induced agglomerates.

Finally, the agglomeration index (AI) was explored further to calculate stability ratio, a parameter for defining slurry stability independent of shear rate. Stability ratio showed that it is constant for a given slurry condition and does not change with shear rates. The values of stability ratios are 1.26 - 16.53 depending upon slurry conditions and higher the value of stability ratio implies higher is the slurry stability. Based on comparison of stability ratios with previous work on agglomeration index and CMP polished wafers using silica slurries; it is seen that for 10-wt% particle loading, 35 nm basic pH silica slurry is the most stable and 35 nm acidic pH slurry and 135 nm basic pH slurry are the most unstable among the set of slurries that were studied. Thus, AI was used to calculate stability ratio that defines CMP slurry stability under varied shear environment.

LIST OF REFERENCES

- [1] S. M. Sze, *VLSI Technology*, 2nd ed. New York: McGraw Hill, 1988.
- [2] R. K. Singh and R. Bajaj, "Advances in chemical-mechanical planarization," *MRS Bulletin*, vol. 27, pp. 743-751, 2002.
- [3] I. M. Steigerwald, Murarka, S.P., Gutmann, R.J., *Chemical-Mechanical Planarization of Microelectronic Materials*. New York: John Wiley & Sons, 1997.
- [4] F. C. Chang, S. Tanawade, and R. K. Singh, "Effects of Stress-Induced Particle Agglomeration on Defectivity during CMP of Low-k Dielectrics," *Journal of the Electrochemical Society*, vol. 156, pp. H39-H42, 2009.
- [5] A. E. Braun, "CMP becomes gentler, more efficient," in *Semiconductor International*, vol. 24, Nov. 2001, pp. 54-61.
- [6] V. Shannon, Smith, D.C., "Copper Interconnects for High-Volume Manufacturing," in *Semiconductor International*, vol. 24, May 2001, pp. 93-97.
- [7] S. Wolf, Tauber, R.N., *Silicon Processing for the VLSI Era: Process Technology*, vol. 1, 2nd ed. Sunset Beach, CA: Lattice Press, 1999.
- [8] F. B. Kaufman, Thompson, D.B., Broadie, R.E., Jaso, M.A., Guthrie, W.L., Pearson, D.J., Small, M.B., "Chemical-Mechanical Polishing for Fabricating Patterned W Metal Features as Chip Interconnects," *Journal of Electrochemical Society*, vol. 138, pp. 3460-3465, Nov. 1991.
- [9] F. Preston, "The Traction of Glass Polishing," *Journal of the Society of Glass Technology*, vol. 12, pp. 3-6, 1928.
- [10] N. J. Brown, Baker, P.C., Maney, R.T., "Optical Polishing of Metals," presented at Contemporary Methods of Optical Fabrication, SPIE - The International Society for Optical Engineering Bellingham, Bellingham, WA, 1981.
- [11] L. M. Cook, "Chemical processes in glass polishing," *Journal of Non-Crystalline Solids*, vol. 120, pp. 152-171, 1990.
- [12] M. Elimelech, J. Gregory, X. Jia, and W. R.A, "Particle Deposition and Aggregation - Measurement, Modelling and Simulation," Elsevier, 1998.
- [13] H. Stechemesser, Dobias, B., *Coagulation and Flocculation*, Second ed. Boca Raton: CRC Press, Taylor and Francis Group, 2005.
- [14] K. O. Higashitani, Ryuji; Hosokawa, Gijiro; Matsuno, Yoshizo "Kinetic theory of shear coagulation for particles in a viscous fluid " *Journal of Chemical Engineering of Japan* vol. 15, pp. 299-304, 1982.

- [15] U. Mahajan, Biemann, M., Singh, R.K., "Dynamic Lateral Force Measurements during Chemical Mechanical Polishing of Silica," *Electrochemical and Solid State Letters*, vol. 2, pp. 80-82, Feb. 1999.
- [16] M. Biemann, Mahajan, Y., Singh, R.K., "Effect of Particle Size during Tungsten Chemical Mechanical Polishing," *Electrochemical and Solid State Letters*, vol. 2, pp. 401-403, Aug. 1999.
- [17] R. K. Singh, Bajaj, R., Moinpour, M., Meuris, M., *Chemical-Mechanical Polishing 2000 - Fundamentals and Materials Issues*, vol. 613, 2001.
- [18] M. Biemann, Mahajan, Y., Singh, R.K., Agarwal, P., Mischler, S., Rosset, E., Landolt, D., *Chemical- Mechanical Polishing - Fundamentals and Challenges*, vol. 566. Warrendale, PA., 2000.
- [19] G. B. Basim, J. J. Adler, U. Mahajan, R. K. Singh, and B. M. Moudgil, "Effect of Particle Size of Chemical Mechanical Polishing Slurries for Enhanced Polishing with Minimal Defects," *Journal of The Electrochemical Society*, vol. 147, pp. 3523-3528, 2000.
- [20] S.-M. Lee, Choi, W., Craciun, V., Jung, S. -H., Singh, R.K., , "Electrochemical Measurements to Understand the Dynamics of the Chemically Modified Surface Layer Formation During Copper CMP," presented at Materials Research Society, San Francisco, CA, April 2002.
- [21] S. Mischler, Debaud, S., Landolt, D., "Wear-Accelerated Corrosion of Passive Metals in Tribocorrosion Systems," *Journal of the Electrochemical Society*, vol. 145, pp. 750-758, Mar. 1998.
- [22] R. J. Hunter, *Foundations of colloid science / Robert J. Hunter*. Oxford ; New York : Oxford University Press, 2001.
- [23] M. J. Rosen, *Surfactants and Interfacial Phenomena*: John Wiley & Sons, Inc., 2004.
- [24] G. B. Basim, I. U. Vakarelski, and B. M. Moudgil, "Role of interaction forces in controlling the stability and polishing performance of CMP slurries," *Journal of Colloid and Interface Science*, vol. 263, pp. 506-515, 2003.
- [25] I. D. Morrison, Ross, S., *Colloidal suspensions: Suspensions, Emulsions, and Foams*: John Wiley and Sons Inc., 2002.
- [26] D. H. Napper, *Polymeric stabilization of colloidal dispersions* Academic Press, London, New York, 1983.
- [27] B. J. Palla and D. O. Shah, "Stabilization of High Ionic Strength Slurries Using the Synergistic Effects of a Mixed Surfactant System," *Journal of Colloid and Interface Science*, vol. 223, pp. 102-111, 2000.

- [28] T. Y. Teo, W. L. Goh, V. S. K. Lim, L. S. Leong, T. Y. Tse, and L. Chan, "Characterization of scratches generated by a multiplaten copper chemical--mechanical polishing process," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, vol. 22, pp. 65-69, 2004.
- [29] "Interconnect," *International Technology Roadmap for Semiconductors*, pp. 1-67, 2007.
- [30] F. C. Chang, "Externally Induced Agglomeration During Chemical Mechanical Polishing of Metals and Dielectrics," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2008, pp. 1-123.
- [31] G. B. Basim and B. M. Moudgil, "Effect of soft agglomerates on CMP slurry performance," *Journal of Colloid and Interface Science*, vol. 256, pp. 137-142, 2002.
- [32] F. C. Chang and R. K. Singh, "Method for Quantifying the Degree of Agglomeration in Highly Stable Chemical Mechanical Polishing Slurries," *Electrochemical and Solid State Letters*, vol. 12, pp. H127-H130, 2009.
- [33] P. Bowen, "Particle Size Distribution Measurement from Millimeters to Nanometers and from Rods to Platelets," *Journal of Dispersion Science and Technology*, vol. 23, pp. 631 - 662, 2002.
- [34] D. F. Nicoli, K. Hasapidis, P. O'Hagan, D. C. McKenzie, J. S. Wu, Y. J. Chang, and B. E. H. Schade, "High-Resolution Particle Size Analysis of Mostly Submicrometer Dispersions and Emulsions by Simultaneous Combination of Dynamic Light Scattering and Single-Particle Optical Sensing," in *Particle Size Distribution III*, vol. 693, *ACS Symposium Series*: American Chemical Society, 1998, pp. 52-76.
- [35] P. Nicomp, "Accusizer 780 APS Manual," PSS Nicomp.
- [36] P. Paar, "Rheometer UDS 200 Manual."
- [37] "Interconnect," *International Technology Roadmap for Semiconductors*, pp. 1-178, 2002.
- [38] R. A. A. Sorooshian, H. K. Choi, M. Moinpour, A. Oehler, A. Tregub "Effect of Particle Interaction on Agglomeration of Silica-Based CMP Slurries," presented at Materials Research Society (MRS), San Francisco, 2004.
- [39] T. R. Camp, "Flocculation and flocculation basins," presented at ASCE, 1953.
- [40] L. Shon-Roy, "CMP: Market Trends and Technology," in *Solid State Technology*, vol. 43, 2000, pp. 67.
- [41] K. D. Beyer, *IBM Micronews*, vol. 5, 1999.

- [42] T. Tucker, Plenary Talk, "Key Issues related to CMP Market Segments," in *Chemical Mechanical Polishing 2001- American Vacuum Society*. San Jose, October 2001.
- [43] G. Vasilopoulos, et al., "STI CMP Defect Reduction with Slurry Filtration," presented at VLSI Multilevel Interconnect Conference (VMIC), June 2000.
- [44] T. Nishiguchi, "CMP Consumable Technologies in PERL Hitachi," presented at ERC Retreat & IAB Meeting, 2001.
- [45] K. Nicholes, et al., "Analysis of Wafer Defects Caused by Large Particles in CMP Slurry using Light Scattering and SEM Measurement Techniques," presented at Eight International Chemical-Mechanical Planarization for ULSI Multilevel Interconnection Conference (CMP-MIC), Marina Del Ray, CA, Feb. 2003.
- [46] B. Johl, Singh, R., "Optimum Process Performance Through Better CMP Slurry Management," in *Solid State Technology*, vol. 46, Aug. 2003.
- [47] B. Johl, et al., "Dynamic Pot-Life and Handling Evaluation of EPL2362 First Step Copper Slurry," presented at 8th International CMP Conference, Marina Del Ray, CA, Feb. 2003.
- [48] B. Johl, Buley, T., "Dynamic Pot-Life and Handling Evaluation of Rodel CUS1351 Copper Barrier Slurry," presented at 7th International CMP Conference, San Jose, 2002.
- [49] B. Johl, et al., "Accelerated Aging and Handling Evaluation of Rodel CUS1201 Second Step Slurry in BOC Edwards Bulk Delivery System," presented at VMIC Conference, 2001.
- [50] B. Johl, Singh, R., "Characterization of a Silica Based STI CMP Slurry in a Vacuum-Pressure Dispense Slurry Delivery System and Pump Loop," presented at VMIC Conference, 2001.
- [51] B. Johl, Bare, J.P., "Accelerated Aging and Handling Evaluation of Rodel ILD1300 Oxide CMP Slurry," presented at AVS N. California CMPUG Annual Symposium, CA, 1997.
- [52] B. Johl, Bare, J.P., "Comparison of Humidified vs. Non-humidified Vacuum Pressure CMPS Slurry Distribution System," presented at VMIC Conference, 1998.
- [53] B. M. Moudgil, "Stability of Colloidal Suspensions for CMP Applications," presented at Levitronix CMP Users Conference, Santa Clara, CA, Feb. 2005.
- [54] J. Bare, Johl, B., Lemke, T., "Comparison of Vacuum-Pressure vs. Pump Dispense Engines for CMP Slurry Distribution," in *Semiconductor International*, Jan. 1999.

- [55] J. Schlueter, presented at SemiCon Southwest, 1995.
- [56] G. B. Basim, "Formulation of Engineered Particulate Systems for Chemical Mechanical Polishing Applications," in *Materials Science & Engineering*, vol. Ph.D. Gainesville, Florida: University of Florida, 2002, pp. 1-141.
- [57] "Material Safety Data Sheet for Semi-Sperse 12 and 25 Aqueous Dispersions," Cabot Corporation Microelectronics Division, Aurora, IL 2000.
- [58] W. J. Patrick, W. L. Guthrie, C. L. Standley, and P. M. Schiabile, "Application of Chemical Mechanical Polishing to the Fabrication of VLSI Circuit Interconnections," *Journal of The Electrochemical Society*, vol. 138, pp. 1778-1784, June 1991.
- [59] F. White, W. Hill, S. Eslinger, E. Payne, W. Cote, B. Chen, and K. Johnson, "Damascene stud local interconnect in CMOS technology," presented at Electron Devices Meeting, 1992. Technical Digest., International, 1992.
- [60] J. Givens, Geissler, S., Cain, O., Clark, W., Koburger, C., Lee J., "A Low-Temperature Local Interconnect Process in a 0.25 μm Channel CMOS Logic Technology with Shallow Trench Isolation," presented at Proceedings of the 11th International VLSI Multilevel Interconnection Conference, 1994.
- [61] S. Hayashi, Poust, B., Heying, B., Goorsky, M.S., "Silicon Carbide and Related Materials 2003," *Trans Tech Publications*, pp. 1605, 2004.
- [62] C. Lian, Xing, H., Wang, S., McCarthy, L., Brown, D., "DC Characteristics of AlGaAs/GaAs/GaN HBTs Formed by Direct Wafer Fusion," *IEEE Electron Device Letters*, vol. 28, pp. 8-10, 2007.
- [63] A. Tauzin, Akatsu, T., Rabarot, M., Dechamp, J., Zussy, M., Moriceau, H., Michaud, J.F., "Transfers of 2-inch GaN films onto sapphire substrates using Smart CutTM technology," *Electronics Letters*, vol. 41, pp. 668-670, 2005.
- [64] L. Jay, Ma, Y., Wang, Y., Bajaj, R., Redekar, F., "Process and Material Challenges for 0.1- μm Copper Technology," presented at Presented at 5th International Symposium on Chemical-Mechanical Polishing, Lake Placid, NY, Aug. 2000.
- [65] R. Bajaj, Redekar, F., Wijekoon, K., "Unlocking the Damascene Puzzle," presented at VMIC Conference, Santa Clara, CA, Jun. 2000.
- [66] S. V. Babu, Cadien, K.C., Yano, H., , *Chemical-Mechanical Polishing 2001-Advances and Future Challenges*, vol. 671. Warrendale, PA, 2001.
- [67] S. Tsai, [CD-ROM], presented at Proceedings IITC Conference, IEEE Electron Devices Society, Piscataway, NJ, 2002.

- [68] C.-C. Chang, [CD-ROM] presented at Proceedings IITC Conference, IEEE Electron Devices Society, 2002.
- [69] K. C. Yu, [CD-ROM], Piscataway, NJ., 2002.
- [70] W. B. Russel, Saville, D. A., Schowalter, W. R., *Colloidal Dispersions*. United Kingdom: Cambridge University Press, 1989.

BIOGRAPHICAL SKETCH

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