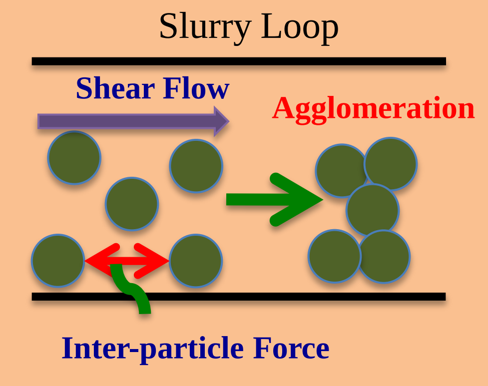
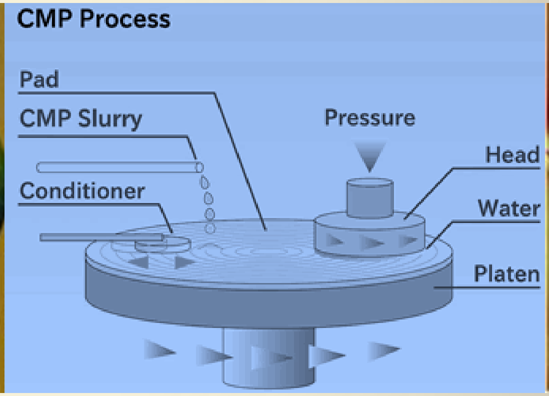
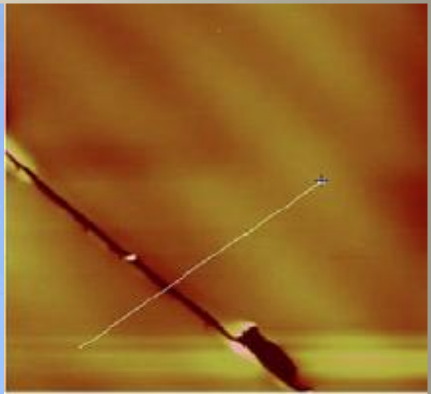
QUANTIFICATION OF PARTICLE AGGLOMERATION DURING CHEMICAL MECHANICAL POLISHING OF METALS AND DIELECTRICS


Slurry Loop


CMP Process



Aniruddh J. Khanna, Rajiv K. Singh

Materials Science & Engineering,

University of Florida

Sinmat Inc

UNIVERSITY OF FLORIDA
The Foundation for The Gator Nation.

Overview: Sinmat Inc.

- University of Florida Spin-off. Developing planarization technologies the semiconductor industry
- Winner of four R&D 100 Awards 2004 & 2005, 2008, 2009
- Employees: 25
- Approx 50 % revenue from commercial products
- Developing several CMP centric technologies - LEDs; Power/RF devices; Ultra large wafer polishing

2004, 2005, 2008, 2009

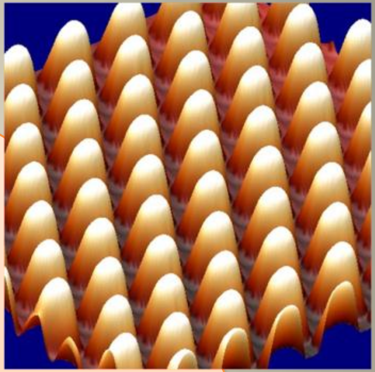
President Obama congratulates Sinmat at White House for transforming R&D into clean energy jobs (March 2009)

Sinmat’s Core Competency

Develop A High Quality, Affordable Supply Of Innovative Surface Preparation-Promoting Products To Serve A Variety Of Markets

Sinmat’s Core Business

Chip Mfg Markets
- Intel
- Samsung
- Texas Instrument
- Toshiba

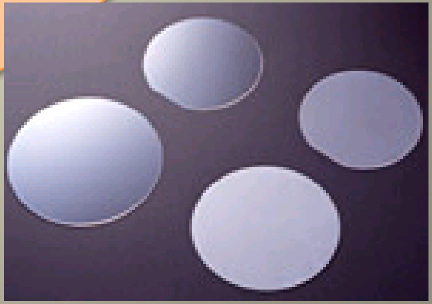


Power Device Markets
- Cree
- RF Micro
- Raytheon
- Rohm

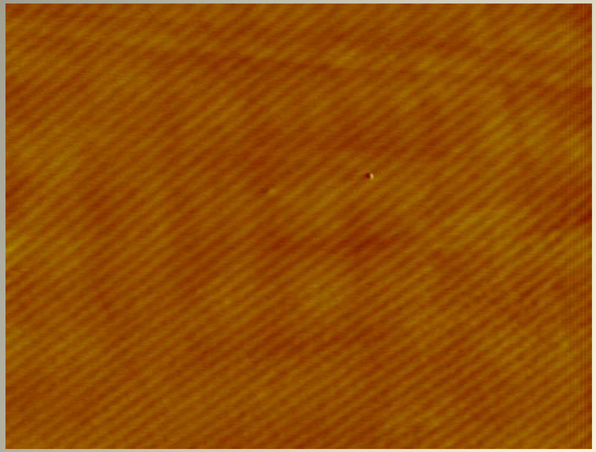
High Quality, Affordable Supply of Innovative Engineered Surface Promoting Products

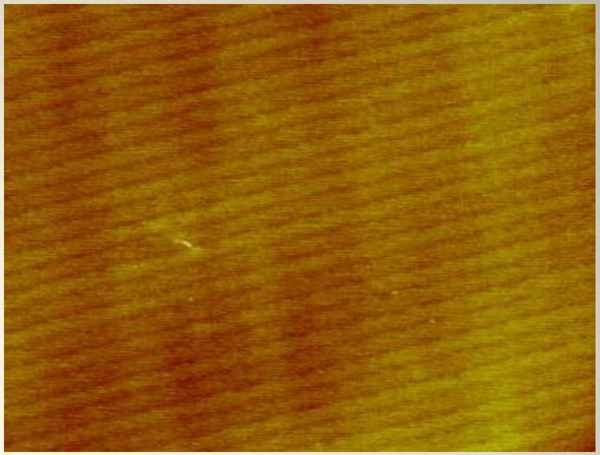
LED Markets
- Cree
- Philips
- Osram
- Nichia
- Kyocera

Solar Device Mfg Markets
- First Solar
- Unisolar
- Helio Volt
- Solo Power



Surface Finish of SiC/GaN

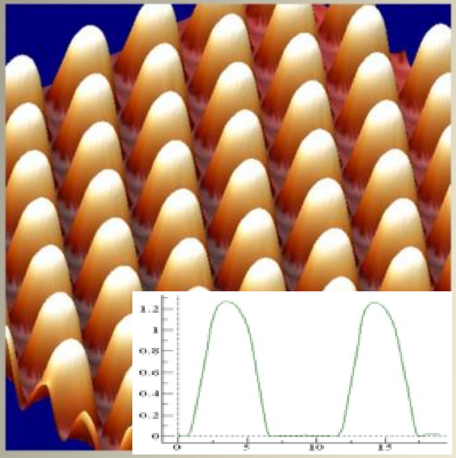


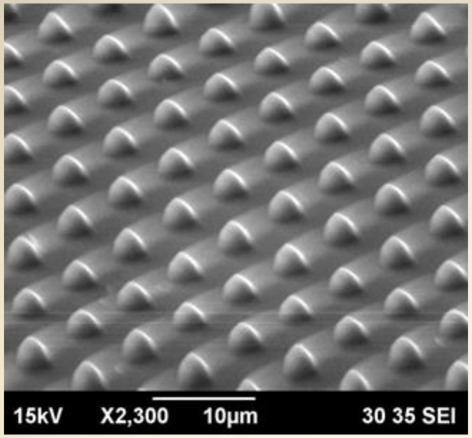


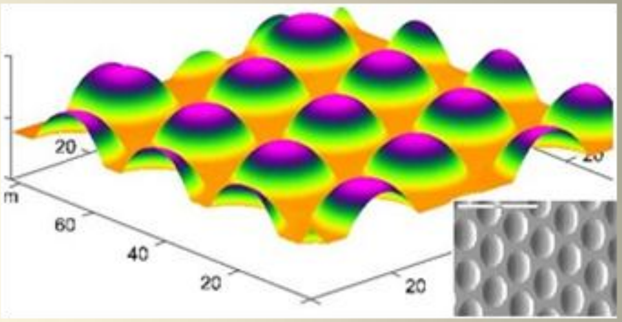
- **Polishing rate 10 x to 50 X higher**
- **High Performance at Reduced Costs**
- **Sinmat is the currently the largest global supplier of WBG CMP slurries (SiC and GaN)**
- **Recently Introduced Sapphire Slurries (Substrate market > 1.5 B in 5 years)**

Engineered Patterned Sapphire Substrates (150 mm)

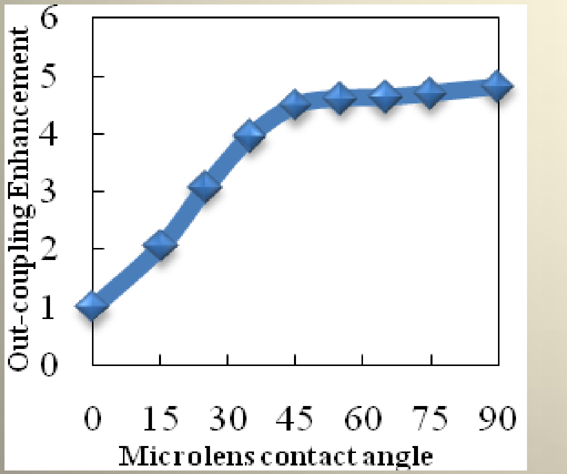
Microlens on Sapphire and Substrates

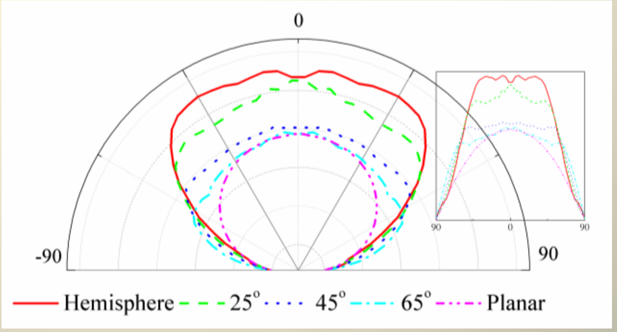




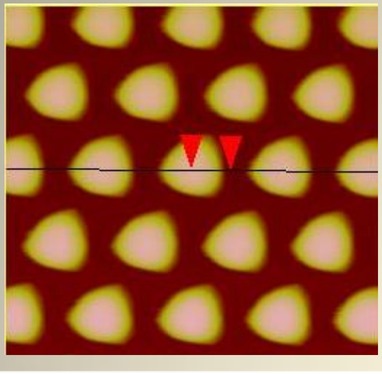


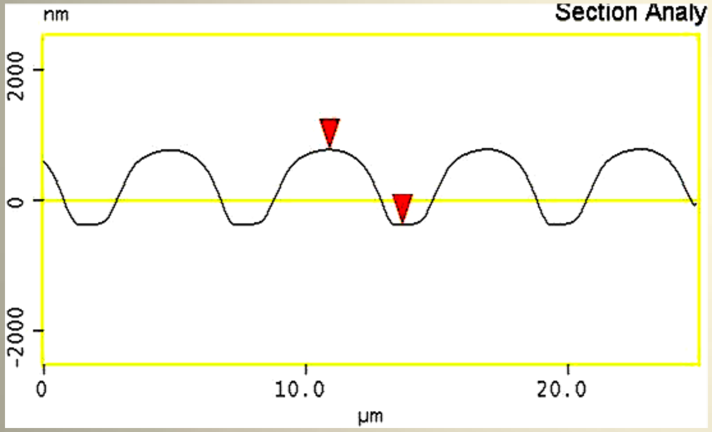
Light Extraction Enhancement (Simulation)





6 inch Patterned Sapphire Substrates (PSS)



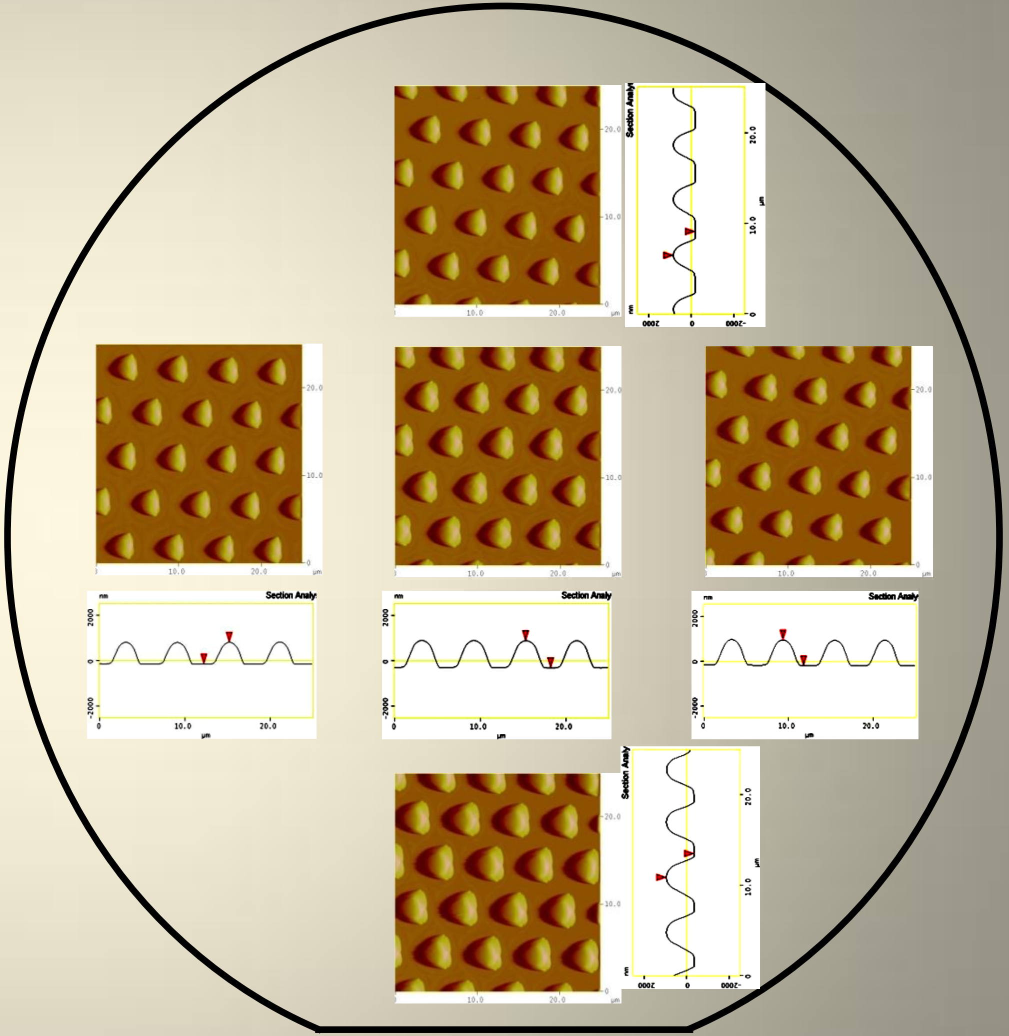


6 inch PSS substrates using the CMP process

Improved epi growth

Low Cost

Enhanced light extraction

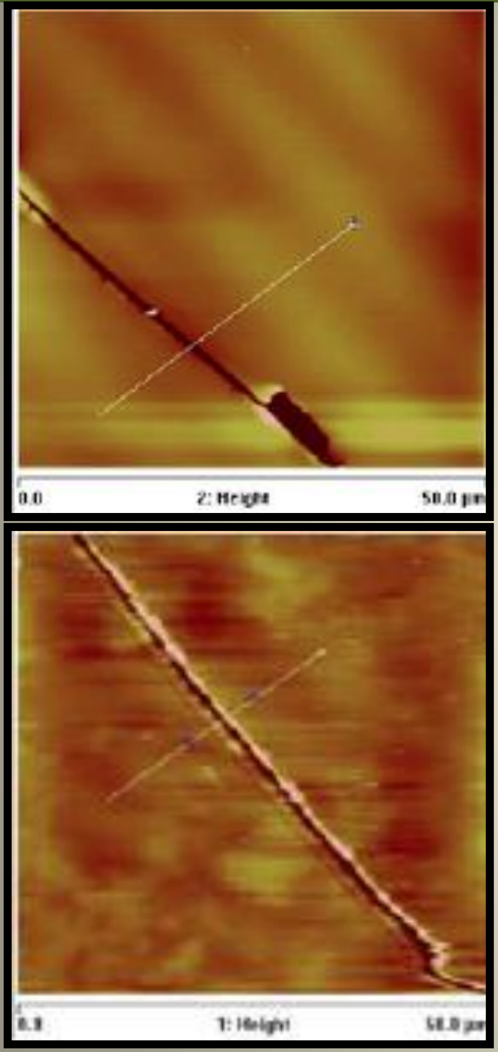


Singh et. al US patent application 61/185,476 (2010)

Outline

- ❖ Method to quantify stress response of CMP slurries
  - ✓ **Engineering of Slurry Delivery System**
- ❖ Measurement of stability ratio for determining slurry stability
  - ✓ **Better Quality Control Over Incoming Slurries**
- ❖ Characterization of the nature of agglomerates in CMP slurries
  - ✓ **Defectivity from Different Slurries**
- ❖ Conclusions

Defectivity Due to Oversize Particles (> 0.5 µm)



F. Chi. et al. "Externally Induced agglomeration during CMP of metals and dielectrics"

Defects during CMP

Killer defects, Arc scratches, Voids or pits, Embedded particle

Typical problems due to defects

- Electrical short circuit (defects in metal interconnects)
- Increase in leakage current
- Unpredictable dielectric breakdown

Critical for Low-K Dielectrics

- More susceptible to damage from oversize particles

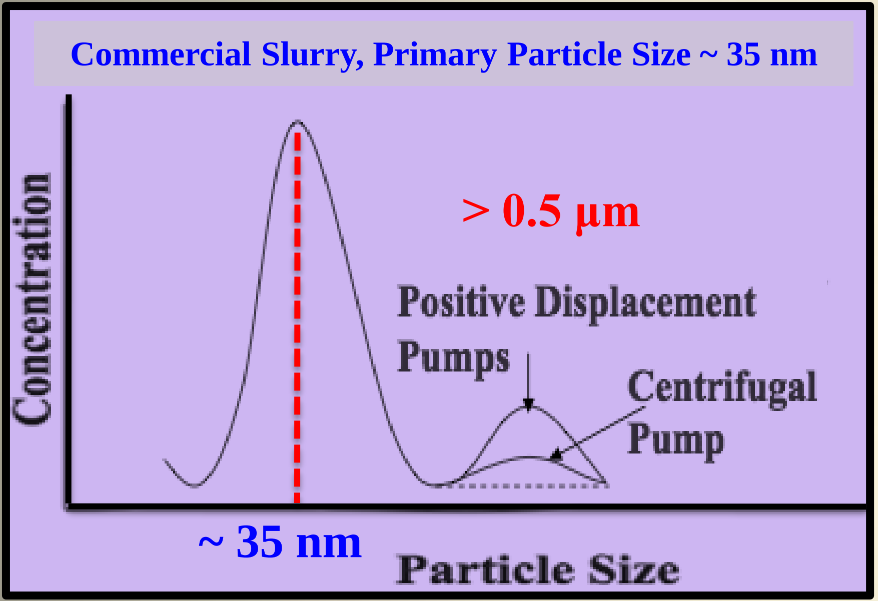
➢ Oversize particles are prime contributors of defectivity during CMP

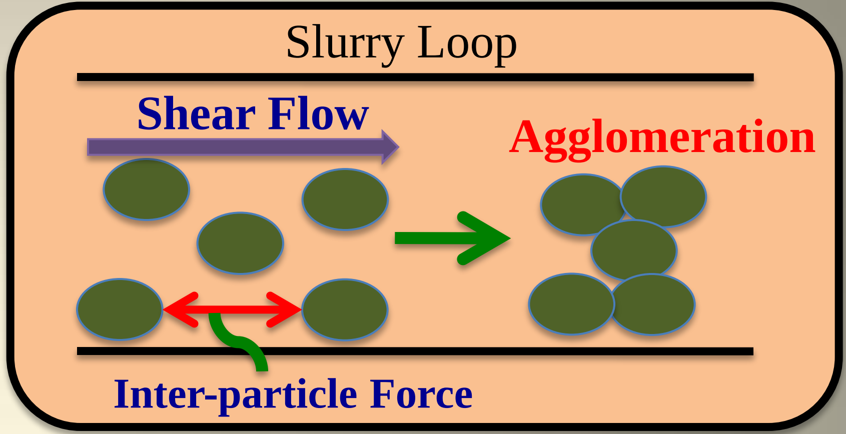
➢ Need to reduce formation of oversize particles

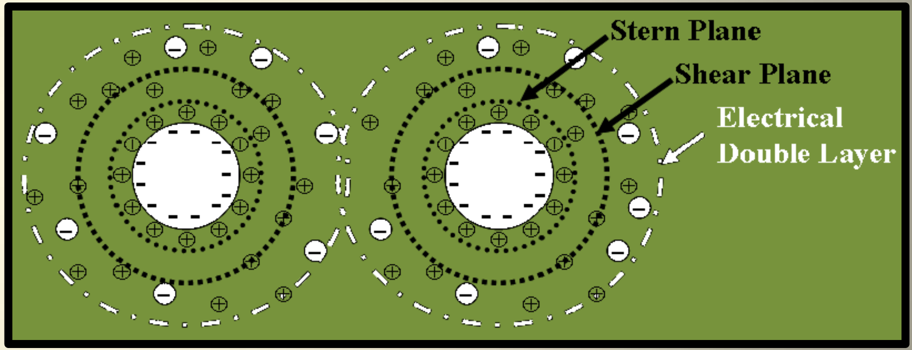
Sources of Oversize Particles – (I) External Forces

External Shear Stress

Pumps used for slurry delivery







Magnetically Levitated Centrifugal Pumps reduce over-size particles

Chang et al., J. ECS, vol 156, pp H39-H42, 2009

Need to quantify stress response of CMP slurries for engineering slurry delivery systems

Types of Oversize Particles

Soft Agglomerates

Large particles that can be broken down to smaller agglomerates or particles by

- ➢ Light mechanical forces or
- ➢ Hydrodynamic stress

M.L. Eggersdorfer et al. / Journal of Colloid and Interface Science 342 (2010) 261–268

Hard Agglomerates

- Large coarse particles
- Cannot be broken down to small size particles
- Closely held by strong attractive forces
- Strong shear forces cannot break these gritty lumps

Hard agglomerates lead to defectivity during CMP

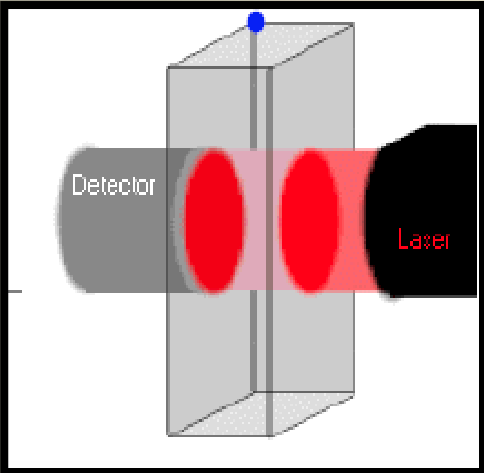
Need to characterize nature of agglomerates to understand defectivity during CMP resulting from stressed slurries

Measurement of Oversize Particles

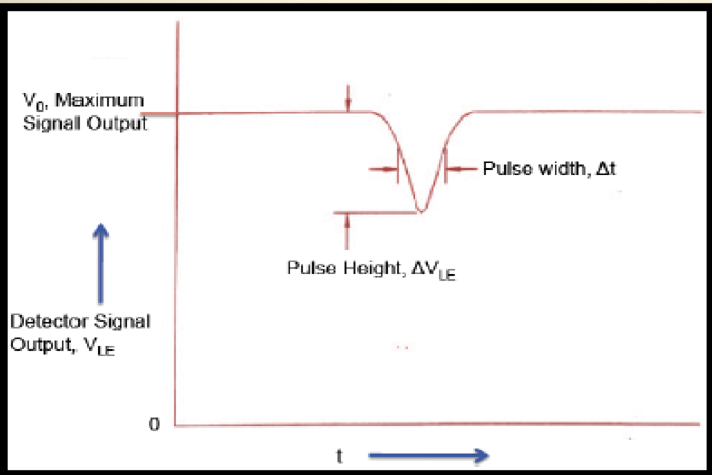
Single Particle Optical Sensing (SPOS) System (Accusizer 780)

- Measures number of particles in size 0.5 – 200 µm
- Physics: Light scattering (< 1.3 µm) and Refraction (> 1.3 µm)
- Voltage signal pulse is proportional to particle diameter
- **Cannot predict stress response of slurries and formation of resulting oversize particles**

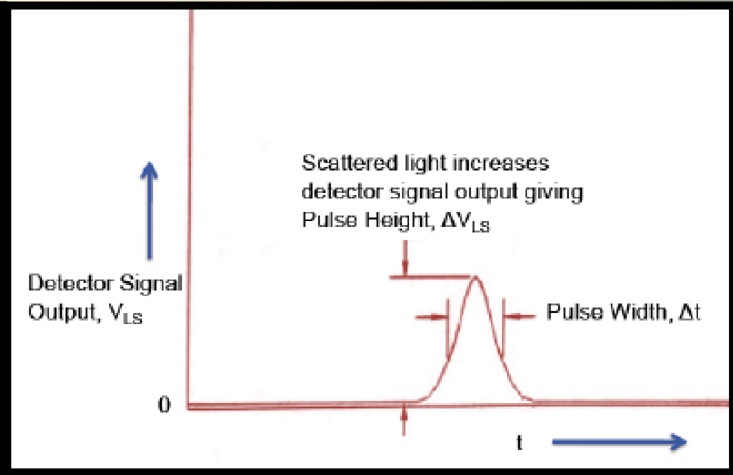
SPOS unable to predict defectivity due to stress induced in slurry



PSS Nicomp, Accusizer Manual



Light Extinction



Light Scattering

Need for better metrology tool for quality control over incoming slurries

Objectives

1. Quantify stress response of CMP slurries for engineering of slurry delivery system
2. Develop metrology tool for better quality control over incoming slurries
3. Identify conditions for formation of soft and hard agglomerates

Experimental Procedure

Rheometer

- Viscosity → *f* (Shear Rate)
- Paar Physica UDS 200 rheometer:
  - Temperature Control
  - Shear Rates up to 5000 s^{-1}

STEP 1 Measure cumulative concentration of as-received slurry (C_{ar})

STEP 2 Subject as-received slurry to different shear rates

Shear Rates 100 – 3000 s^{-1}

Time 100 - 2500 s

STEP 3 Measure cumulative concentration of stressed slurry (C_s)

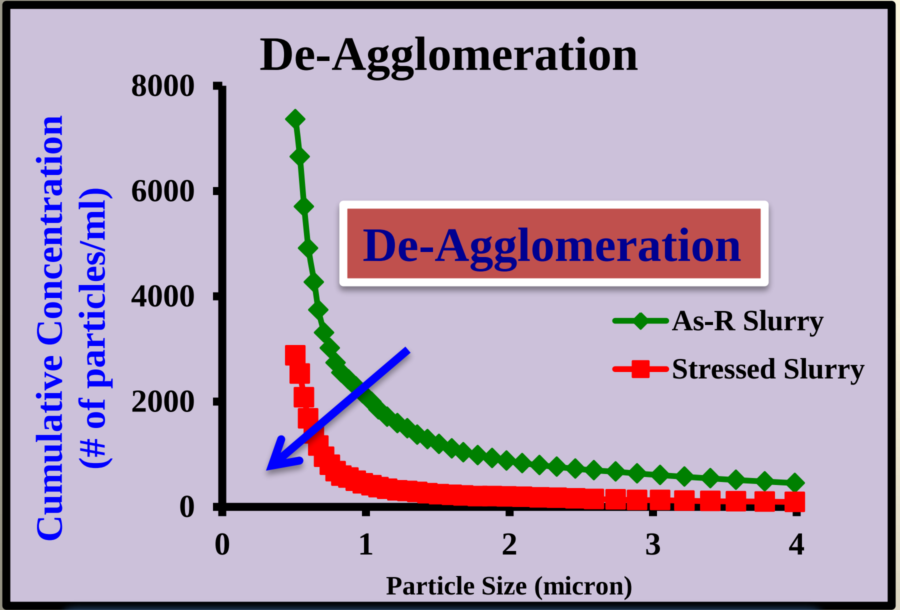
As-Received Slurry

Silco EM-3530K
- Colloidal Silica
- 35 nm
- 10-wt% solids
- pH 2, 7 and 11

Data Analysis

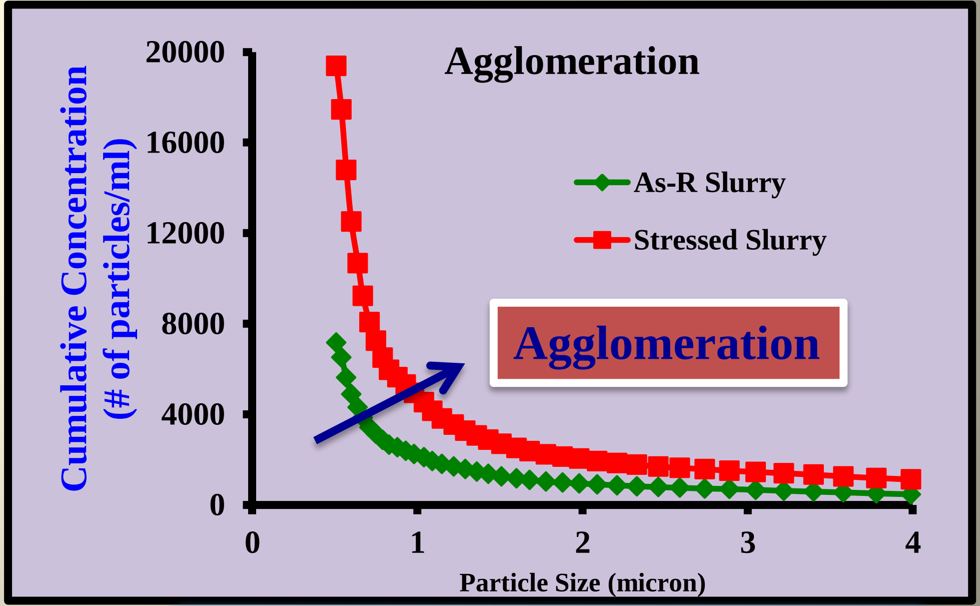
Normalized Concentration (C_s/C_{ar}) = $$\frac{\text{Cumulative Conc. of Stressed Slurry } (C_s)}{\text{Cumulative Conc. of As-Received Slurry } (C_{ar})}$$

De-Agglomeration



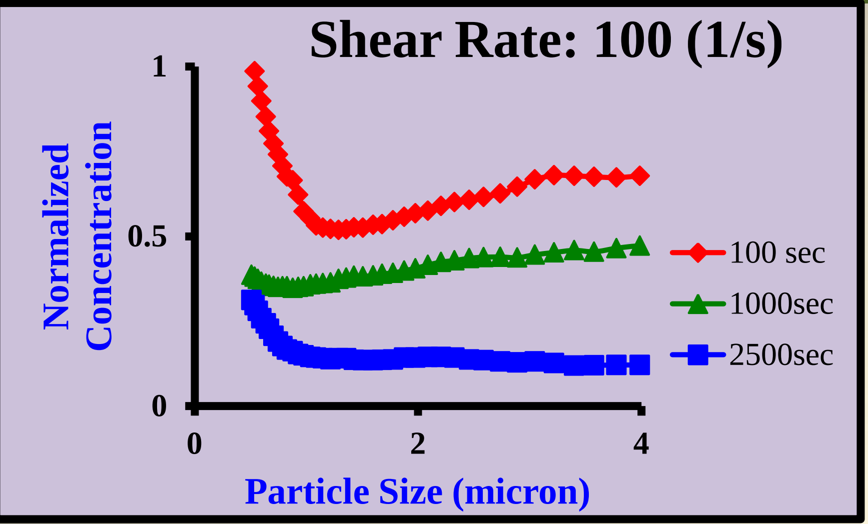
Normalized Concentration < 1

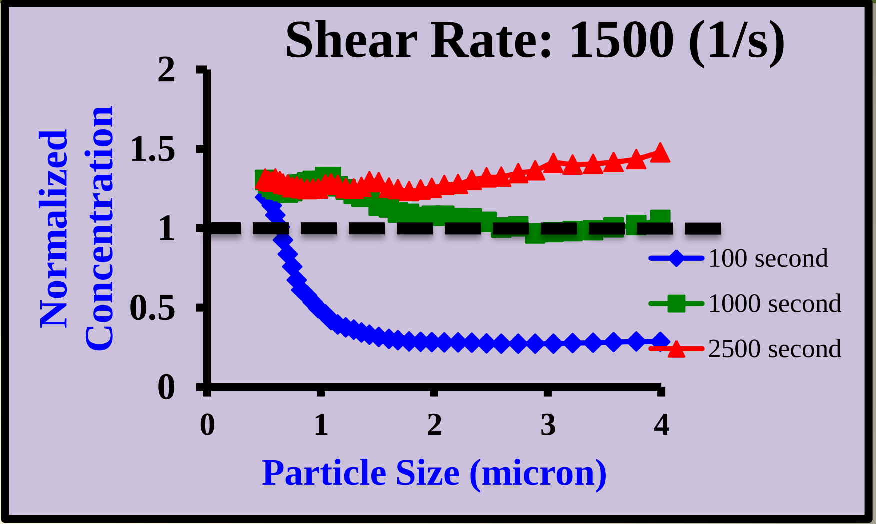
Agglomeration

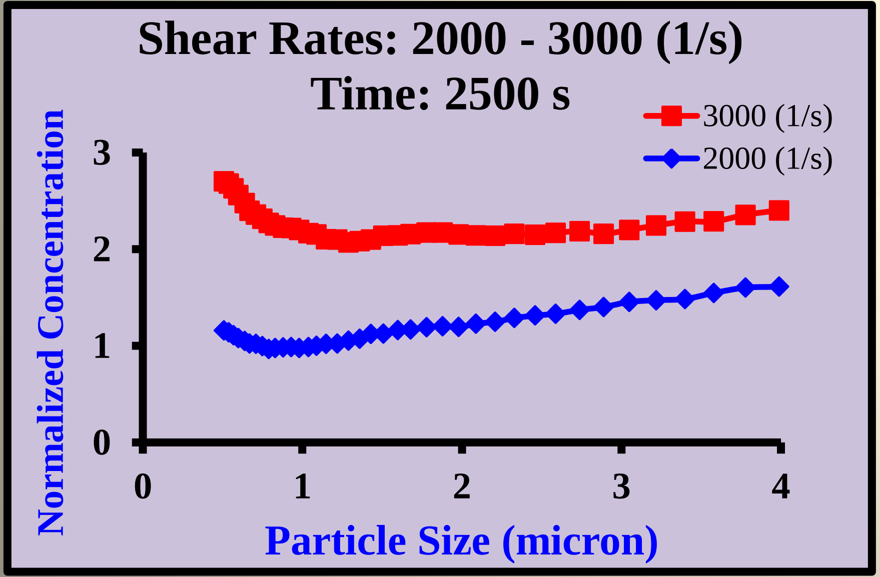


Normalized Concentration > 1

Results







Camp Number

(Low Shear Rate) x (Higher time) = (High Shear Rate) x (Lower time)

Basic pH Silica Slurry

De-Agglomeration

Shear Rate: 100 – 1000 s^{-1}
Time: 100 – 2500 s

Agglomeration

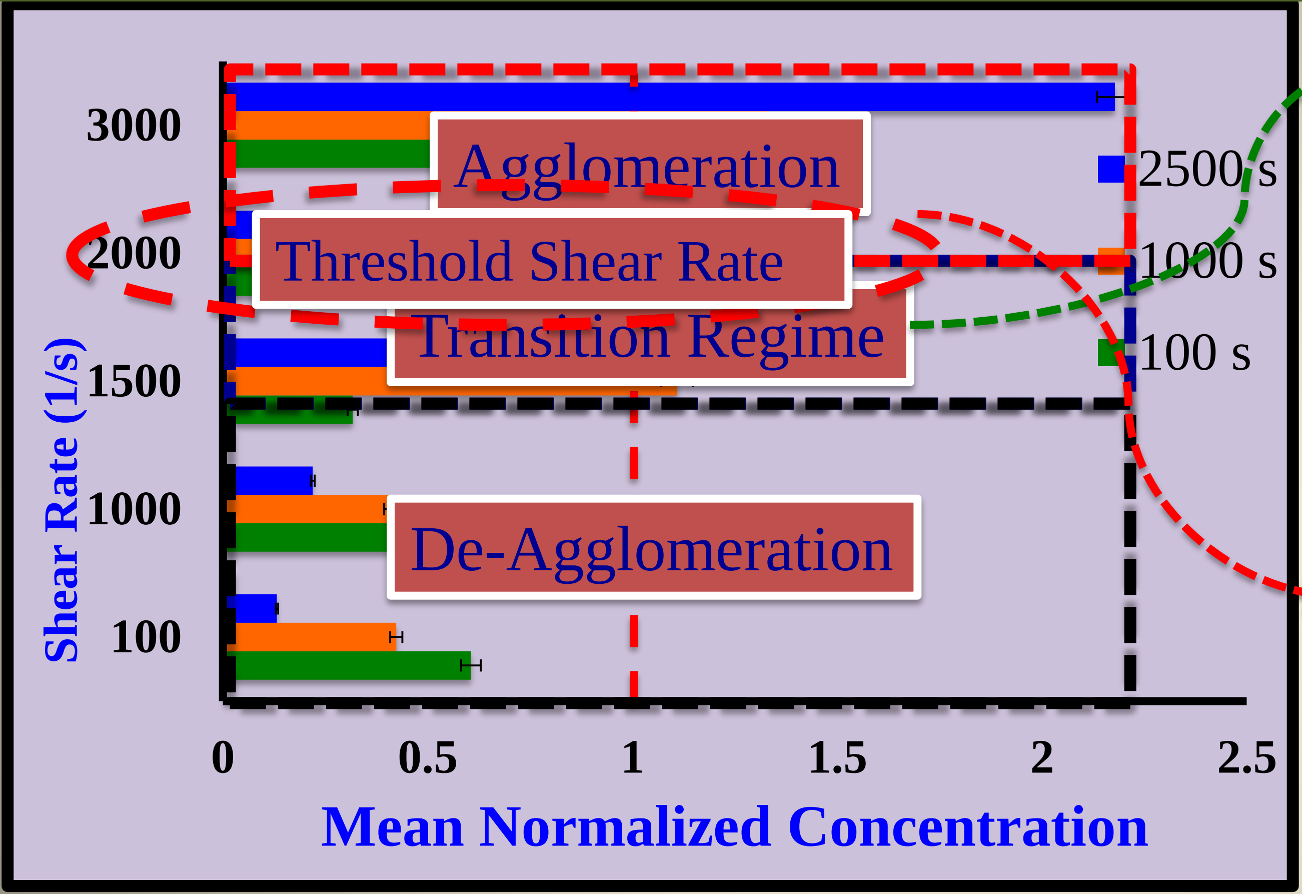
Shear Rate: 2000 – 3000 s^{-1}
Time: 100 – 2500 s

Transition Region

De- Agglomeration
1500 s^{-1} for < 1000 s

Agglomeration
1000 – 2500 s

Mean value of Normalized Concentration
Basic Silica Slurry (pH ~11, 35 nm, 10wt% solids)



Transition Region

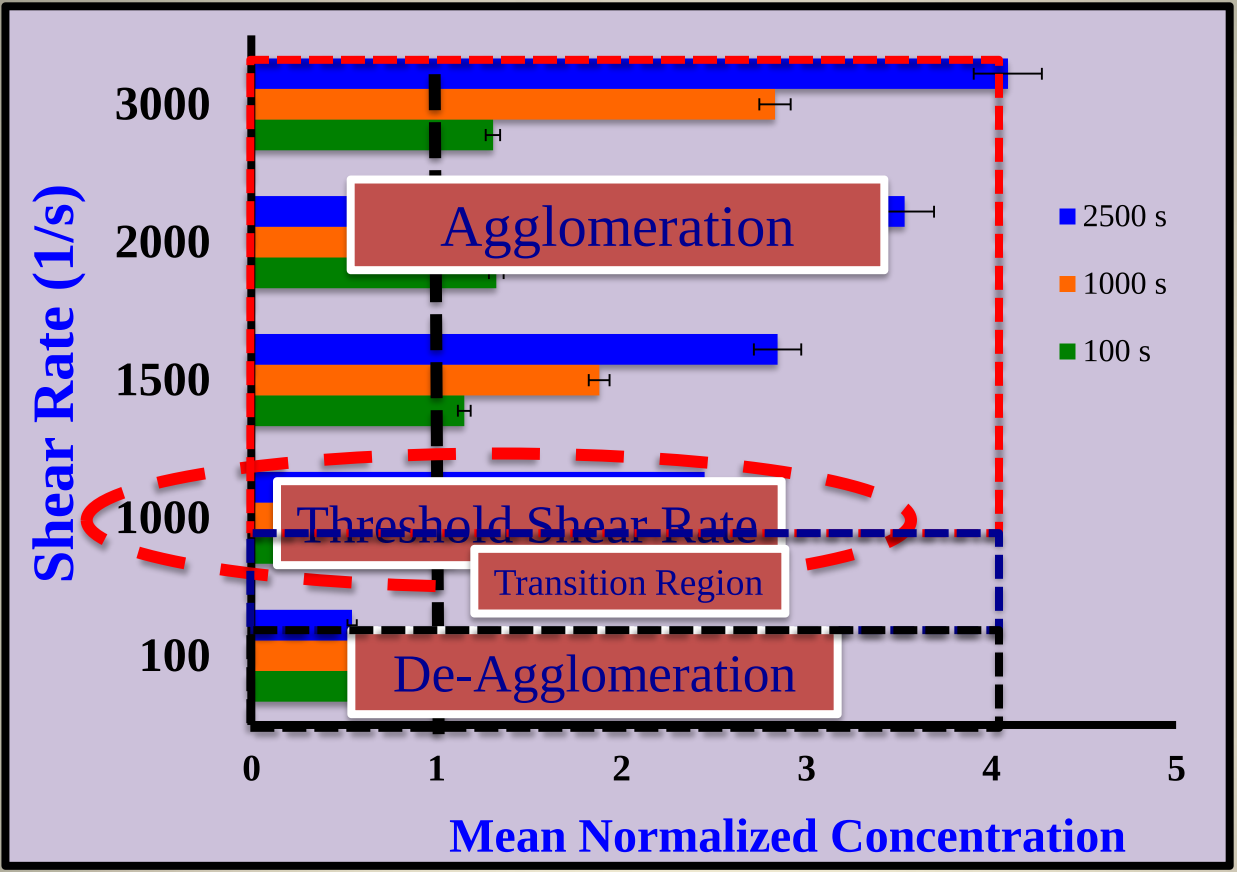
- De-agglomeration for smaller duration (up to 1000 s)
- Agglomeration for longer duration (1000 s and above)

Threshold Shear Rate

Shear Rate for which agglomeration occurs for any duration

Stress Response of slurry: De-Agglomeration, Transition Region, Agglomeration
Threshold shear rate for basic silica slurry is 2000 s^{-1}

Mean value of Normalized Concentration
Acidic Silica Slurry (pH ~2, 35 nm, 10wt% solids)



De-Agglomeration

Shear Rate: 100 – 500 s^{-1}
Time: 100 – 2500 s

Transition Region <u>700 s^{-1}</u>

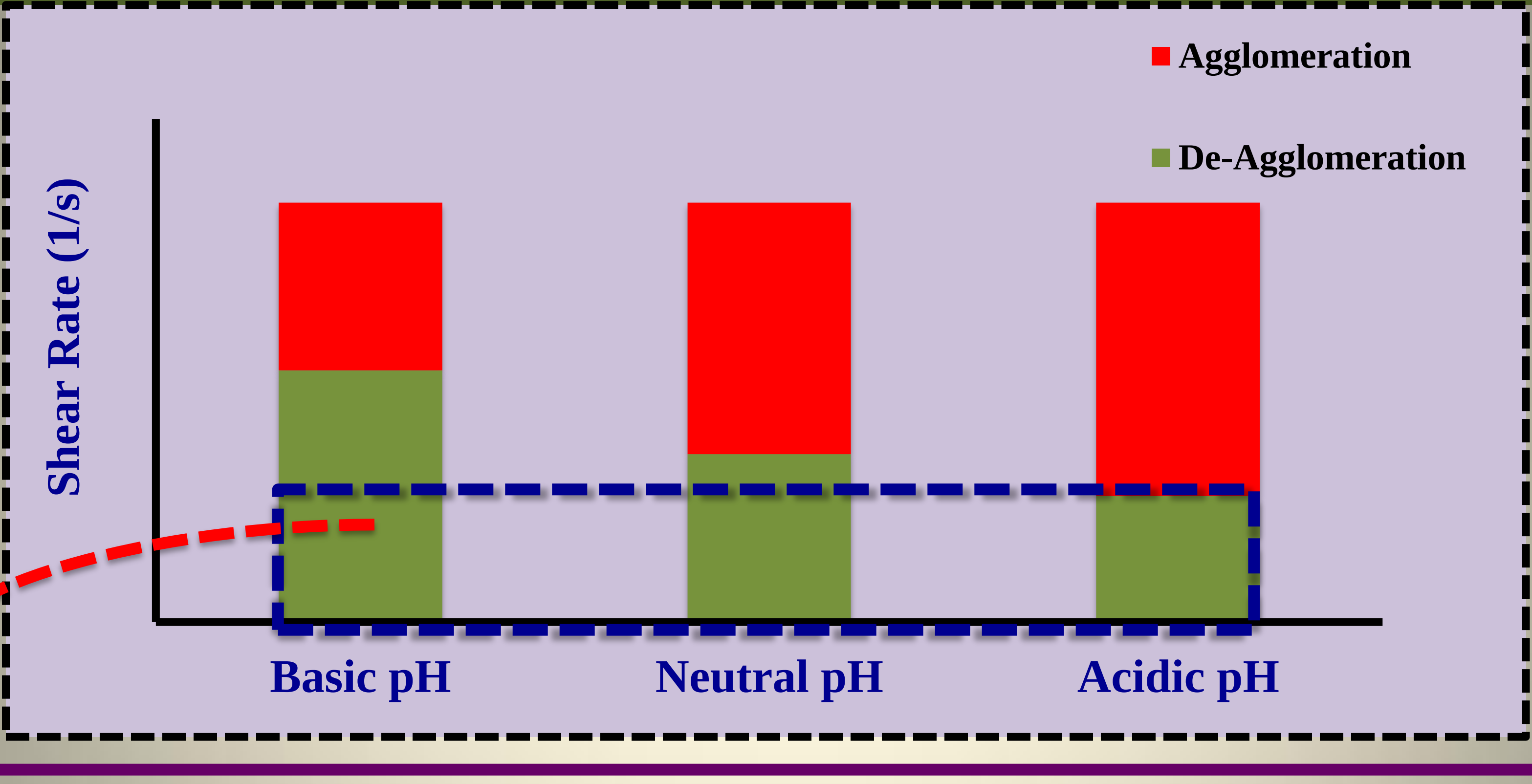
De- Agglomeration for < 1000 s
Agglomeration 1000 – 2500 s

Agglomeration

Shear Rate: 1000 – 3000 s^{-1}
Time: 100 – 2500 s

Threshold shear rate for acidic silica slurry is 1000 s^{-1}

Behavior of Different Silica Slurries



- Select operating shear rate in De-Agglomeration region for engineering slurry delivery system
  - ✓ Provides control over formation of oversize particles in these slurries
  - ✓ Reduces concentration of existing oversize particles

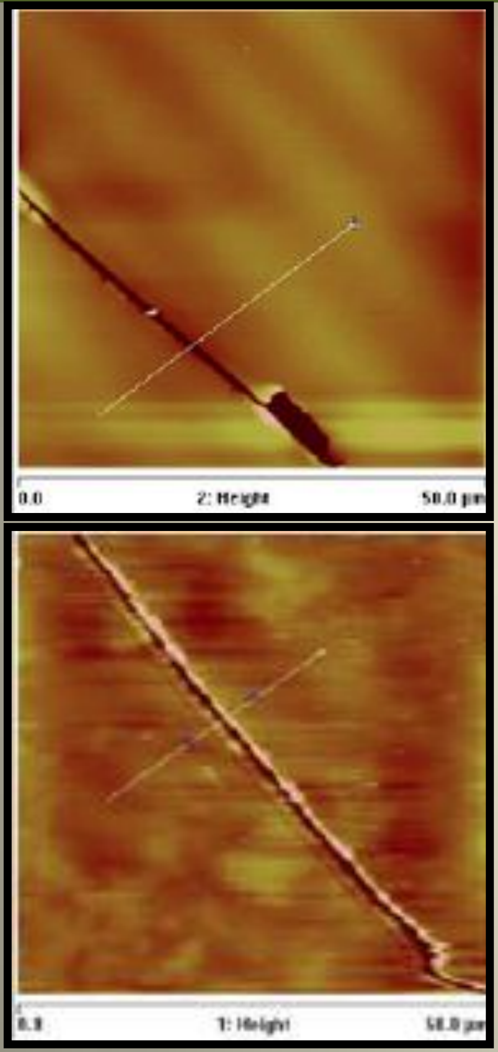
Quantified stress response of slurry aids in engineering of slurry delivery system

Part II

Measurement of stability ratio for determining CMP slurry stability

- ✓ **Better metrology quality control over incoming slurries**

Defectivity



F. Chi. et al. “Externally Induced agglomeration during CMP of metals and dielectrics”

Defects during CMP

Killer defects, Arc scratches, Voids or pits, Embedded particle

Typical problems due to defects

- Electrical short circuit (defects in metal interconnects)
- Increase in leakage current
- Unpredictable dielectric breakdown

Critical for Low-K Dielectrics

- More susceptible to damage from oversize particles

➢ Oversize particles are prime contributors of defectivity during CMP

➢ Need to reduce formation of oversize particles

Modeling using Smoluchowski's Theory

From Smoluchowski's Theory

Number of k-fold aggregates 'N_k'

k: 0.5 – 4 µm

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

$$\tau = \frac{3}{4\,(G/W) N_0 R_{ij}^3}$$

Stability Ratio 'W'

- Particle Size 'a'
- Slurry chemistry 'd'
- Temperature 'T'

Variables:

- Initial particle concentration (N_0)
- Aggregation time (t),
- Half life 'τ'
- Particle radius (R_{ij})
- Shear Rate 'G'

➢ Calculation of N_k gives $N_{0.5}$, $N_{0.75}$…………..$N_{4.0}$

➢ N_k / *Total Particle Concentration* → Modeled Tail Distribution

Stability Ratio 'W' is the curve fitting parameter for experimental and modeled tail distribution

Stability Ratio

Stability Ratio ‘W’

$$W = 2\int_0^\infty \frac{\exp(V_{total}/KT)}{(u+2)^2}du$$

where,
‘V_{total}’ - total interaction energy
‘T’ - temperature (kept constant)
u = d/a
‘d’ – inter-particle distance,
‘a’ - particle

Stability Ratio ‘W’ depends on slurry properties only

Previous Work

AI= log (G/W)

where,
‘AI’ – Agglomeration index
‘G’ – Shear Rate (1/s)
‘W’ – Stability Ratio

- Pumps were used to calculate AI
- Shear rate of pump was unknown
- **(G/W)** - fitting parameter
- Different pumps → Diff. AI

Need of a parameter that defines slurry stability independent of shear rate

Determination of Stability Ratio

STEP 1 Measure cumulative concentration of as-received and stressed slurry

STEP 2 Calculate : $\dfrac{\text{Part Conc.}}{\text{Total Particle Conc.}}$

STEP 3 Model final tail distribution by solving Smoluchowski's Theory

STEP 4 Curve fitting of modeled and experimental tail distribution

As-Received Slurry

Silco EM-3530K
- Colloidal Silica
- 35 nm
- 10-wt% solids
- pH 2, 7 and 11

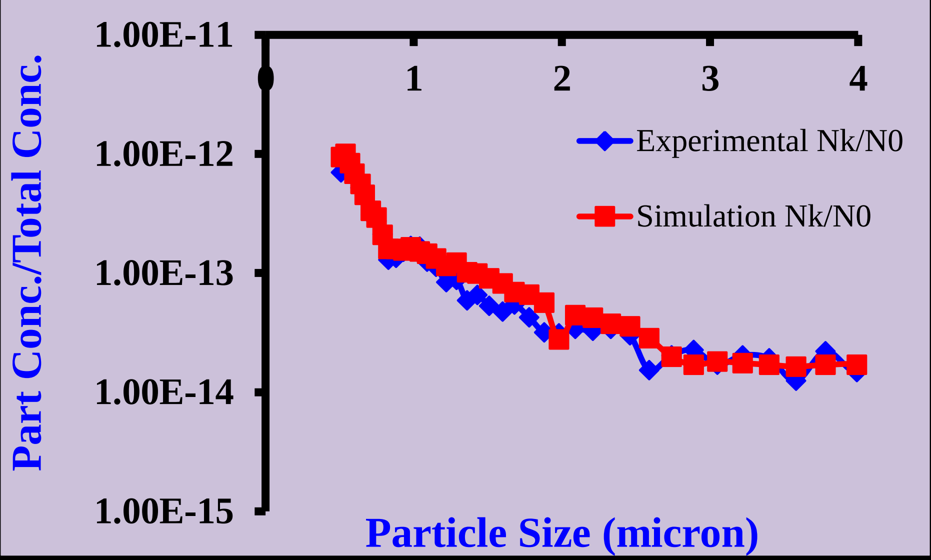
Shear Rates

1500 – 3000 s^{-1}

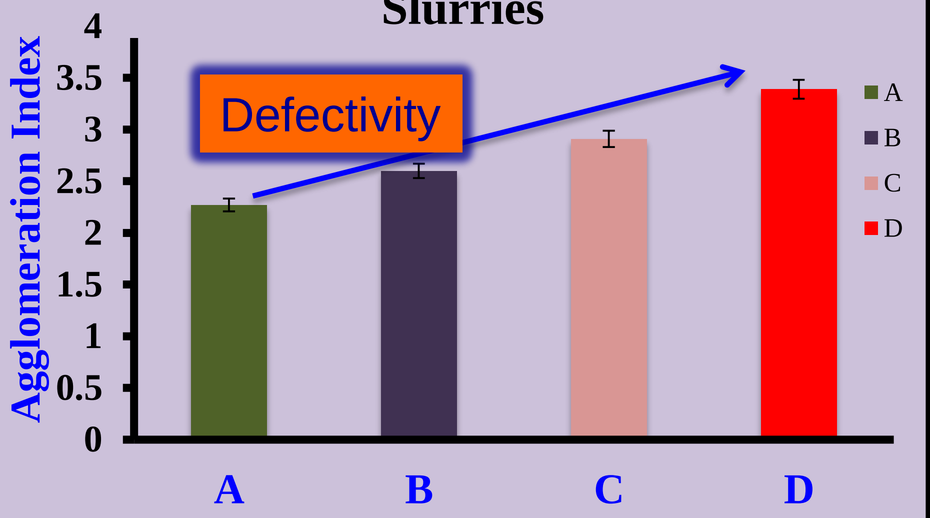
Part Conc.

Number of particles of different sizes from 0.5 – 200 µm

Agglomeration Index of Different Slurries at 3000 s^{-1}



Curve Fitting to obtain A.I.



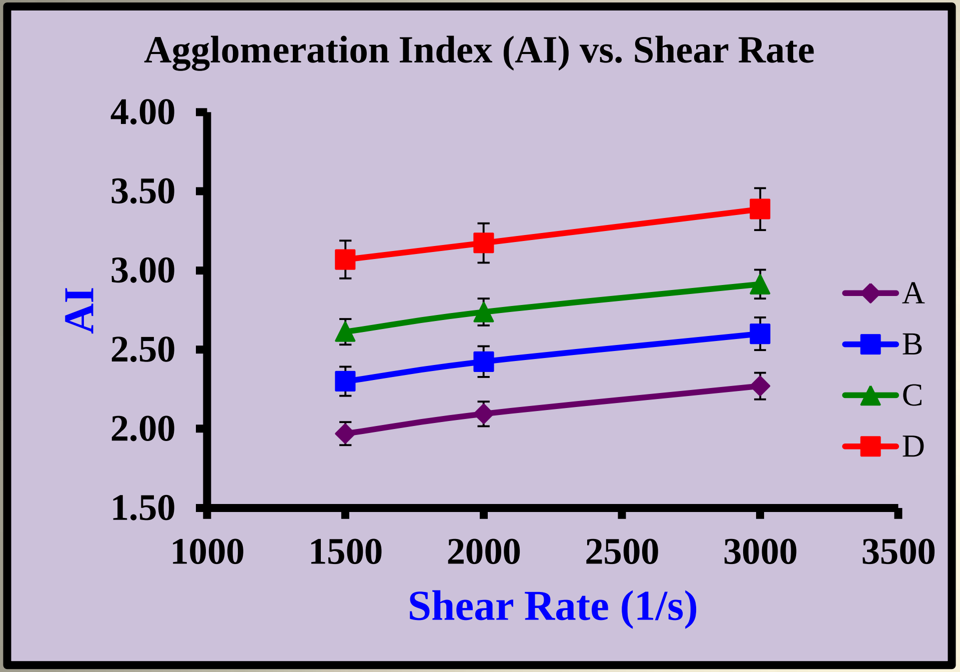
Agglomeration Index for Different Slurries

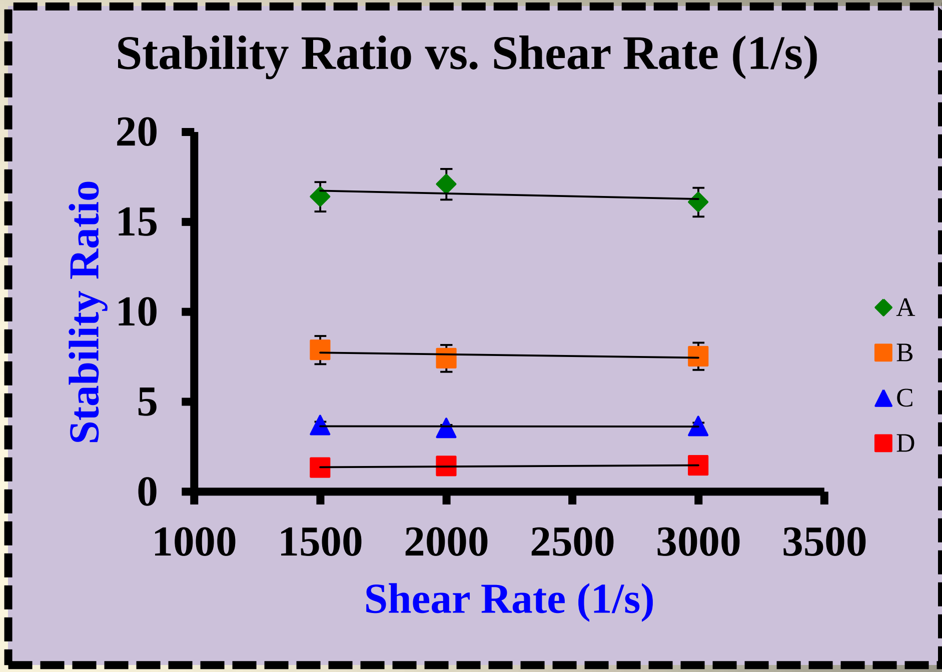
Slurry Type	Assigned Name
Silica: pH 10, 35nm	A
Silica: pH 7, 35nm	B
Silica: pH 2, 35nm	C
Silica: pH 2 + 0.1M KCl, 35nm	D

$$AI = \log (G/W)$$

Agglomeration index gives relative slurry stability

Stability Ratio vs. Agglomeration Index at Different Shear Rates



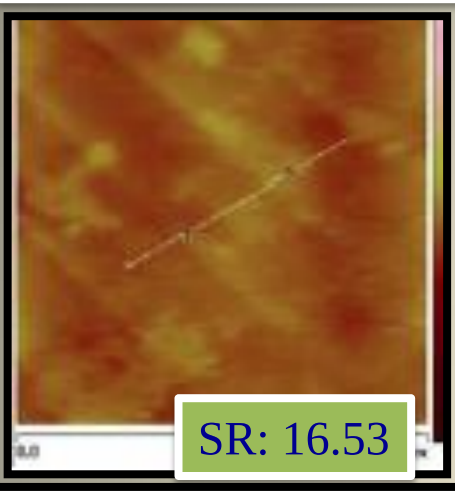


Agglomeration index changes with shear rate

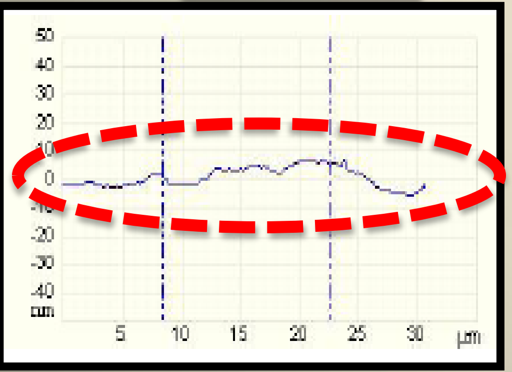
Stability ratio is independent of shear rate and a better parameter than agglomeration index

Relating Stability Ratio (SR) to CMP Performance

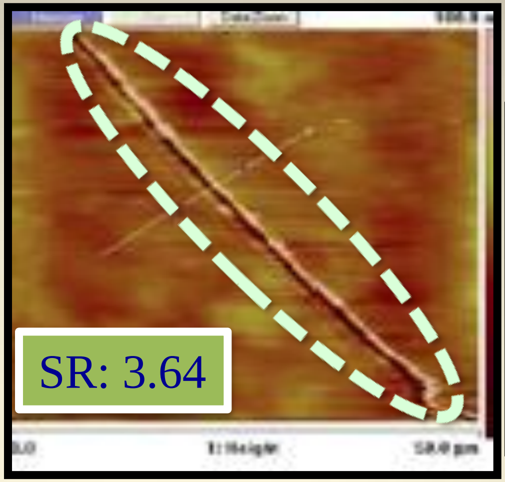
Basic pH Silica Slurry (A)



SR: 16.53



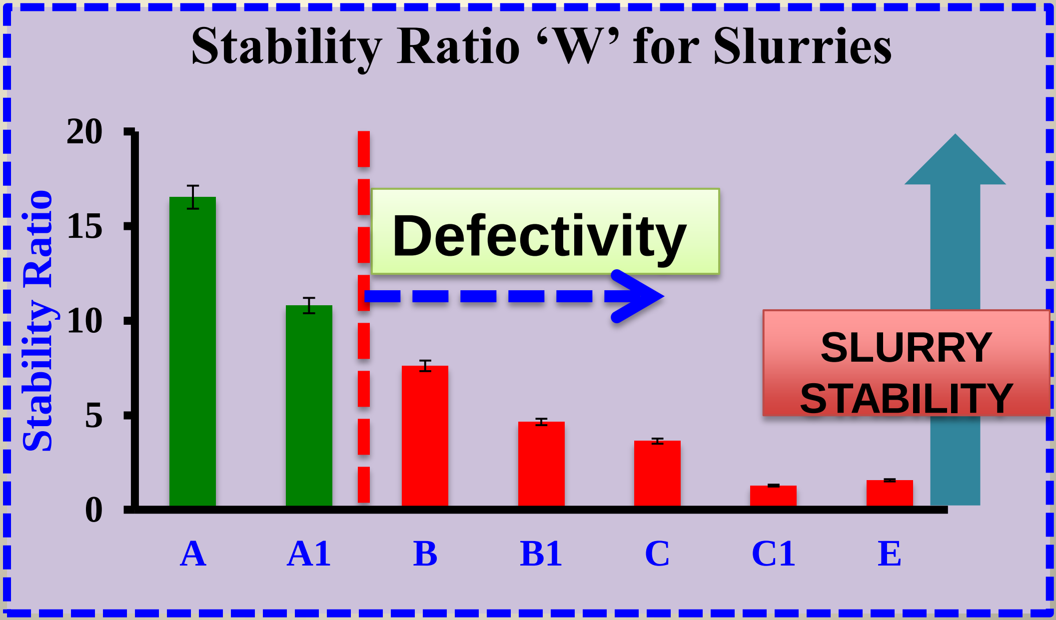
CMP of Cu Wafer



SR: 3.64

Acidic pH Silica Slurry (C)

Stability Ratio ‘W’ for Slurries



Defectivity

SLURRY STABILITY

F.C. Chang and R. Singh, *Electrochem Solid-State Letter*, 12, 2009

Stability ratio predicts relative slurry stability in agreement with earlier work with slurries under identical conditions

Stability Ratio of Different Slurries

Slurry Type		**Stability Ratio**
Silica: pH 11, 35nm	A	16.53
Silica: pH 11 + 0.1M KCl, 35nm	A1	10.8
Silica: pH 7, 35nm	B	7.61
Silica: pH 7 + 0.1M KCl, 35nm	B1	4.65
Silica: pH 2, 35nm	C	3.64
Silica: pH 2 + 0.1M KCl, 35nm	C1	1.42
Silica: pH 10, 135nm	E	1.26

- ‘W’ of tested silica slurries is 1.26-16.53
- Stressed silica slurry with pH 7 and 2, with and without salt caused defects during CMP
- Stability Ratio decreases for these slurries

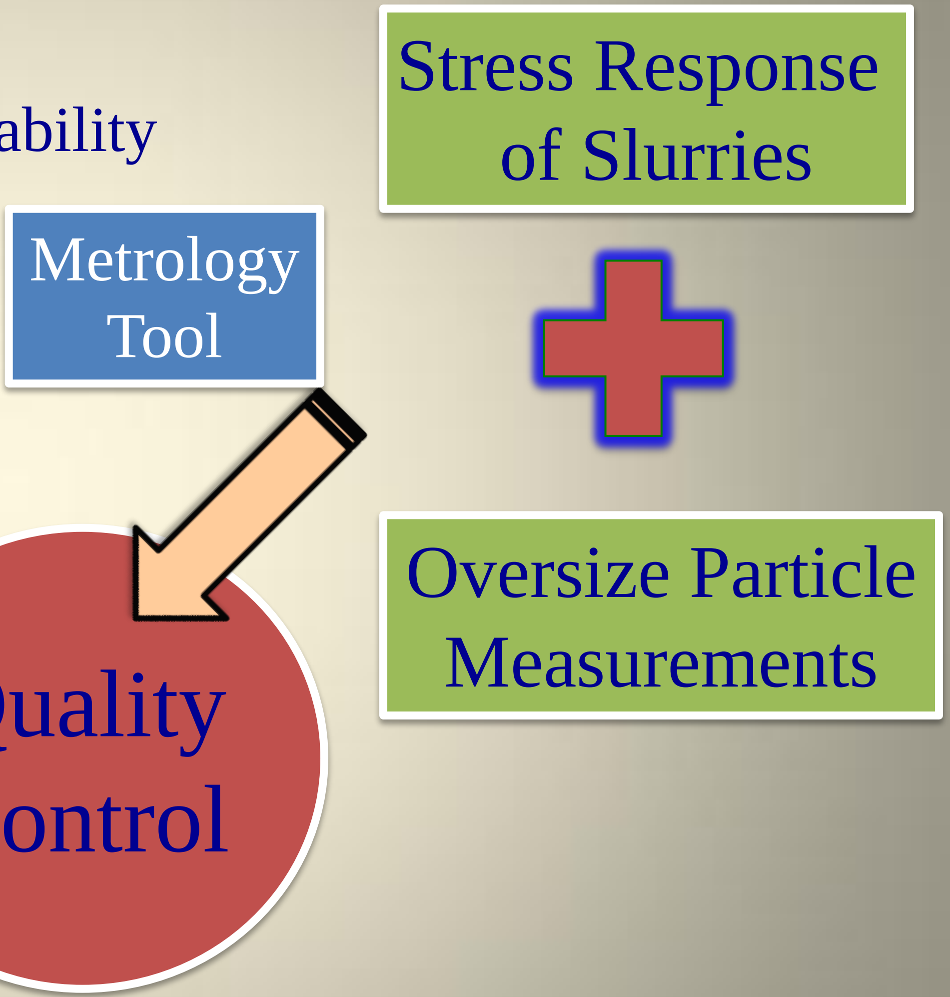
Stability Ratio decreases with increase in tendency of slurry to cause defectivity

Summary of Part II

Stability Ratio (SR)

Better parameter to define slurry stability

- Independent of Shear Rate
- Predicts tendency of slurry to cause defectivity



Stress Response of Slurries

Oversize Particle Measurements

Metrology Tool

Quality Control

Better Quality Control aids in reducing defectivity, better process control and enhanced uniformity

Types of Oversize Particles

Soft Agglomerates

Large particles that can be broken down to smaller agglomerates or particles by

- ➢ Light mechanical forces or
- ➢ Hydrodynamic stress

M.L. Eggersdorfer et al./Journal of Colloid and Interface Science 342 (2010) 261–268

Hard Agglomerates

- Large coarse particles
- Cannot be broken down to small size particles
- Closely held by strong attractive forces
- Strong shear forces cannot break these gritty lumps

Hard agglomerates lead to defectivity during CMP

Need to characterize nature of agglomerates to understand defectivity during CMP resulting from stressed slurries

Experimental Procedure (Part III)

STEP 1

Agglomerate the slurry i.e.
As-Received → Stressed Slurry

STEP 2

De-agglomerate the stressed slurry

Low Shear Rates

100 – 1000 s^{-1}

STEP 3

Compare De-agglomeration in Stressed with As-Received slurry

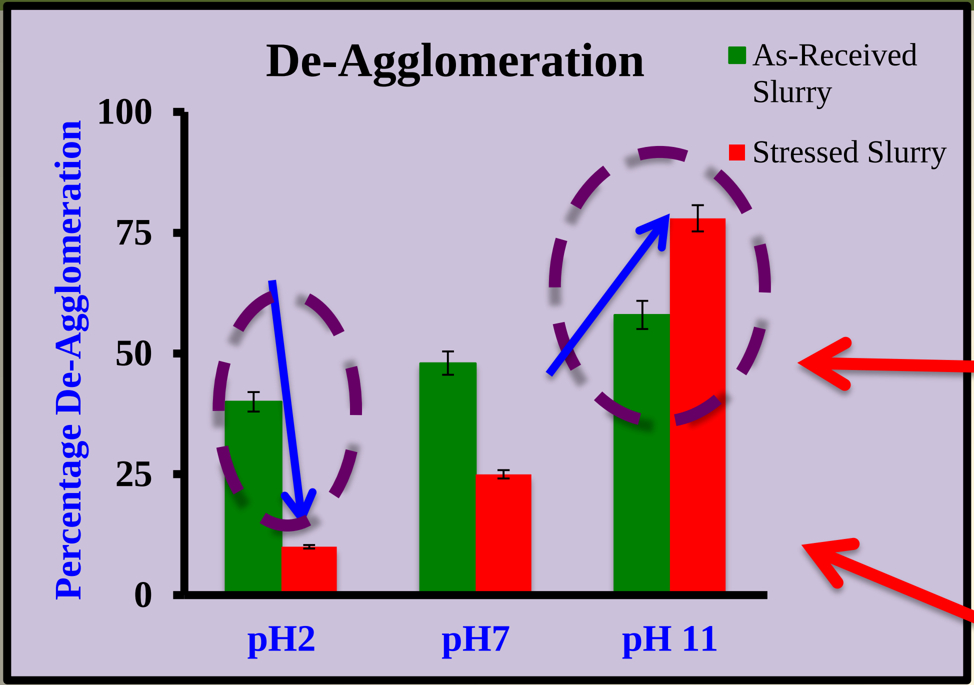
As-Received Slurry

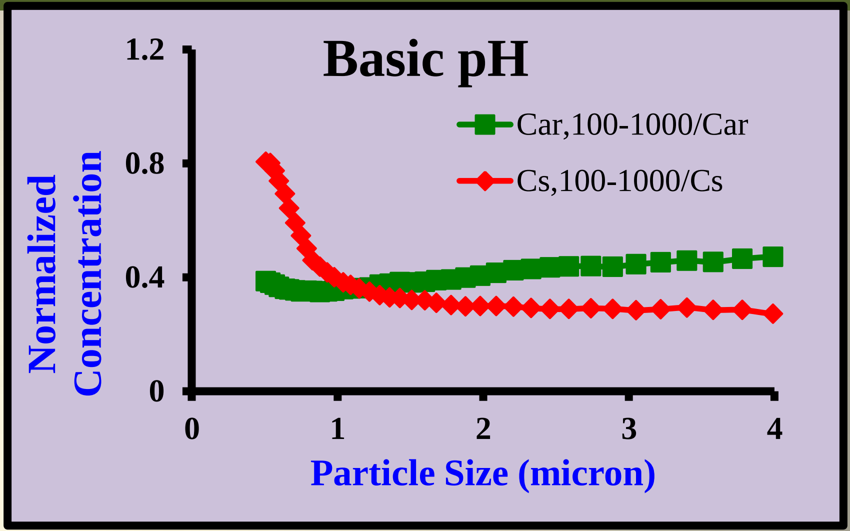
Silco's EM-3530K
- Colloidal Silica
- 35 nm
- 10-wt% solids
- pH 2, 7 and 11

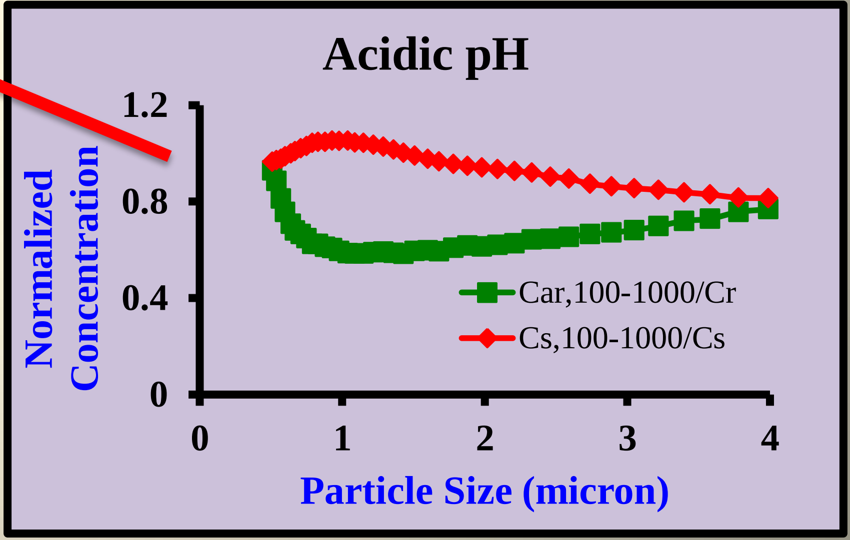
Stressed Slurry

Subject As-Received Slurry to:
3000 s^{-1} for 1000 s

Comparison of De-agglomeration in Stressed & As-Received Slurry







Shear Rate: 100 s^{-1}, **Time:** 1000 s

Basic pH: De-agglomeration in
Stressed slurry > As-received slurry

Neutral & Acidic pH: De-agglomeration in
Stressed slurry < As-received slurry

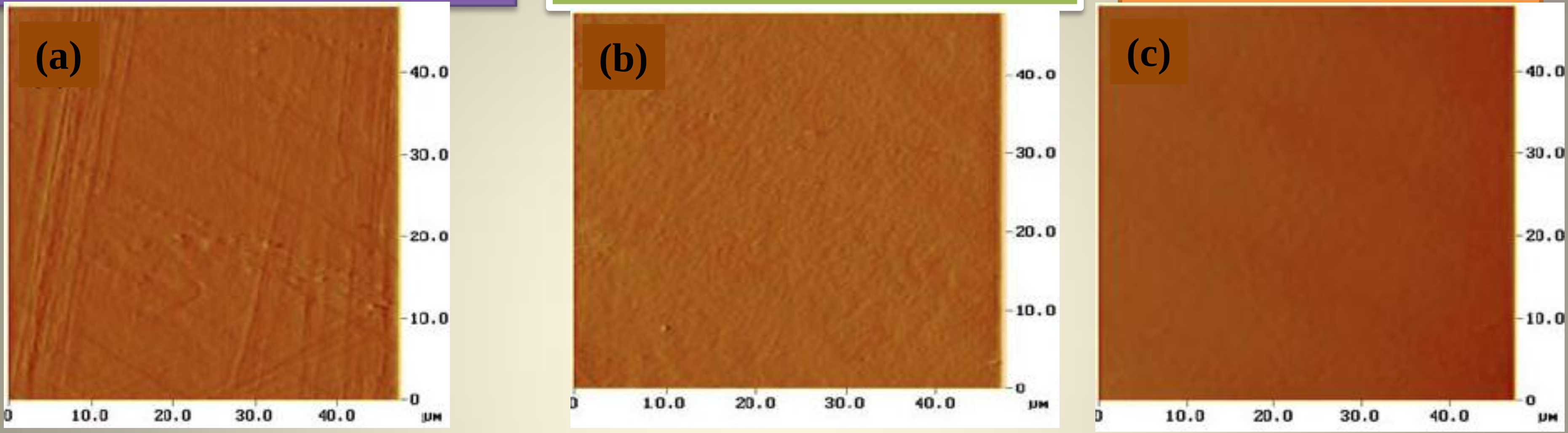
Soft agglomerates - Basic silica slurry
Hard agglomerates – Neutral and Acidic silica slurry

Relating Nature of Agglomerates to CMP Performance

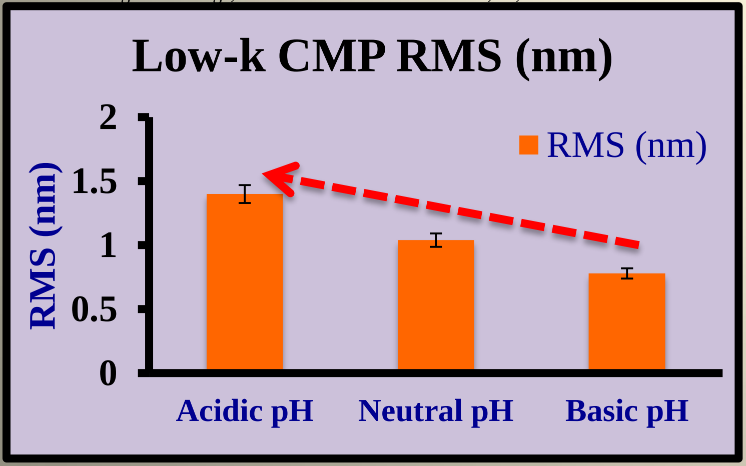
Acidic pH
Hardest Agglomerates

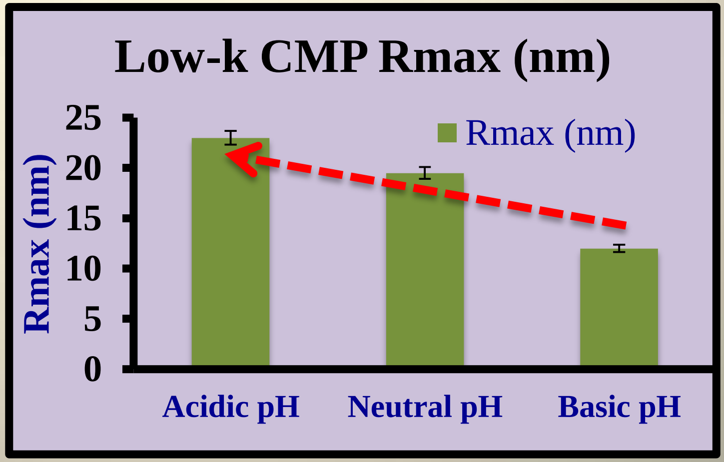
Neutral pH
Hard Agglomerates

Basic pH
Soft Agglomerates



F.C. Chang and R. Singh, *Electrochem. Solid-State Letter*, 12, 2009





CMP of Low-k BD1 Wafers

Presence of hard agglomerates in stressed slurries leads to defectivity

Summary of Part III

Agglomerates

Soft

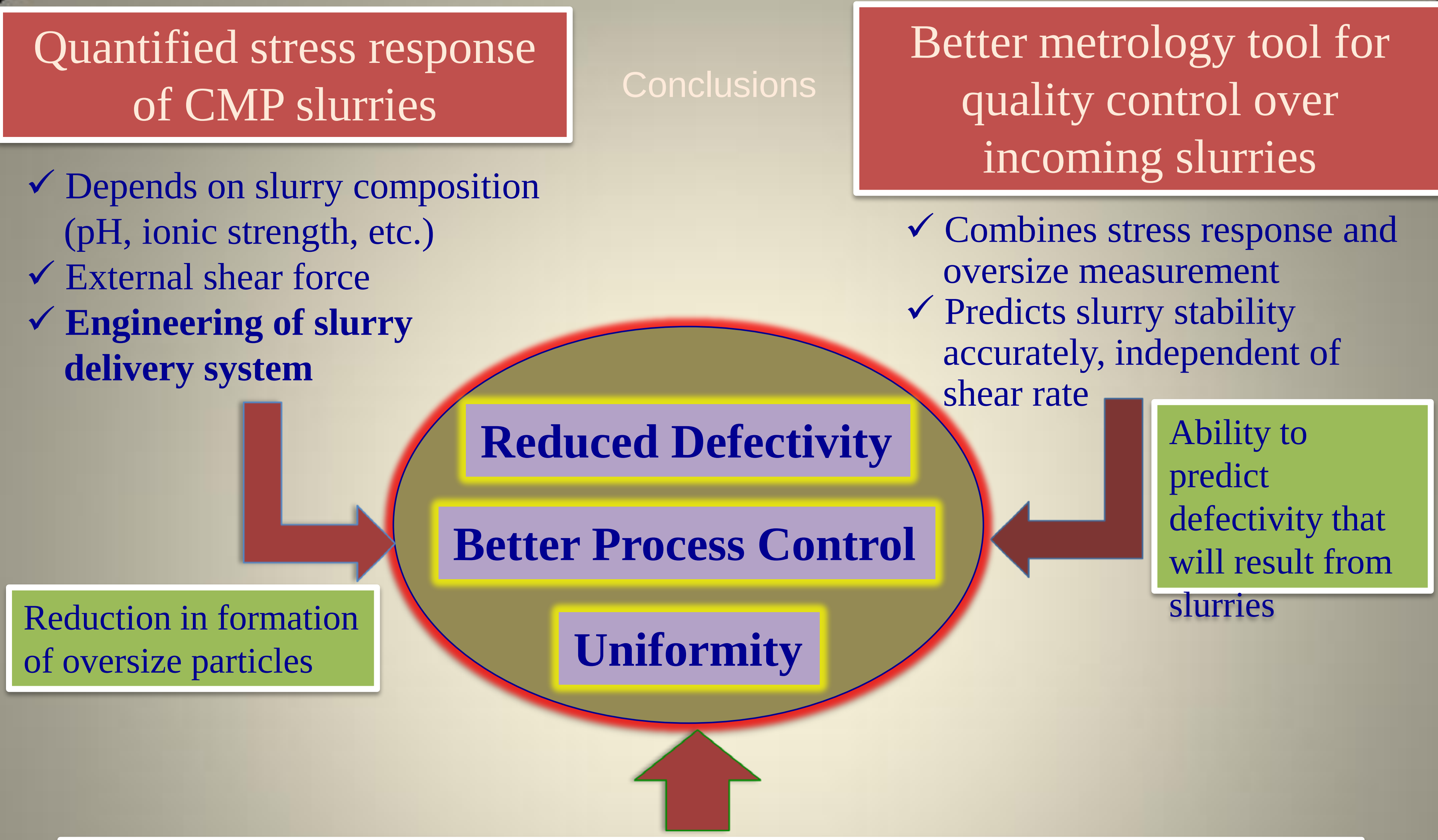
Hard

- ✓ Present in stressed silica slurry for basic conditions
- ✓ Explains why oversize particles in basic pH slurries did not cause defectivity

- ✓ Present in stressed silica slurry for neutral and acidic conditions
- ✓ Explains why oversize particles in neutral and acidic pH slurries cause defectivity

A method was developed to characterize nature of agglomerates in CMP slurries

Conclusions



Quantified stress response of CMP slurries

- ✓ Depends on slurry composition (pH, ionic strength, etc.)
- ✓ External shear force
- ✓ **Engineering of slurry delivery system**

Reduction in formation of oversize particles

Better metrology tool for quality control over incoming slurries

- ✓ Combines stress response and oversize measurement
- ✓ Predicts slurry stability accurately, independent of shear rate

Ability to predict defectivity that will result from slurries

Reduced Defectivity

Better Process Control

Uniformity

Identified conditions for formation of hard and soft agglomerates

- ✓ Hard agglomerates related to defectivity
- ✓ Stricter requirements for monitoring oversize concentration in certain slurries