

# BASF Soft Particles for Metal CMP

Vijay Raman<sup>1</sup>

Claus Poppe<sup>2</sup>

Bastian Noller<sup>3</sup>

Michael Lauter<sup>2</sup>

Yuzhuo Li<sup>2</sup>

BASF SE, Ludwigshafen, Germany

<sup>1</sup> Global Polymer Research – Polymer Colloids

<sup>2</sup> Global Business Unit Electronic Materials

<sup>3</sup> Competence Center Formulation Technologies

BASF SE, Ludwigshafen, Germany



The Chemical Company

# BASF – The Chemical Company

## The world's leading chemical company



- Chemistry is about every aspect of life.
- We are connected to deliver intelligent and sustainable solutions.
- Sales 2009: €50,693 mill.
- EBIT 2009: €3,677 mill.
- Employees (December 31, 2009): 104,779
- About 1,300 new patents filed
- 6 Verbund sites and about 380 production sites



# Electronic Materials by BASF

## Worldwide Presence



# Electronic Materials by BASF

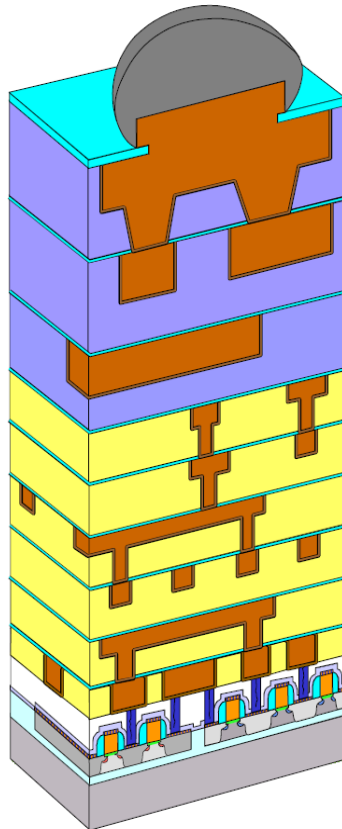
R&D to meet customer needs



- State-of-the-art R&D and application facilities in Europe and Asia
- Presently approx. 100 employees dedicated to the development activities in Electronic Materials
- Part of approx. 9,300 employees in BASF's R&D and technology network
- Collaboration: commercial, academic partners and tool manufacturers
- Some of our R&D projects:
  - Advanced cleaning formulations
  - Copper electroplating
  - New CMP slurries



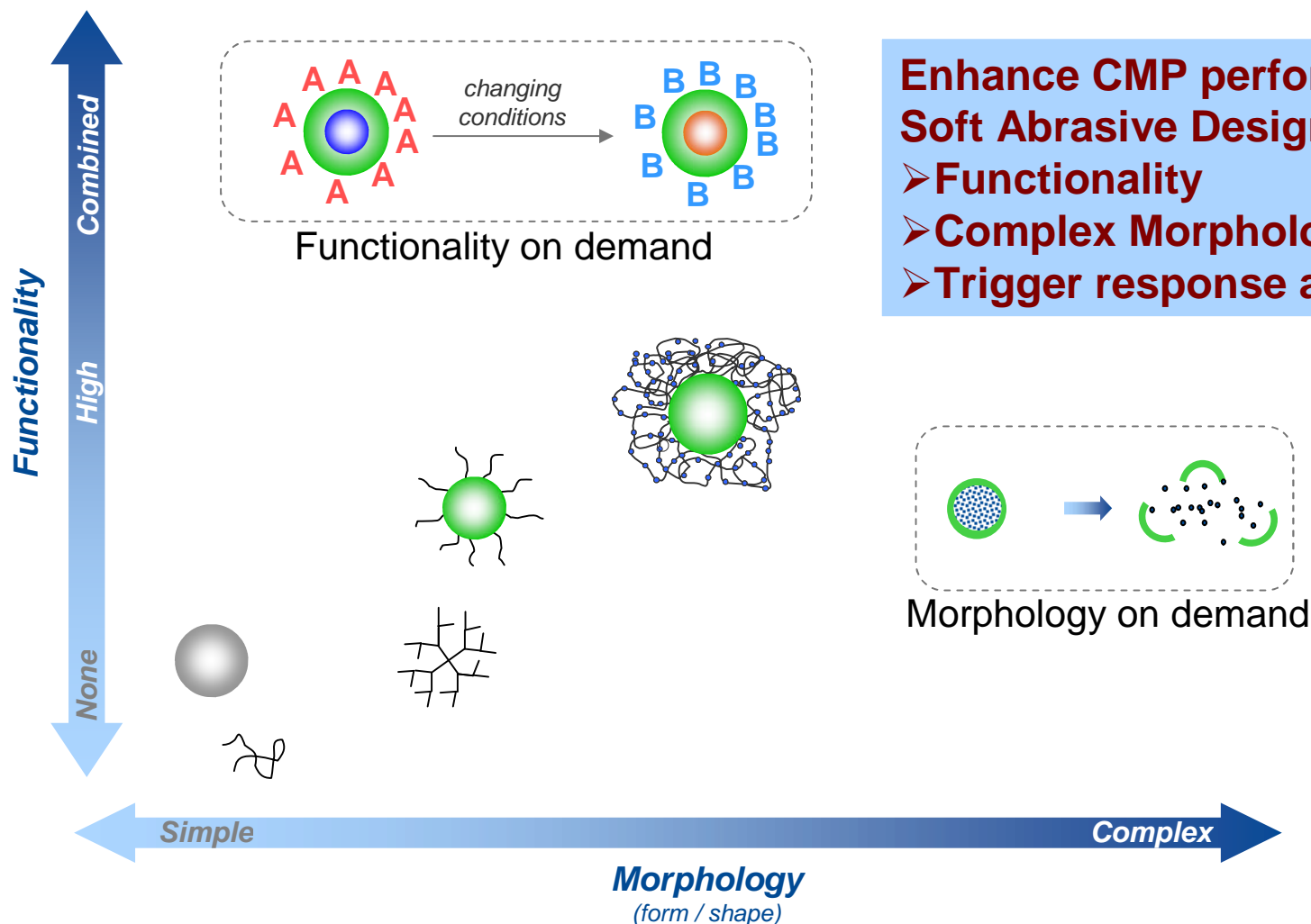
# Overview of BASF CMP Activities



## CMP Slurries

- Cu CMP for 3D TSV
  - Front and back side
- Cu CMP for Interconnect
- Barrier CMP for Interconnect
- Interlayer dielectric (ILD)
- Shallow trench isolation (STI)
  - Nitride and poly Si stopping
- High K metal Gate
  - Poly Si opening

# BASF's intelligent chemistry for CMP: *Functional and Adaptive Particles for Dynamic Conditions*

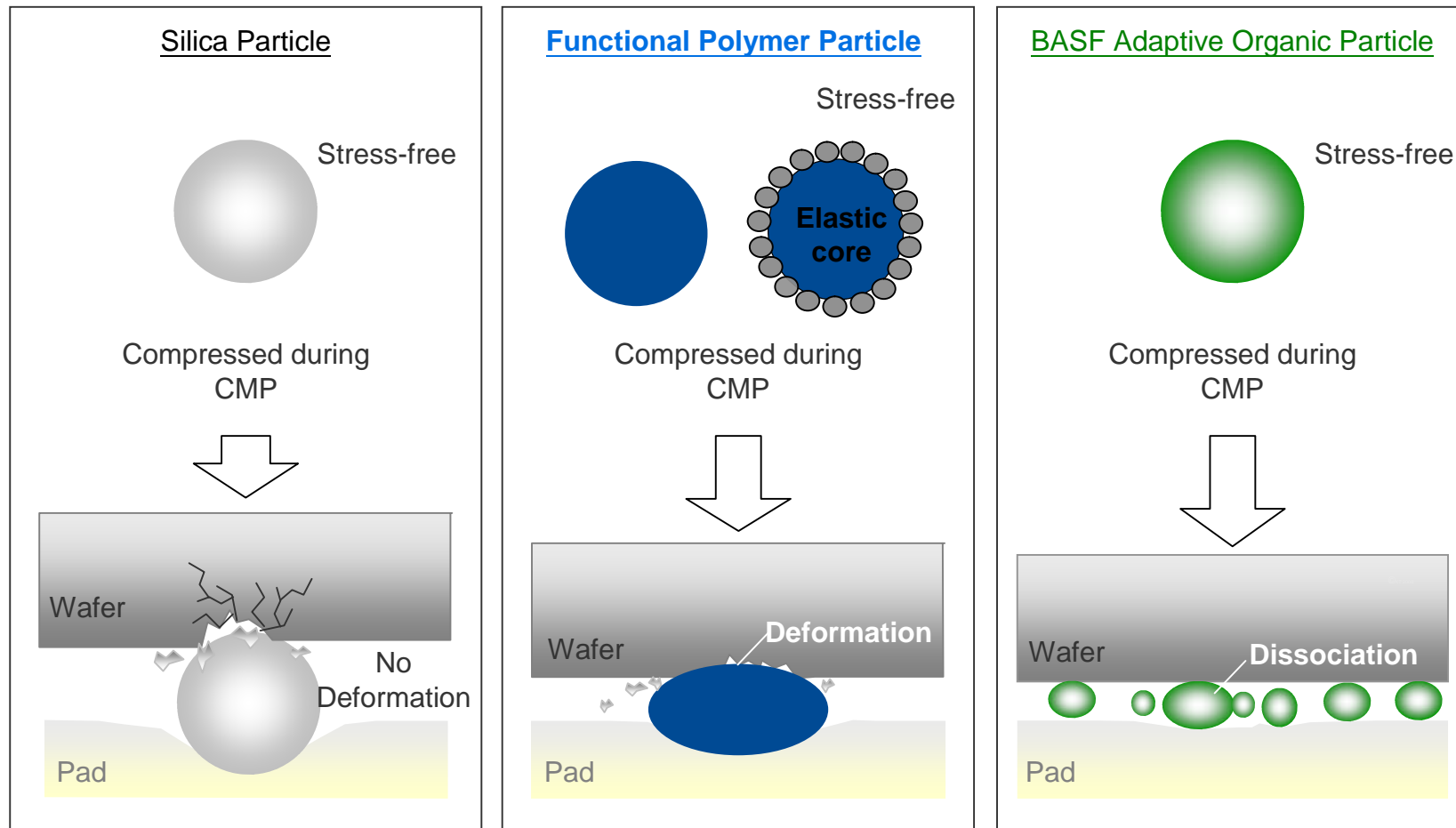


**Enhance CMP performance via Soft Abrasive Design**

- **Functionality**
- **Complex Morphology and**
- **Trigger response ability**

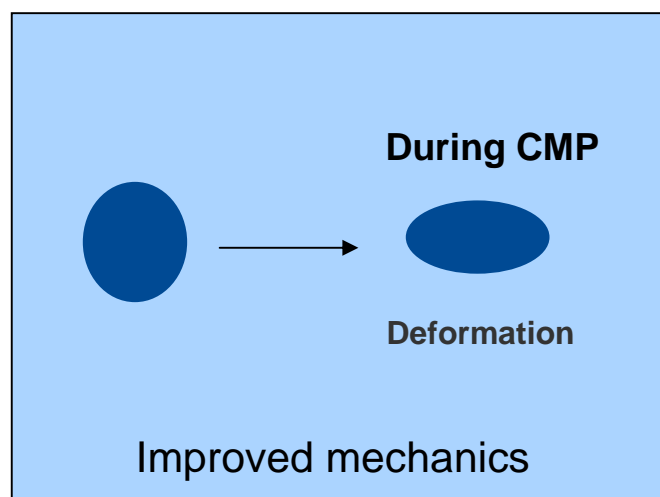


# New Soft Abrasives for CMP

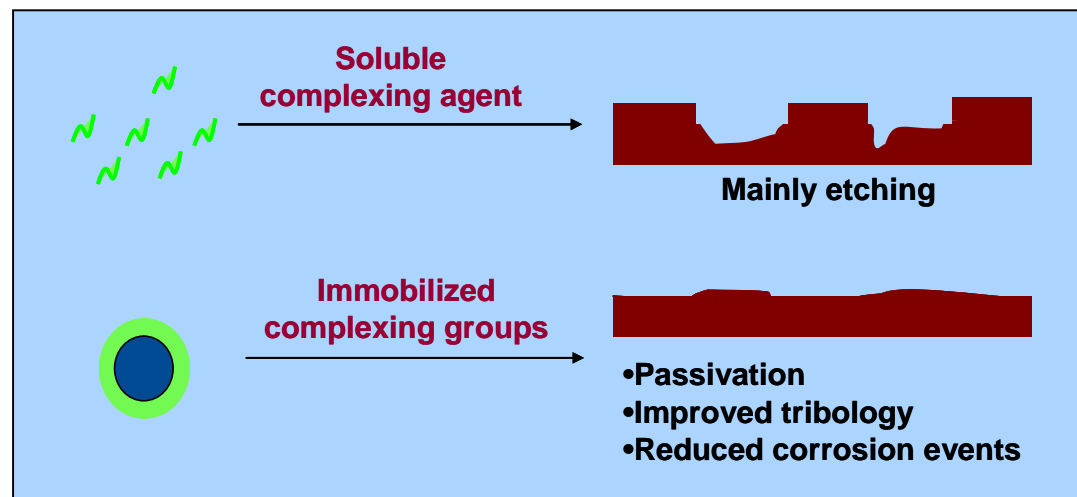


# Concept: Soft Functional Polymer Particles in CMP

## Soft Particle



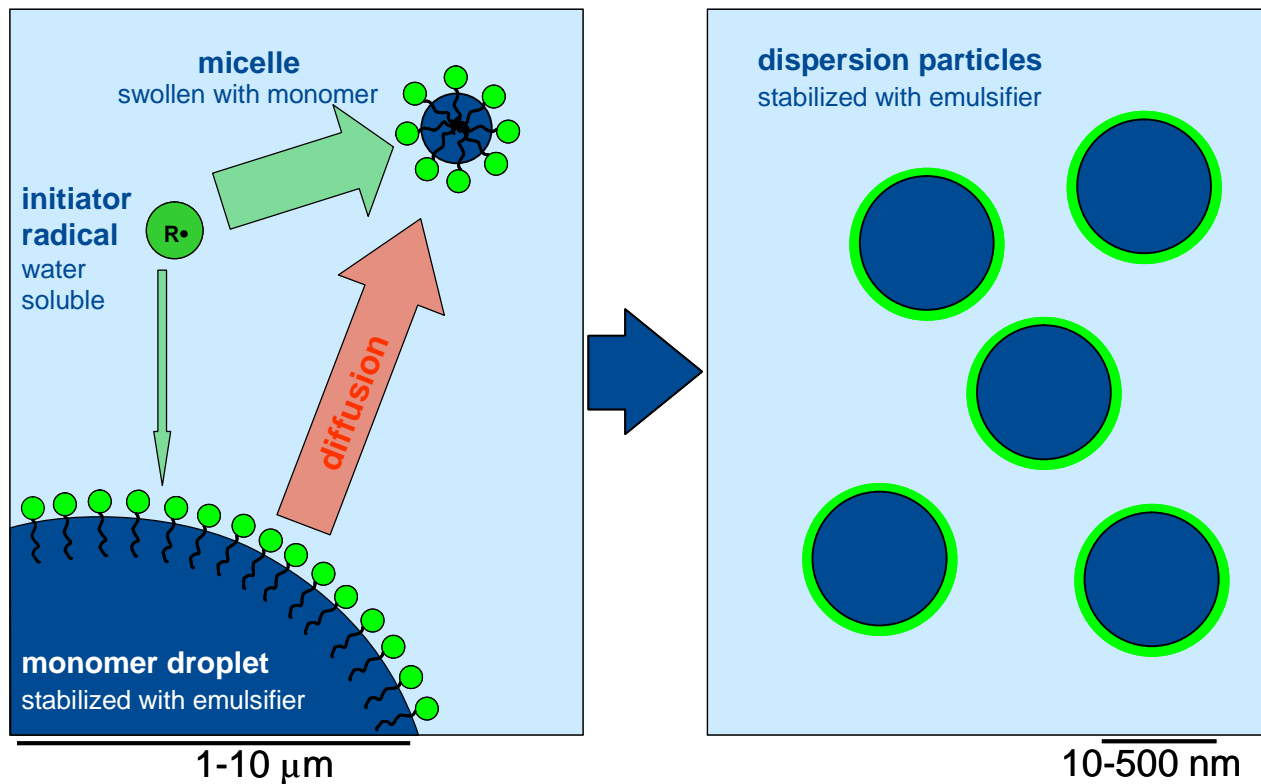
## Soft Functional Particle



# Improved chemical/mechanical balance in CMP



# Designing Polymer Particles via Emulsion Polymerization

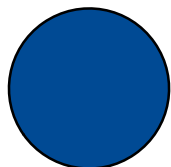


- **Current applications: Adhesives, Paints, Paper and Construction**
- **BASF capacity: > 1 million tons per year**
- **New market opportunity → CMP**

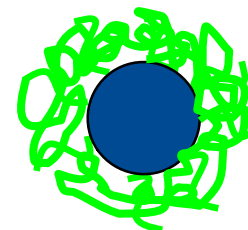
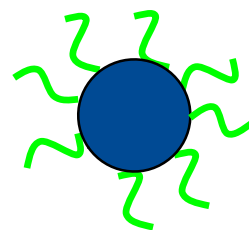
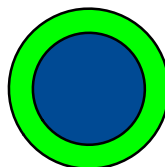
# BASF Polymerization Technologies: Versatile Functionalities and Morphologies



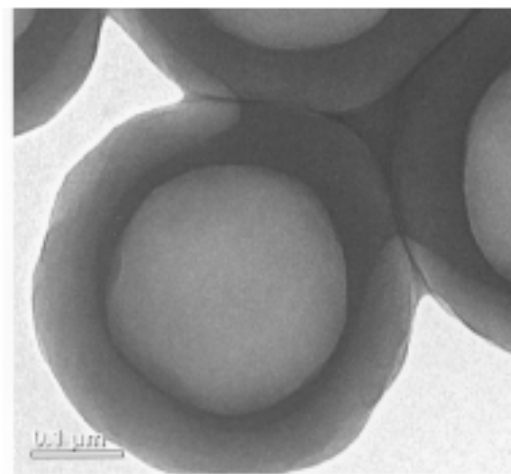
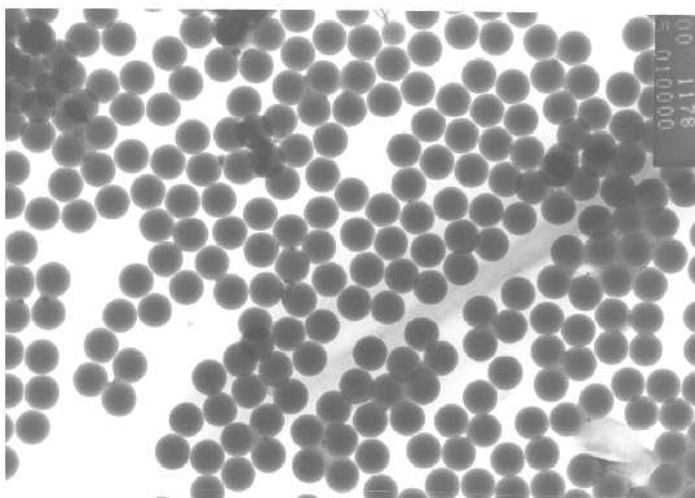
**new functionalized polymer particles with different morphologies**



Non-Functional Particles

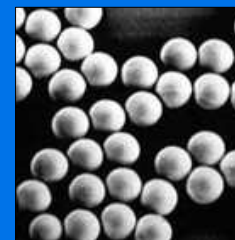


Functional Particles Core-Shell



Vijay Raman and Claus Poppe, BASF SE, Semicon West 2010

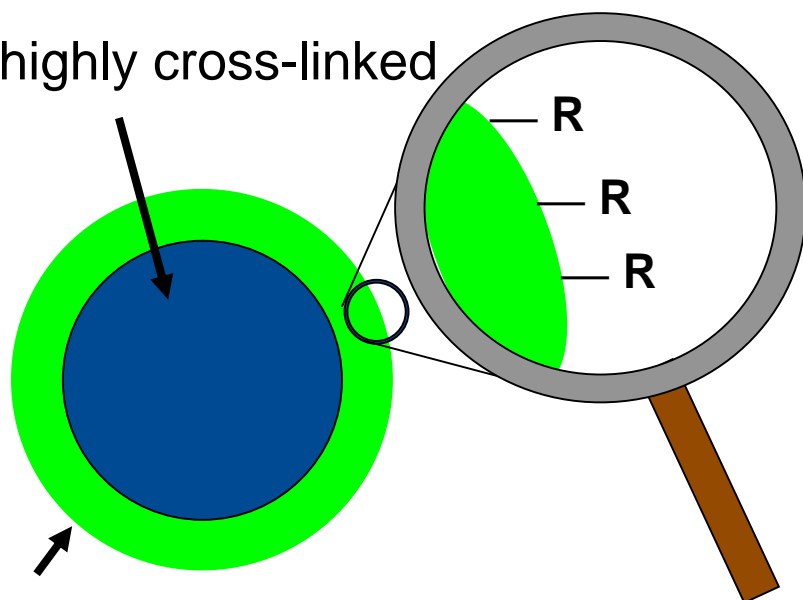
# Overview: Functional Polymer Particles for CMP



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## core:

- highly cross-linked



## shell:

- functional (R)

## Portfolio / Properties

**particle size:** 10nm to 500nm

**Tg:** -30°C to 180°C

**crosslinking:** up to 30%

**functionality (R):** cationic, anionic and non-ionic

**solids:** up to 60%

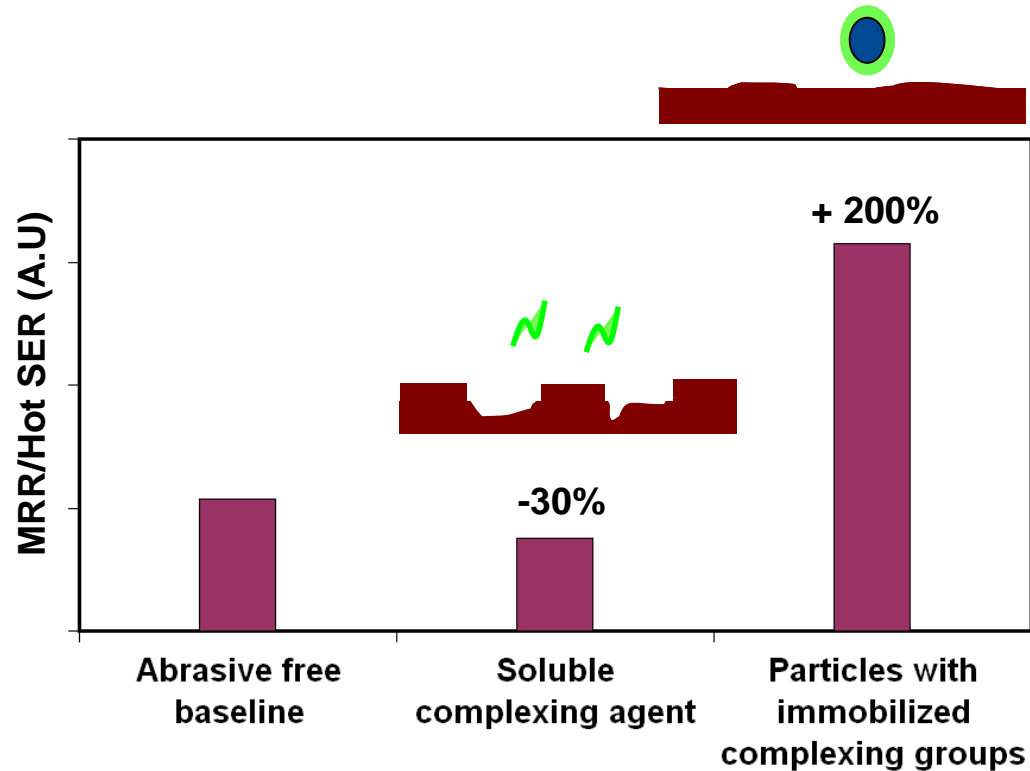
**surfactant:** low as 0,5 %

**stability:** thermal stability >350°C

**coagulum:** < 10 ppm possible

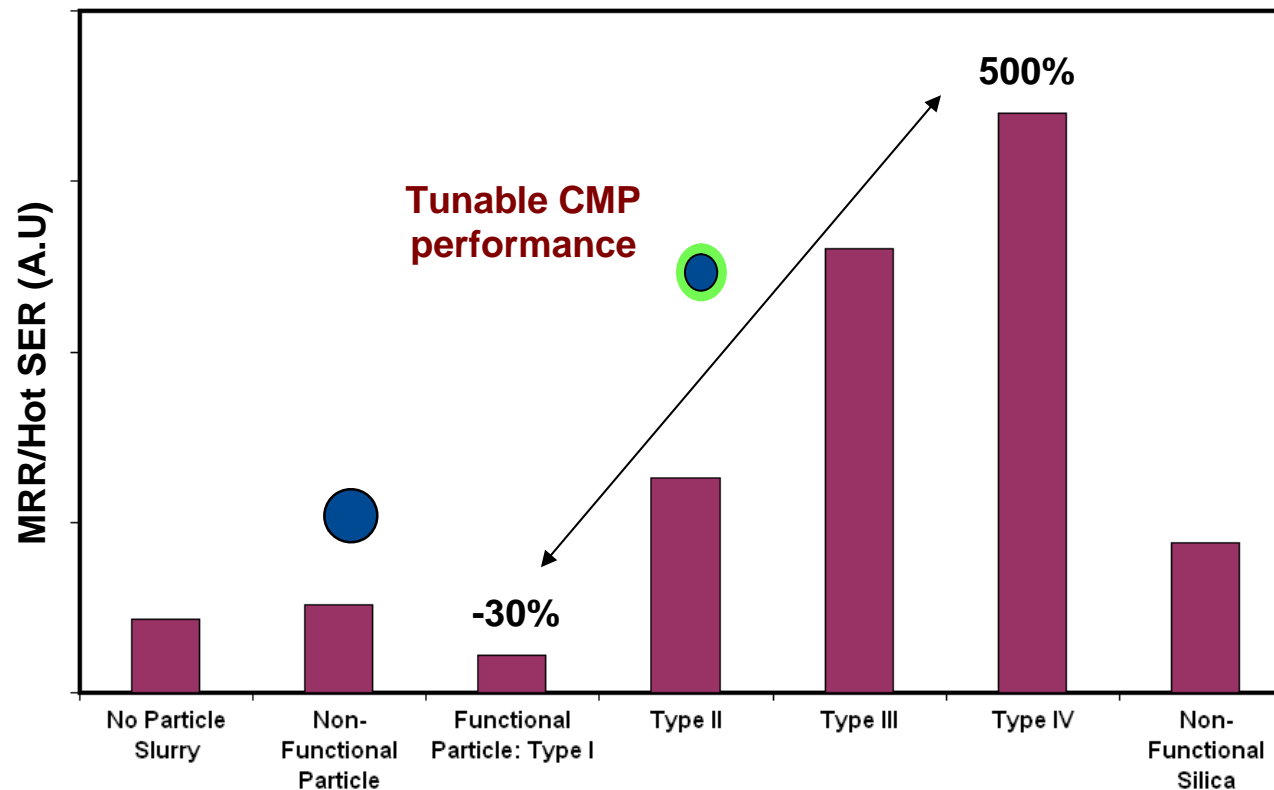
**very low VOC** < 10 ppm

# Proof of Concept: Soft Functional Polymer Particles in CMP



- Lower chemical etching (SER)
- Increased mechanical contribution (MRR)
- Improved Chemical/Mechanical balance

# Tunable CMP Performance via Surface Functionality

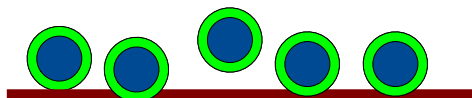


- CMP performance can be tuned via surface functionality
- Functional particle significantly improves the chemical-mechanical balance
- Performance significantly better than non-functionalized silica

# CMP Fundamental Investigations: Interfacial Phenomena

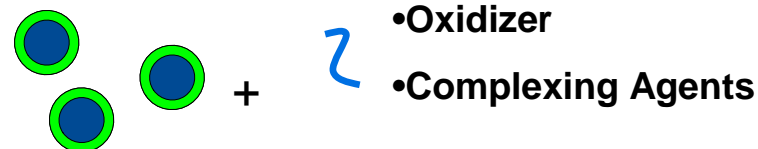
## Polymer Particle- Surface- Slurry Component Interactions

Polymer Particle +  
Surface Interactions



- Mechanics (AFM – Higher Harmonics)
- Surface Adsorption (AFM, QCM)
- (In-situ) IR, XPS

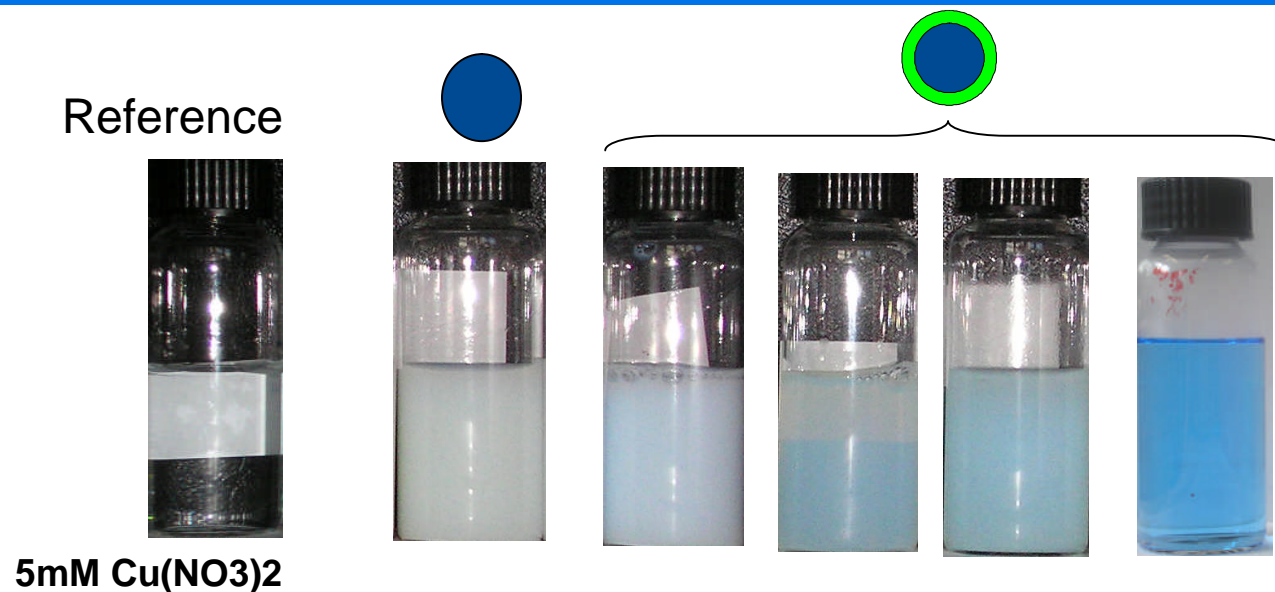
Polymer Particle +  
Slurry Component  
Interactions



- Optical observations
- NMR
- UV-vis, light scattering

**To develop a complete understanding of CMP  
interactions and mechanisms**

# Interactions of Functional Polymer Particles with Slurry Components



## NMR T<sub>2</sub> measurements

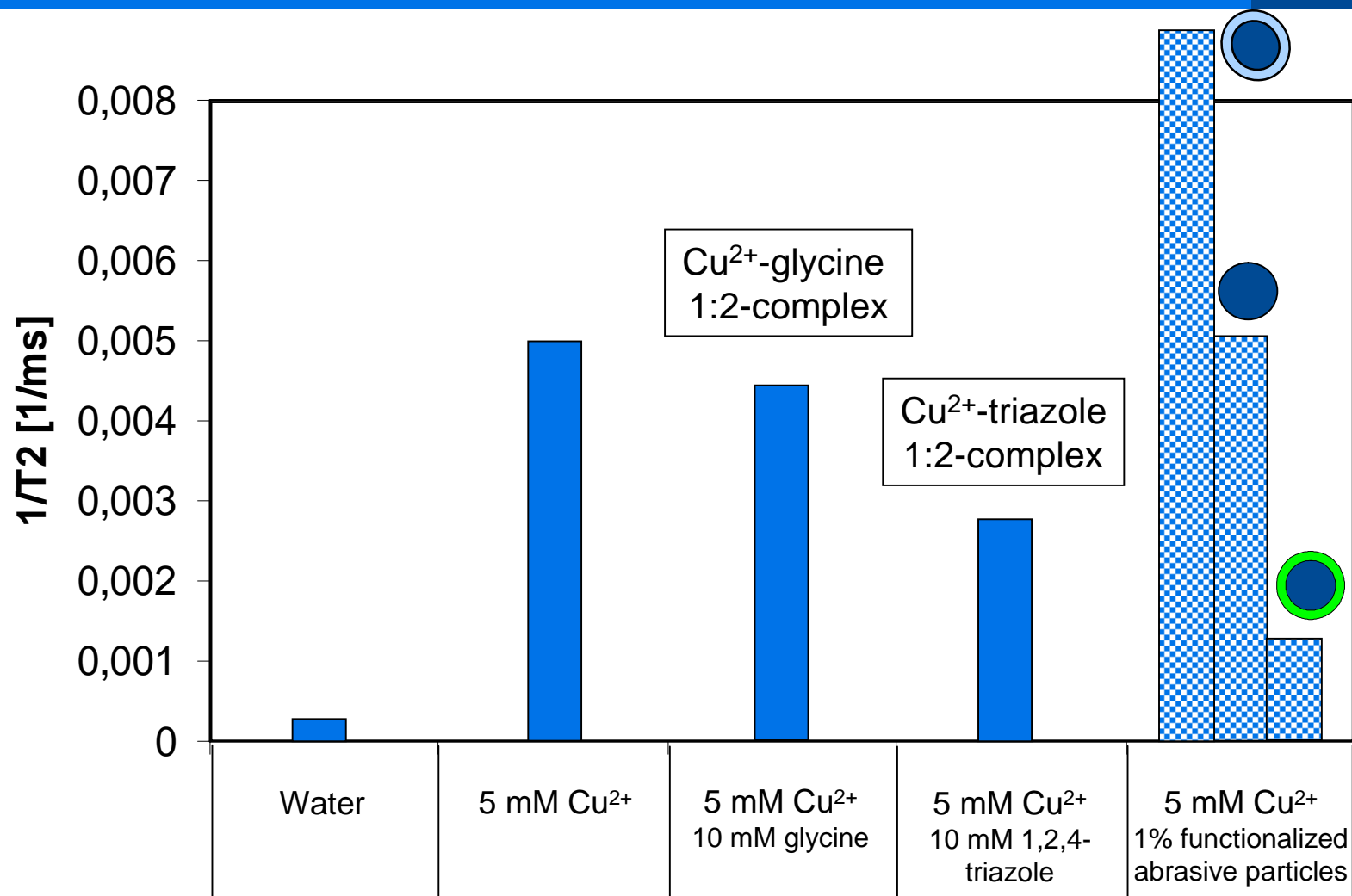
Relaxivity of water protons in presence of paramagnetic species

$$\frac{1}{T_i} = \frac{1}{T_{i,0}} + \rho_{i,para} C_{para}$$

Relaxivity, depends on paramagnetic species, solvent, magnetic field

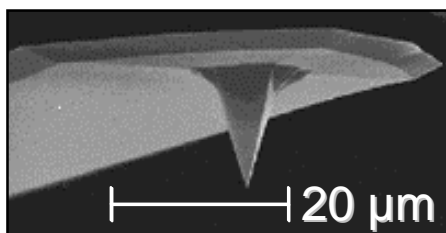


# Functionalized Particles a Versatile Component: Offers a Range of Interactions in Slurry



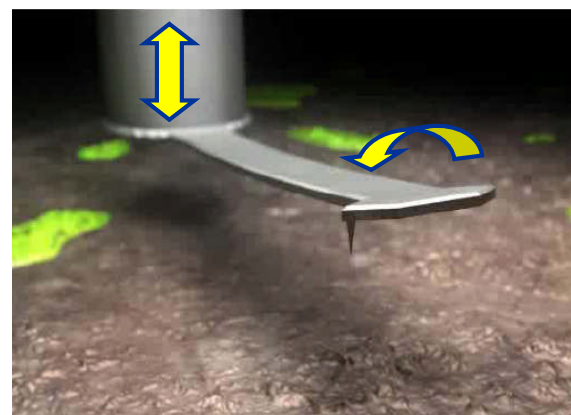
# Higher Harmonic AFM: New Insights Into Mechanical Property of Nanoparticles Adsorbed on Surfaces

Normal AFM Cantilever



**Mechanics possible only on flat surfaces  
/ particles immobilized on tips**

Higher Harmonics: Coupling the normal force on the tip into a torsional motion of the cantilever

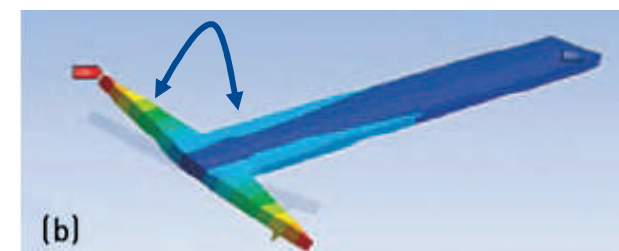


**Mechanics on individual particles adsorbed on  
surfaces – CMP conditions**

tapping 



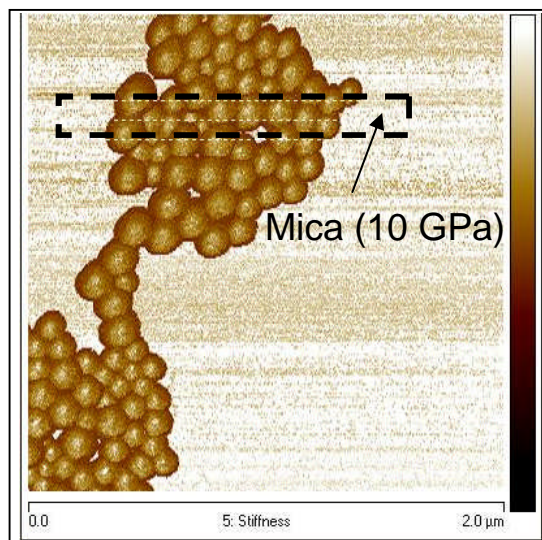
torsional deflection



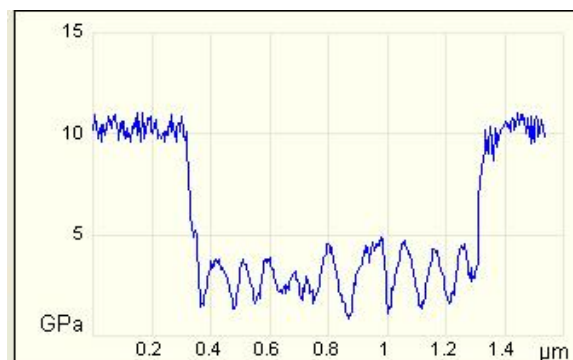
AFM & Nanomechanics Lab – Dr. Sugiharto (GKP/O)

**O. Sahin *et al.*, Nature Nanotechnology (2007) 2: 507 - 514**

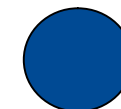
# Higher Harmonic AFM: Mechanics at CMP conditions



21.6 GPa

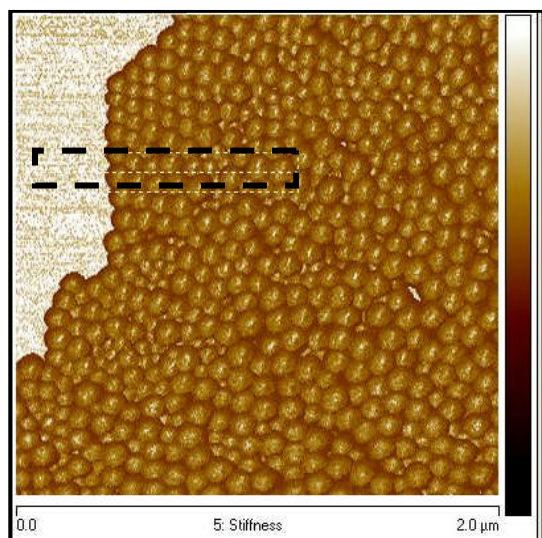


Mean elastic modulus:  
 $4.3 (\pm 0.4)$  GPa;  $n=4$

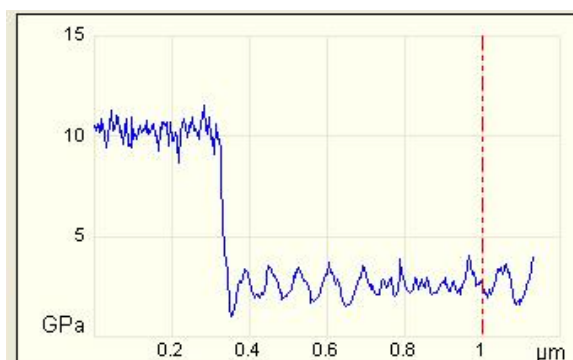


Non-Functionalized Particles

0.0 GPa

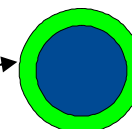


23.7 GPa



Mean elastic modulus:  
 $3.5 (\pm 0.3)$  GPa;  $n=4$

Hydroplasticized  
layer

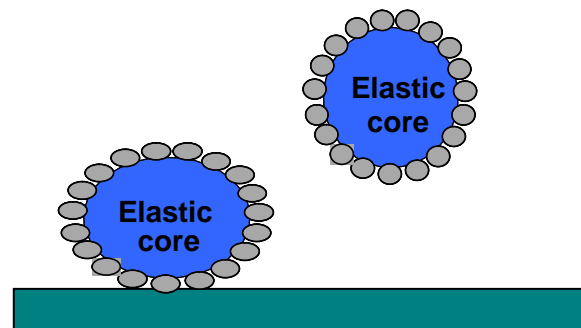


Functionalized Particles

0.0 GPa

Vijay Raman and Claus Poppe, BASF SE, Semicon West 2010 \* E-modulus: 2.4-4 GPa

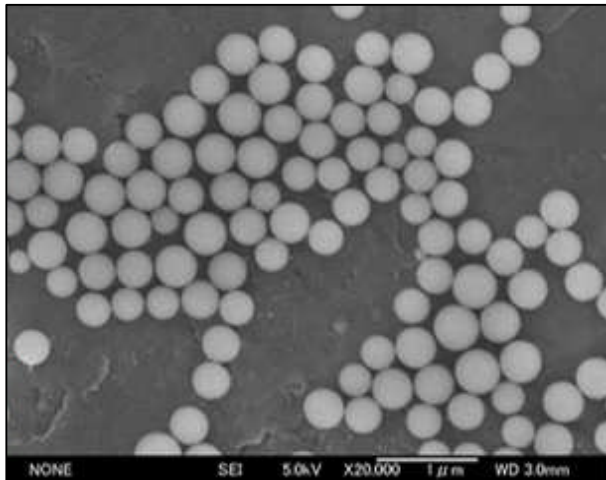
## Composite Abrasive



# Conventional High Purity Colloidal Silica (HPCS) vs. BASF High Purity Composite Abrasive (HPCA)

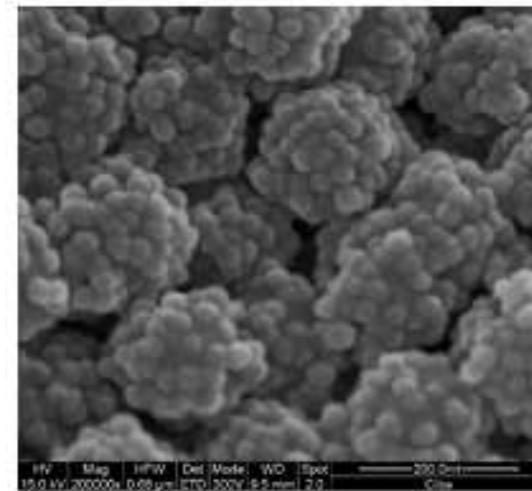


**Typical Colloidal Silica**



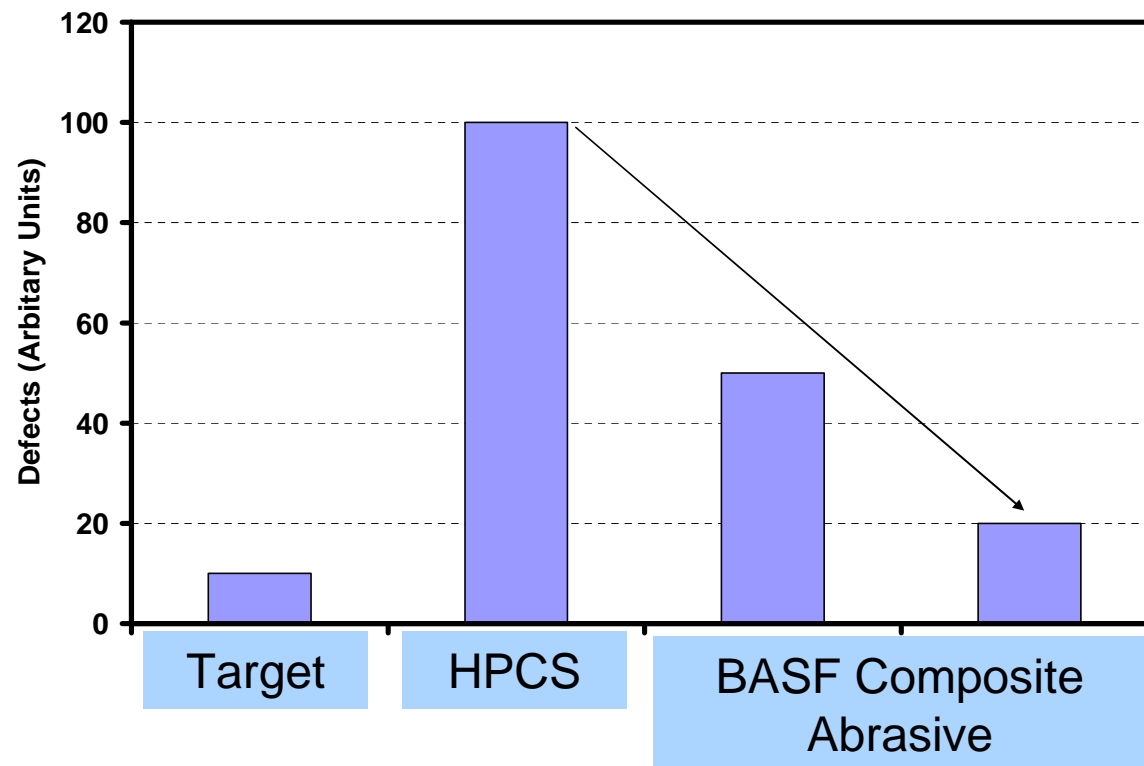
- Conventional Synthesis via TEOS or ion exchange
- High cost due to limited number of suppliers
- High purity
- 30-100 nm available
- Relatively hard
- Non-compressible

**BASF Composite Abrasive**



- Well controlled polymerization process: BASF IP
- Cost effective: HVM for other applications
- High purity possible
- 30 – 100 nm available
- Hardness and morphology tunable
- Compressible => low defect?

# Conventional High Purity Colloidal Silica vs. BASF Composite Abrasive



➤ **Excellent Defectivity Levels Achieved on Metal Layers**

# Conclusions

- **BASF Soft Abrasive Design to Improve CMP performance**
- **Functional Polymer Particles** – a new component for Cu CMP slurry design
  - with improved chemical-mechanical balance
  - tunable CMP performance – via surface functionality
- **Composite abrasive**
  - Industrially feasible composite structures
  - Excellent defectivity with balanced removal rate
- **Fundamental Mechanistic Understanding**
  - AFM higher harmonics – to understand mechanics of particles under CMP conditions
  - Particle-slurry component interactions – functional abrasives offer a range of versatile interactions for slurry design (NMR)



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