GENERAL ENGINEERING AND RESEARCH

National Science Foundation – SBIR Phase II

Nano-Capsule CMP Slurries: Enabling Localized Control of Chemical Exposure

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Outline

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  - Motivation and Objective of Research
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  - Silica particles
  - Nano-capsules
- CMP Experiments
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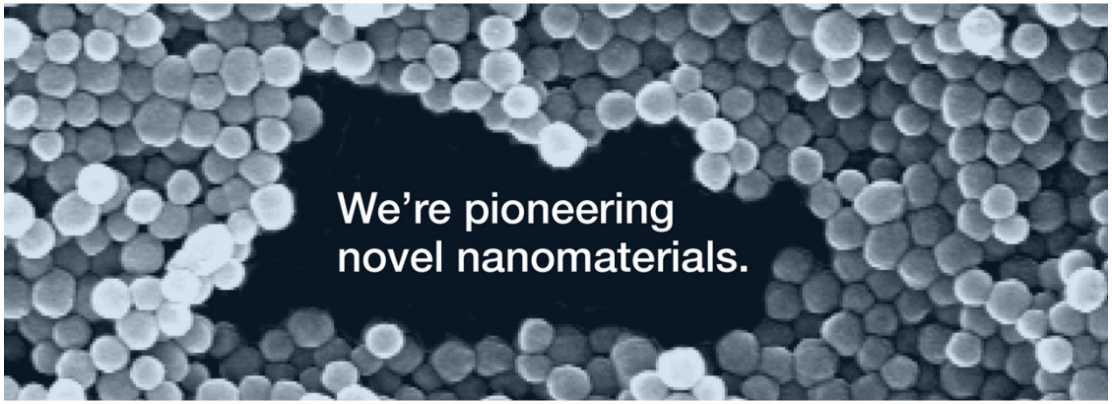
GE&R Background

- Founded in 2009
  - Industry Experience – Semiconductor/ Pharmaceuticals/ Medical Device/ Oil refining
  - PhD on CMP slurries
  - Licensed Patent Agent
  - GE&R Advisor Board
    - Ted Taylor - Micron R&D Fab Manager / Director at Cymer
    - Steve Oldenburg – President of NanoComposix
    - Professor Jan Talbot – Head of UCSD ChemE dept.
- Current employees
  - 5 full time employees , 2 part time, 3 UCSD graduate students, 2 Prof.

- Lab opened in 2012 with Phase I SBIR NSF Grant - $150,000 1yr
  - Development of nano-Capsules
    - CMP slurries
  - Phase II Awarded 2014 - $750,000 – 2yr
- R&D Grant NRL – $2.4M for 6 yrs - Cooling Technology - Collaboration with UCSD
- DOE STTR Awarded June 2012 – Magnetocaloric nanomaterials

Future Research Areas

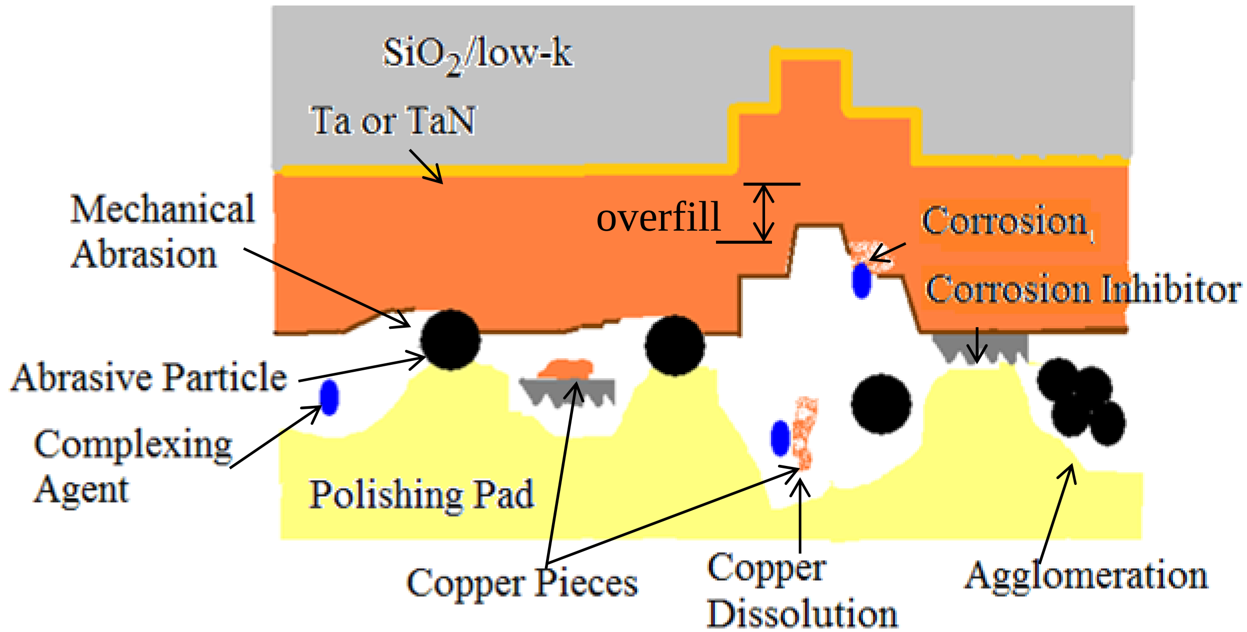
- ☐ Bio applications - Nano-Capsules



Motivation

- CMP - planarize and remove material
- Slurry - mechanical and chemical
- Cu CMP complex - reactive surface

Typical Cu CMP Process

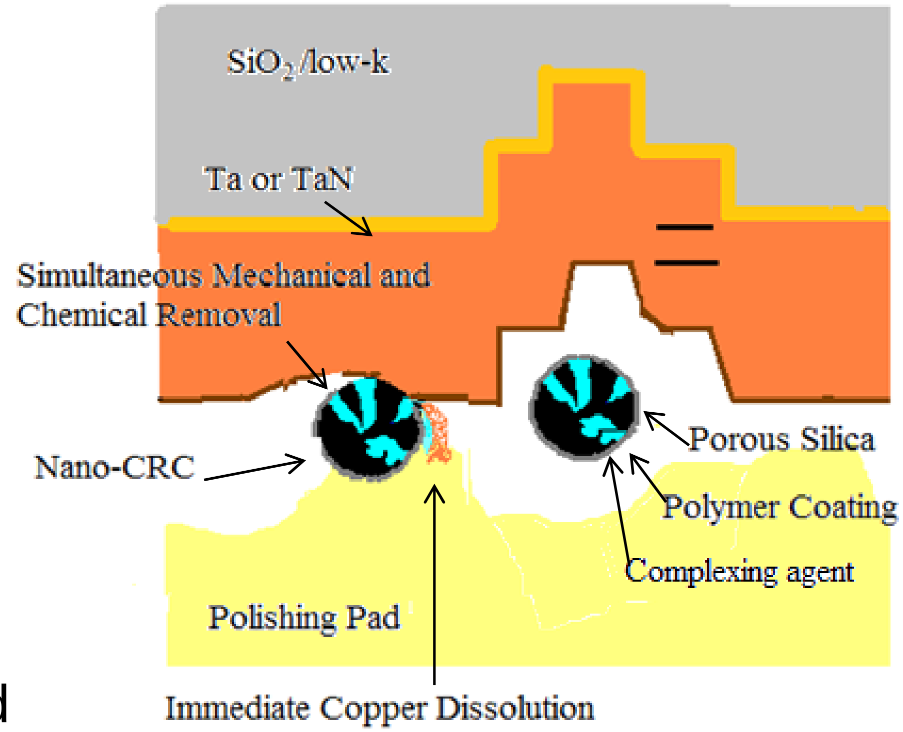


- Current CMP slurries are homogeneous mixtures of nanoparticles and chemicals
  - Chemicals - cause unwanted etching, dishing, oxidation
  - Additional corrosion inhibitors, surfactants – lower MRR
  - As devices scale down – becomes more difficult to achieve planarity
- Need to control exposure of the chemical components
  - reduce/eliminate etching, increase planarization efficiency

Research Objectives

Develop and optimize methods to synthesize nano-capsule slurries

- □Chemical payload encapsulated in the nanoparticle pores
- □Polymer coating that is stable over time – does not allow leakage of payload
- □A polymer soft enough to be torn away with shearing force to release the payload
- □Particles that are easily dispersed – no agglomeration
- □Meet the cost requirements for competitive CMP slurry pricing



For Cu CMP – silica loaded with glycine
- Zero etch rate,
- High MRR
- High PE

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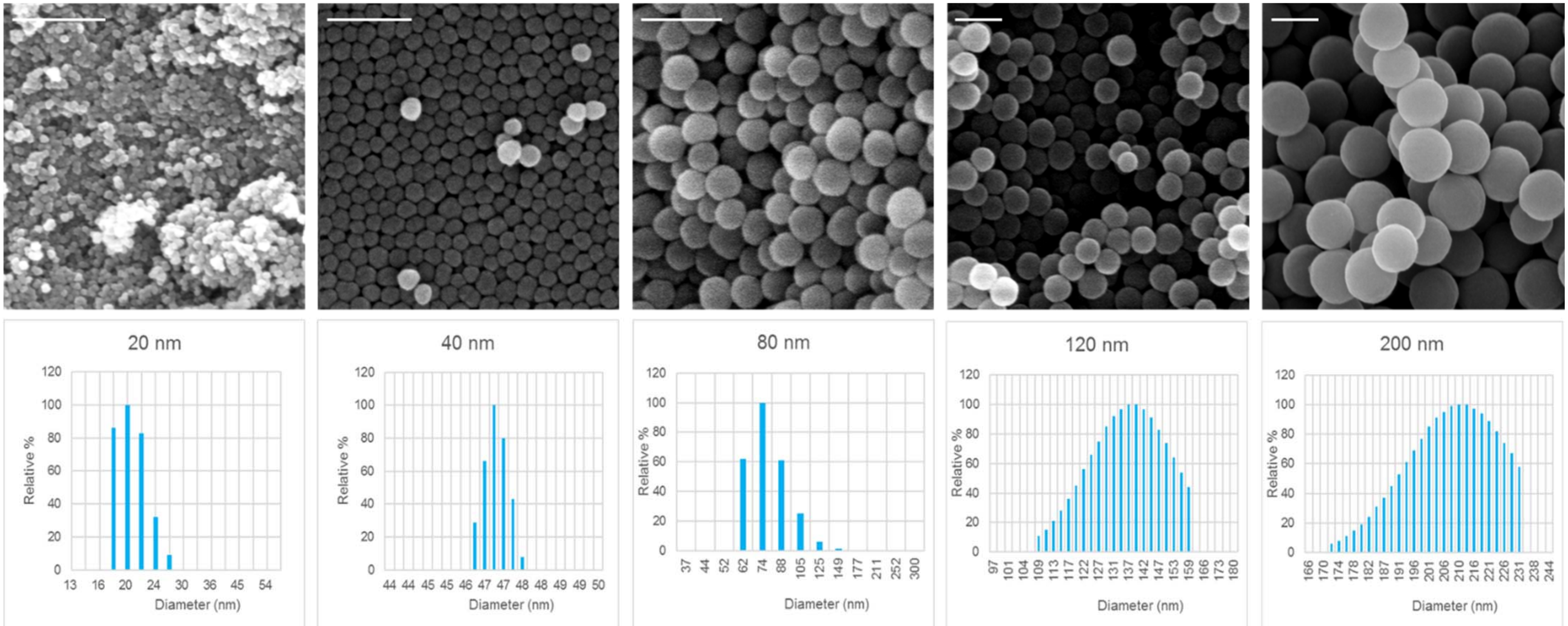
Porous Silica Synthesis

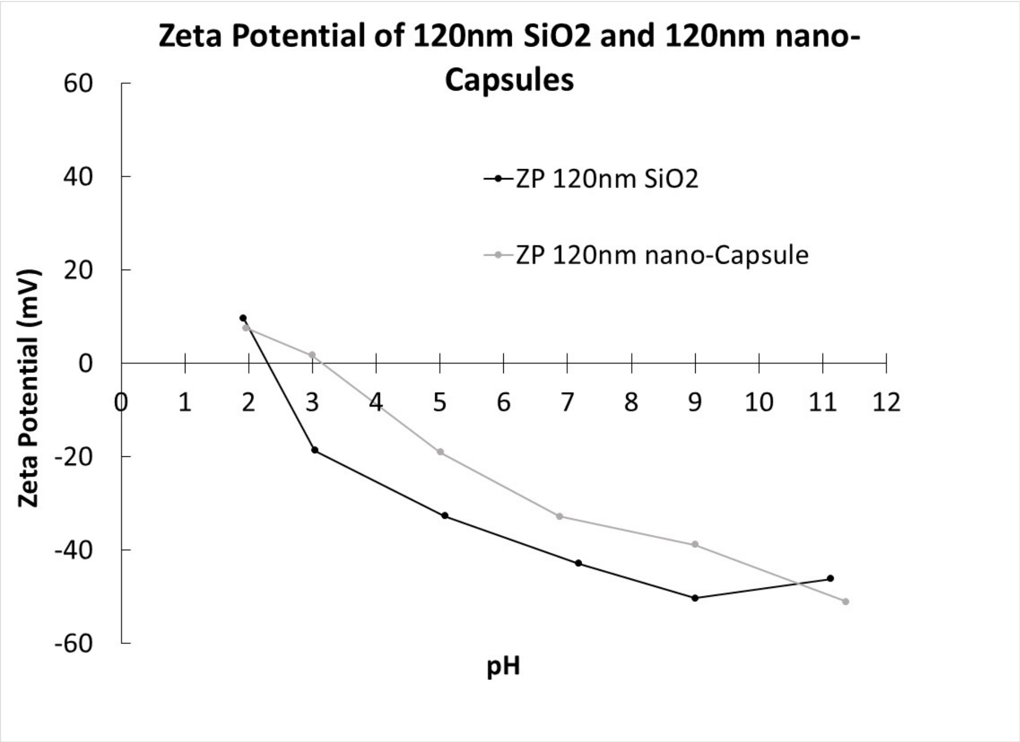


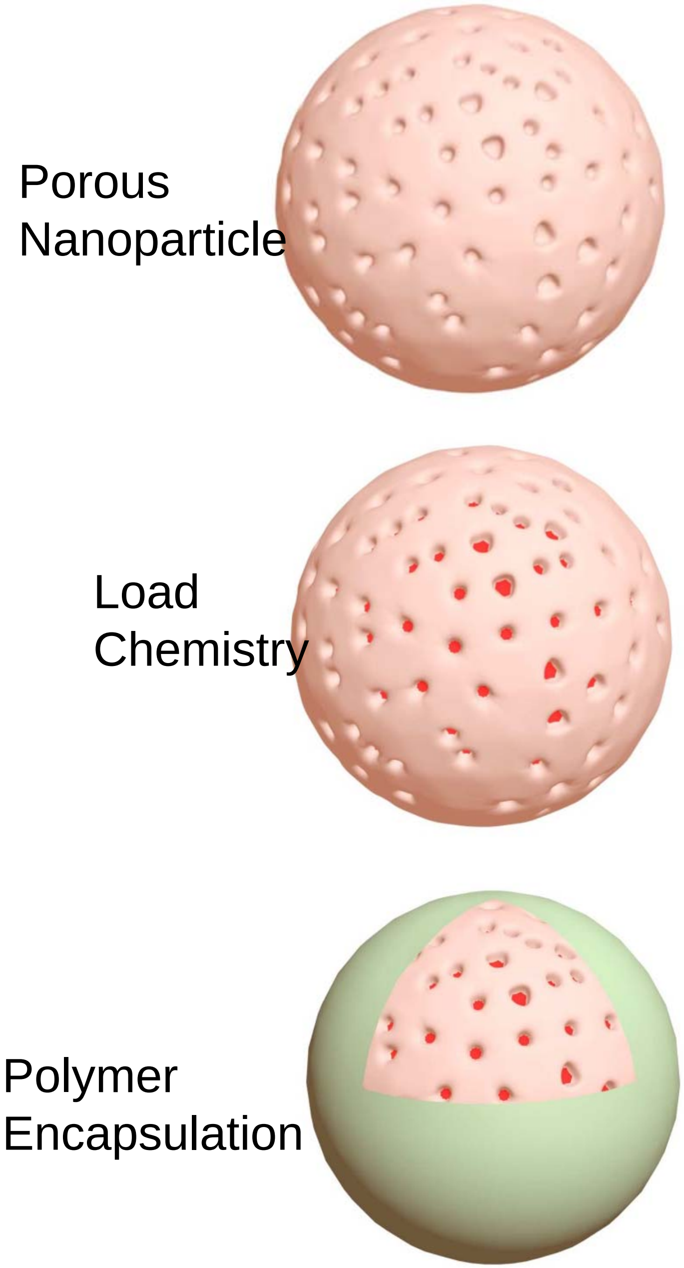
- Modified Stober method
- GE&R Silica is available from 20nm-1000nm
- Cv < 20% (SEM)
- Powder or dispersion

Nano-capsule Synthesis

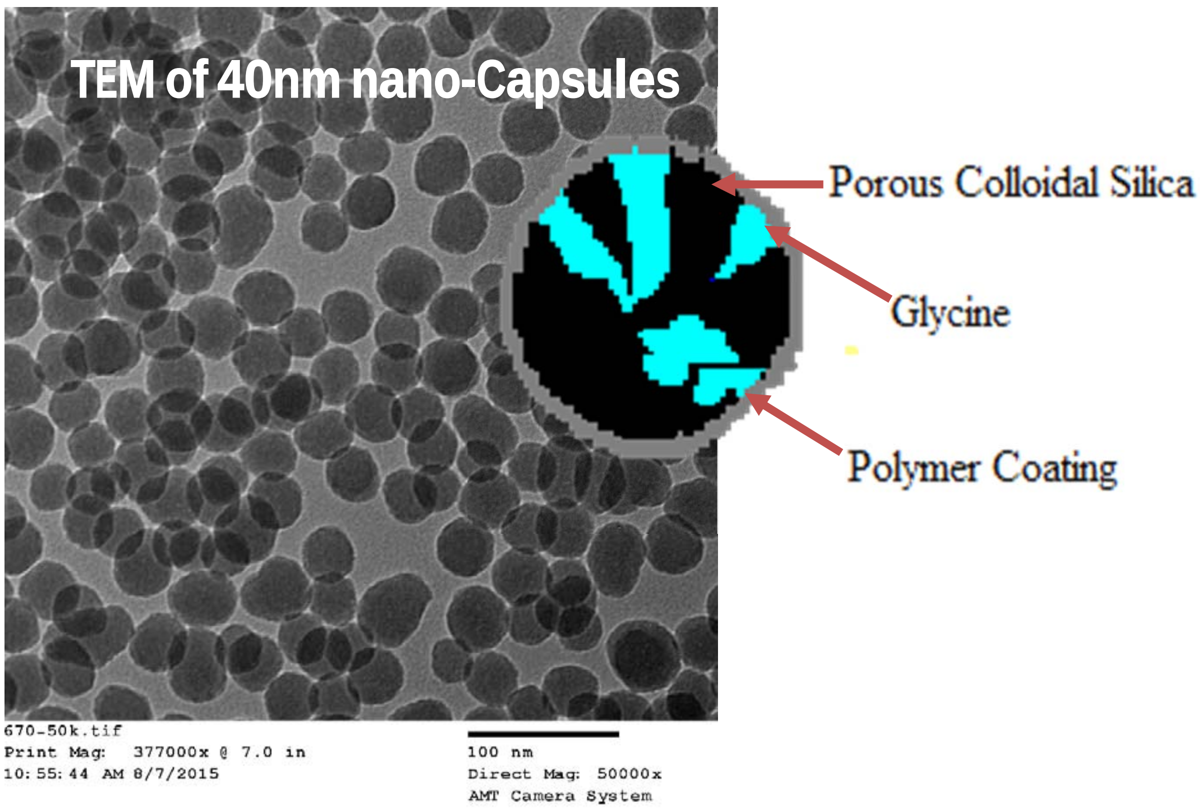
GE&R Synthetic Methods Proprietary

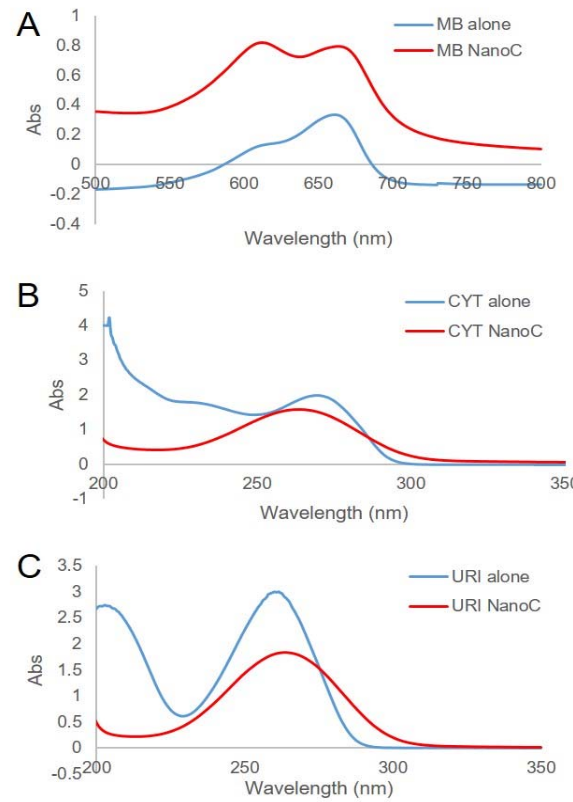
- Loading and coating is simultaneous in solution
- Economical Processing
- Various base particles (silica, alumina, etc.) possible
- Various payloads possible
- Considerations for nano-capsule synthesis
    - Solution pH, nanoparticle IEP, ionic strength, chemical payload interaction with polymer materials





Nano-Capsule Loading





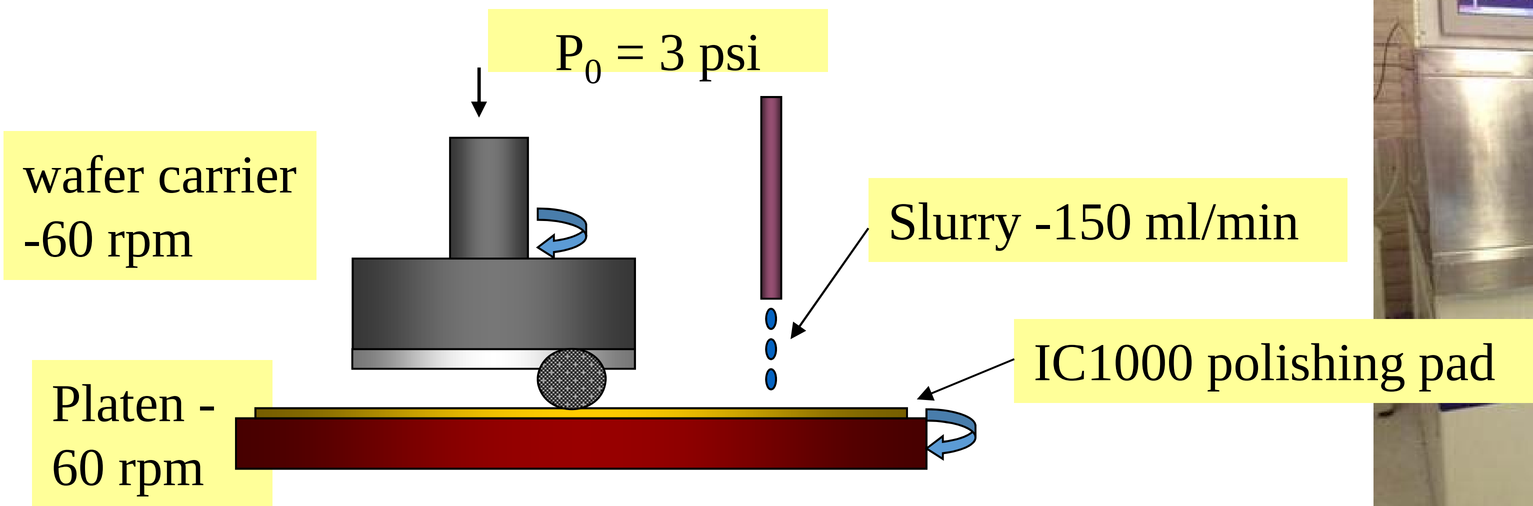
UV-Vis data of a) MB, b) CYT, and c) URI in solution alone and encapsulated into 40nm silica nano-capsules

How much chemical is loaded?

- BET intra - porosity 40nm silica ~ 15-20%
- Glycine + Methylene Blue ~3-15% loading
- Cytidine and Uridine ~3-5%
- Polymer coating not complete encapsulation? Pore Size effects

Experimental Copper CMP

Strasbaugh 6EC CMP Machine

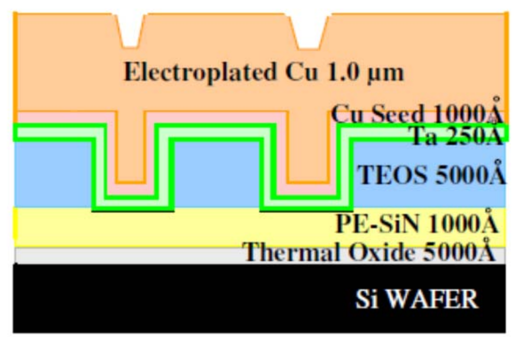


- Addition of hydrogen peroxide (H_2O_2) (oxidizing agent)

Material Removal Rates (MRR) – wafers weighed before and after CMP

Planarization Efficiency (PE) – measured using a Dektak 150 surface profiler

- Test wafers were purchased from SKW Associates, Inc., using MIT854 mask



Cu CMP Data

- Cu CMP of 6in blanket copper wafers on Strasbaugh 6EC CMP machine

Silica loaded with various concentrations of glycine.
(silica at 4wt% and at pH 4.5 with 0.1wt% H_2O_2+1mM KNO_3).

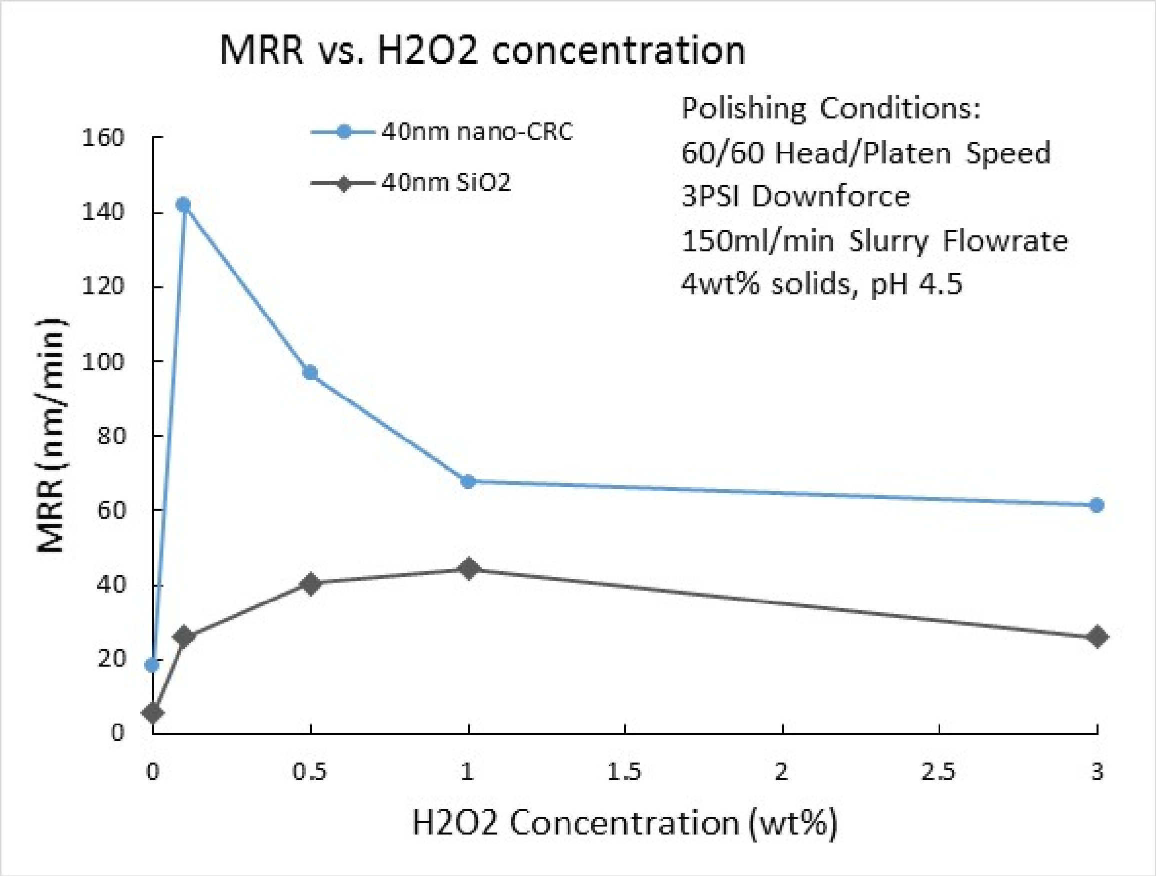
Slurry	MRR (nm/min)
40nm SiO_2 – not coated	44
40nm SiO_2 – polymer coated + 5wt% Glycine	43
40nm SiO_2 – polymer coated + 10wt% Glycine	65
40nm SiO_2 – polymer coated + 15wt% Glycine	94
40nm SiO_2 – polymer coated + 22wt% Glycine	134

Polishing conditions: IC1000 polishing pad, 60rpm platen speed/60rpm head speed, 150ml/min slurry delivery, 3PSI downforce.

- ❑ Glycine concentration limited by solubility in H_2O

Cu CMP Data

- CMP of 6in blanket copper wafers on Strasbaugh 6EC CMP machine



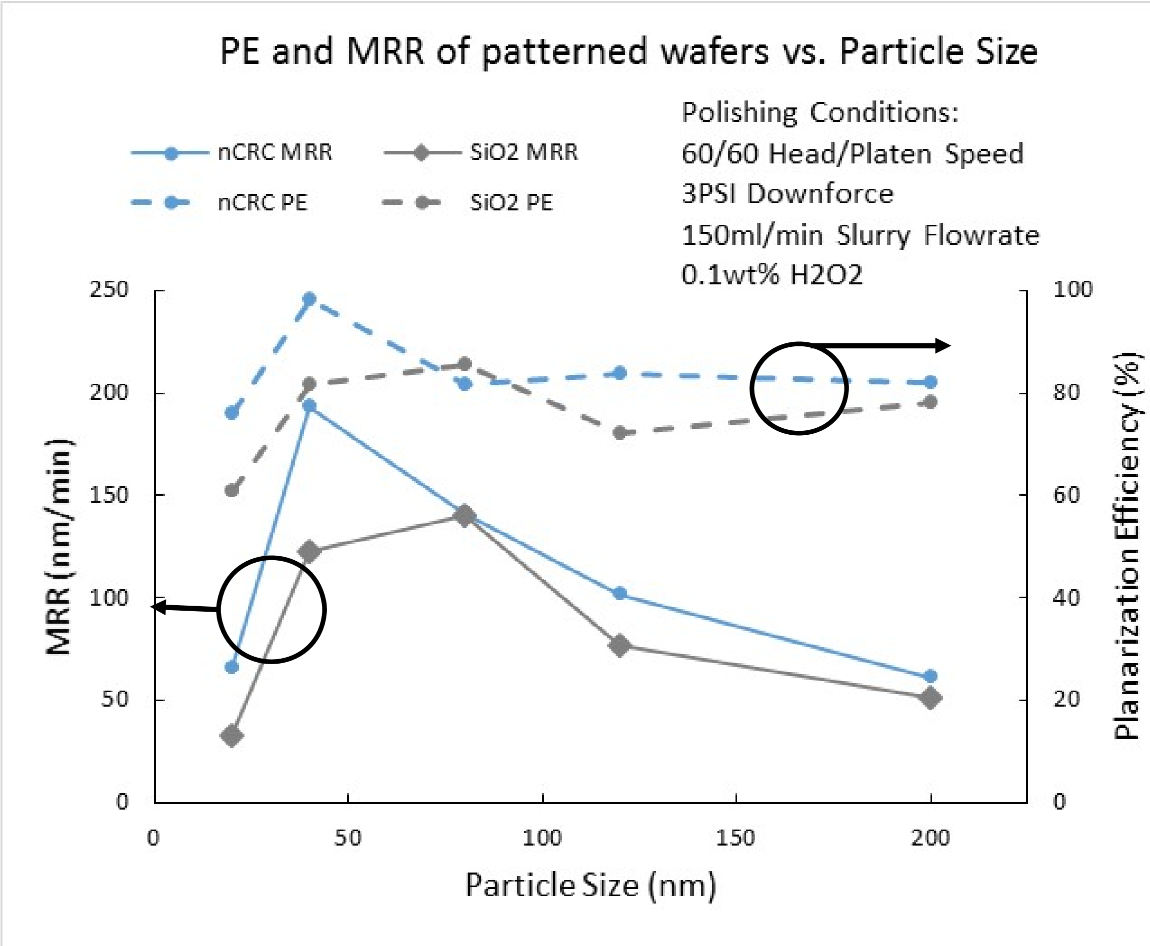
Nano-CRC slurry – 40nm Silica nanoparticles loaded with **glycine** and polymer coated

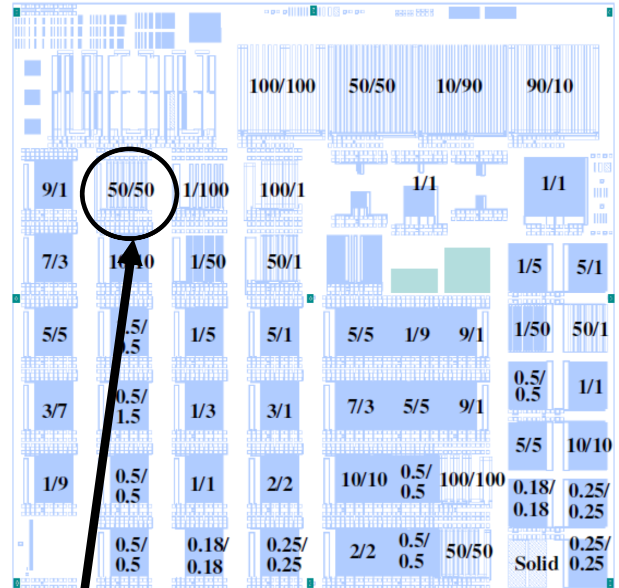
40nm SiO2 slurry – 40nm Silica nanoparticles (no chemistry or coating)

❑ Nano-CRC - very sensitive to H2O2 concentration!

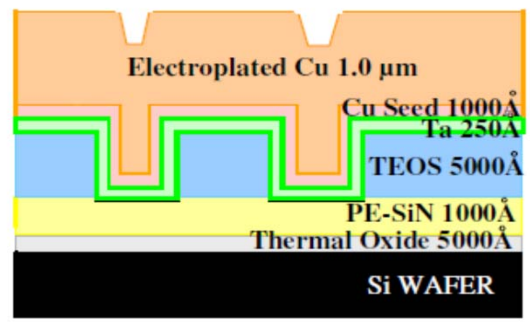
    ❑ Optimal H2O2 concentration ~0.1wt%

Cu CMP Data – Patterned Wafers





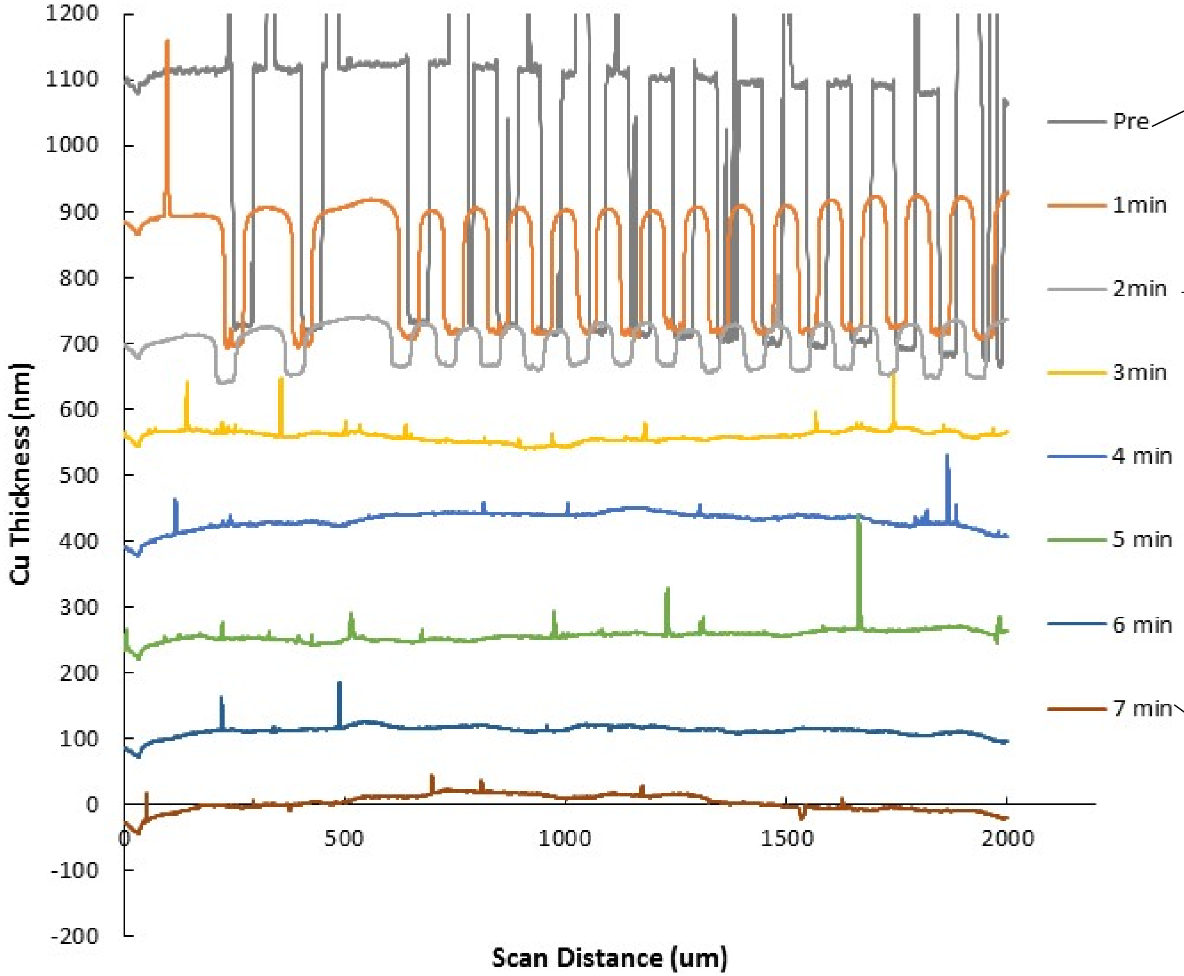
Profile of 50um line space/50um line width feature used to determine PE.

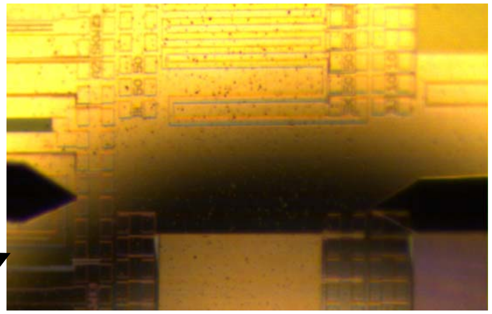


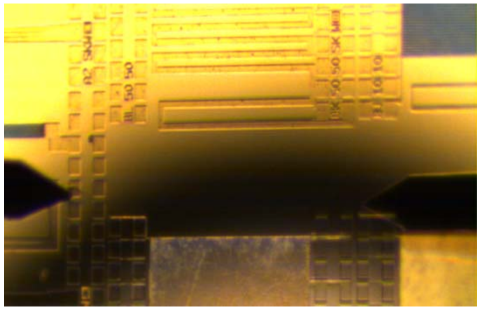
- ❑ Highest PE and MRR - 40nm Nano-CRC Slurry
- ❑ Porosity/Loading changes with PS?

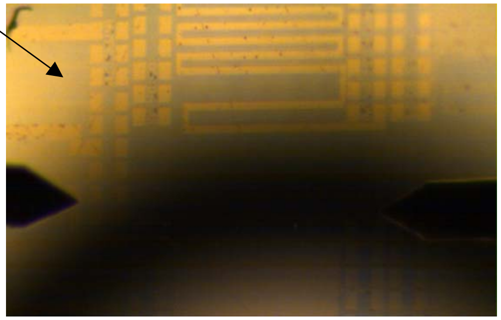
Cu CMP Data – Patterned Wafers

Profile of Middle Site on Patterned Cu wafer before and after CMP using Nano-CRC slurry at pH 4.5 (4wt% 40nm Silica loaded with Glycine and polymer coated , 0.1wt% H_2O_2, 1mmol KNO_3)









- ❑ 40nm Nano-CRC Slurry PE>85%

Other Efforts

- Chemical Payloads
  - Silica – Glycine, Tartaric Acid, acetic acid, potassium persulfate, – all successfully loaded.
- Increasing/controlling the porosity of silica nanoparticles
  - Payload concentration limited by solubility and porosity
  - 80nm SiO2 particles highest MRR but no increase in MRR in nano-CRC form - low porosity?
- Base particles – Colloidal Properties (IEP) limit particle effectivity
  - Commercially available - SiO2, CeO_2, Al_2O_3
  - Low cost Composite Nanoparticles ?

Other nano-capsules – Bring us your ideas!

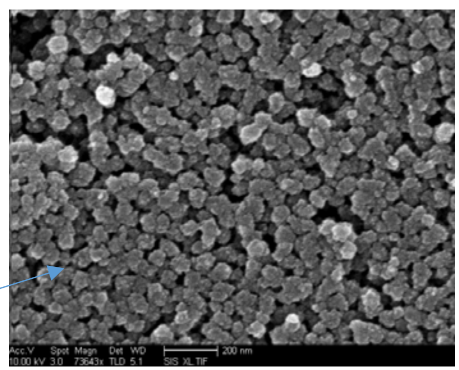
MRR for Ti CMP with nano-CRC

Slurry	MRR (nm/min)
40nm SiO2 – not coated	44
40nm SiO2 – polymer coated + 4wt% $K_2S_2O_8$	118

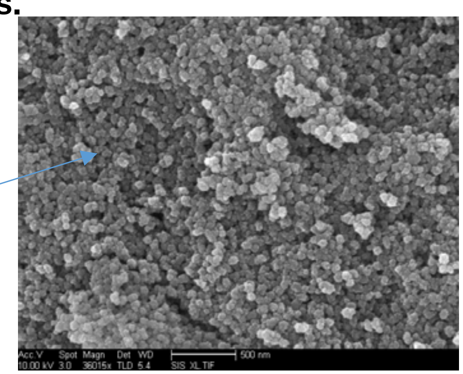
Measured IEP for various nanomaterials synthesized using GE&R proprietary methods.

Material	Measured IEP
SiO_2	2
Si-Al-O	4-5
Al-O	8-9

Material	Measured IEP
$SiZrO_4$	3-4
$Si_{0.5}Zr_{1.5}O_4$	4-5
ZrO_2	5-6



Material	Measured IEP
SiO_2	2
$SiTiO_4$	2-3
$Si_{0.5}Ti_{1.5}O_4$	3-4
$Si_{0.2}Ti_{1.8}O_4$	3-4
TiO_2	~4



Tunable IEP Nanocomposites - Spherical Morphology – low defectivity

Summary

- ❑ High quality monodispersed silica nanoparticles commercially available
- ❑ Processing techniques to form high quality nano-capsule slurries developed
- ❑ Advantages of nano-Capsule slurries
    - ❑ High planarization efficiencies
    - ❑ Enables controlled exposure of chemicals to surface
    - ❑ Environmental – low concentrations of toxic/hazardous payloads possible

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