How Much Do We Really Know About the Chemical Reactions Occurred During Cu CMP?

Prof. Dr. Yuzhuo Li
Global Electronic Business Unit
BASF, Ludwigshafen
Yuzhuo.li@basf.com

BASF
The Chemical Company

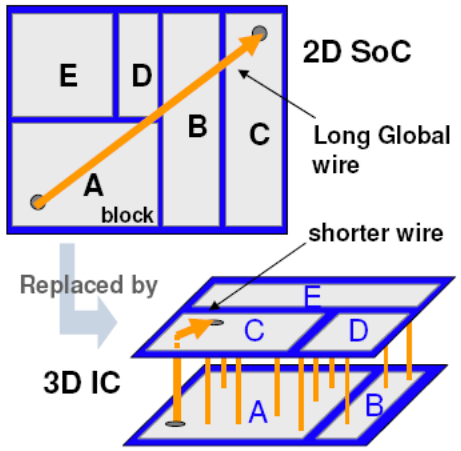
Presentation Outline

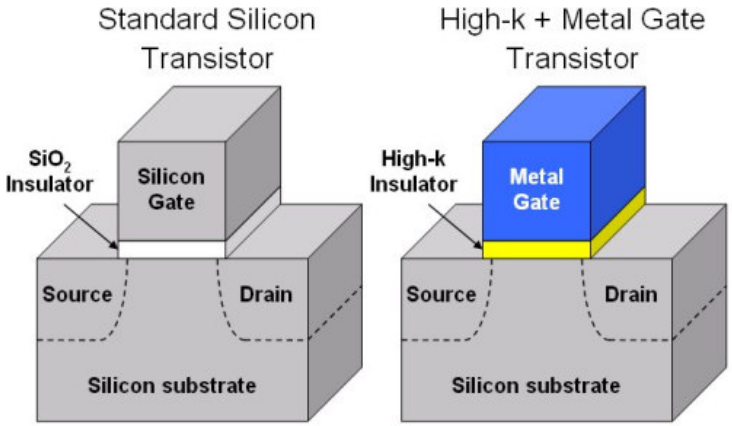
BASF
The Chemical Company

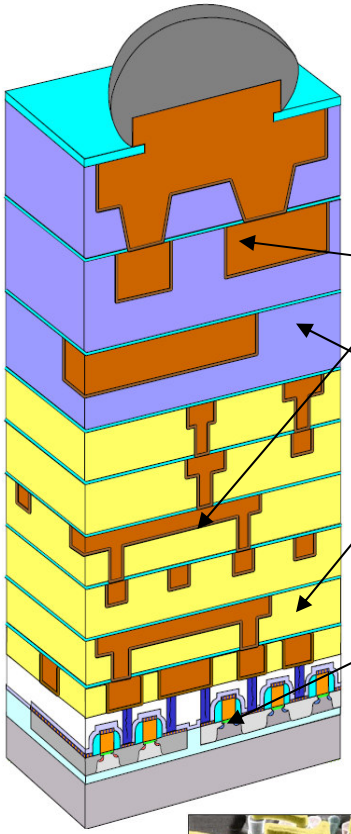
- BASF CMP slurry development setup
- Representative results
  - Innovative particles for copper slurries
  - Progress in barrier slurries
  - Polishing debris management for STI
  - Fundamental understanding of CMP
- Conclusions and Acknowledgement

BASF CMP Slurry Development According to Application

BASF
The Chemical Company







Type of CMP Slurry for:

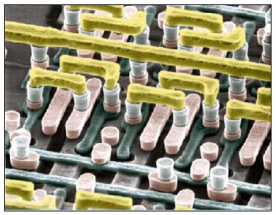
Established Applications

Cu CMP for interconnect (Cu)
Barrier CMP for interconnect

Interlayer dielectric (ILD)

Shallow trench isolation (STI)

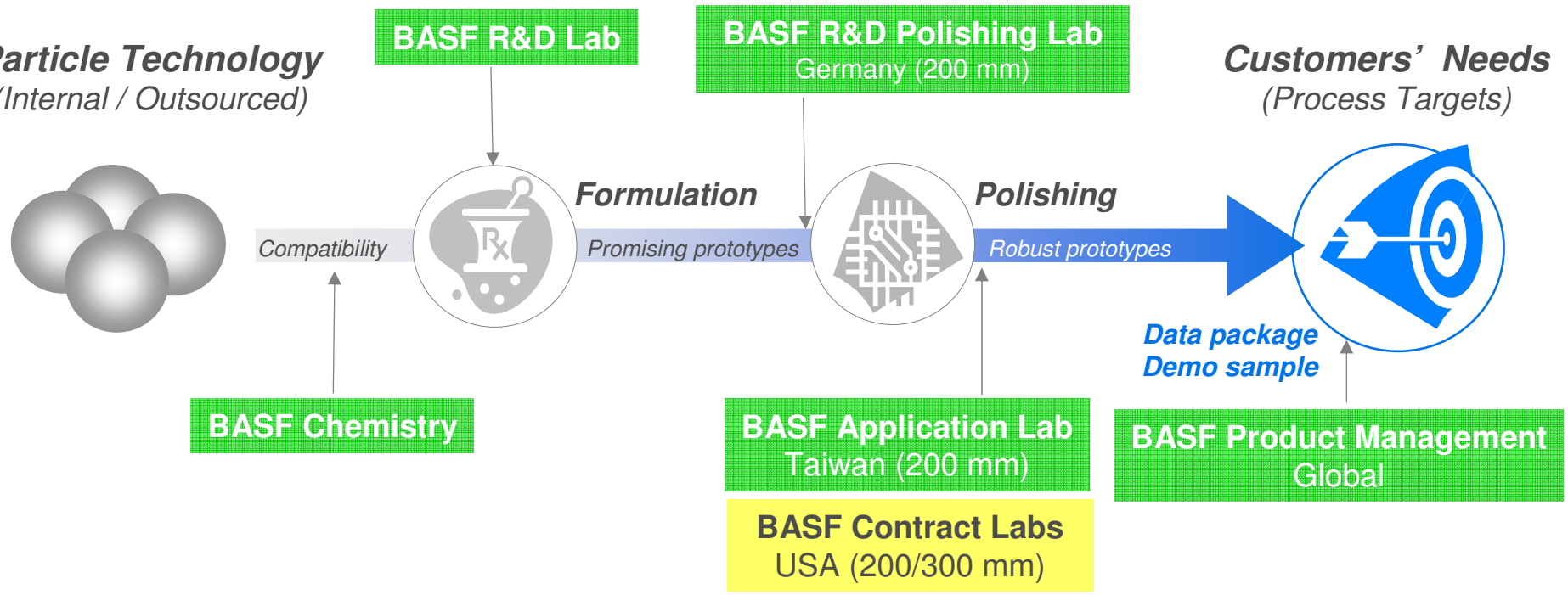
New Applications



TSV for 3D chips

High K metal gate

BASF CMP Slurry Development Setup

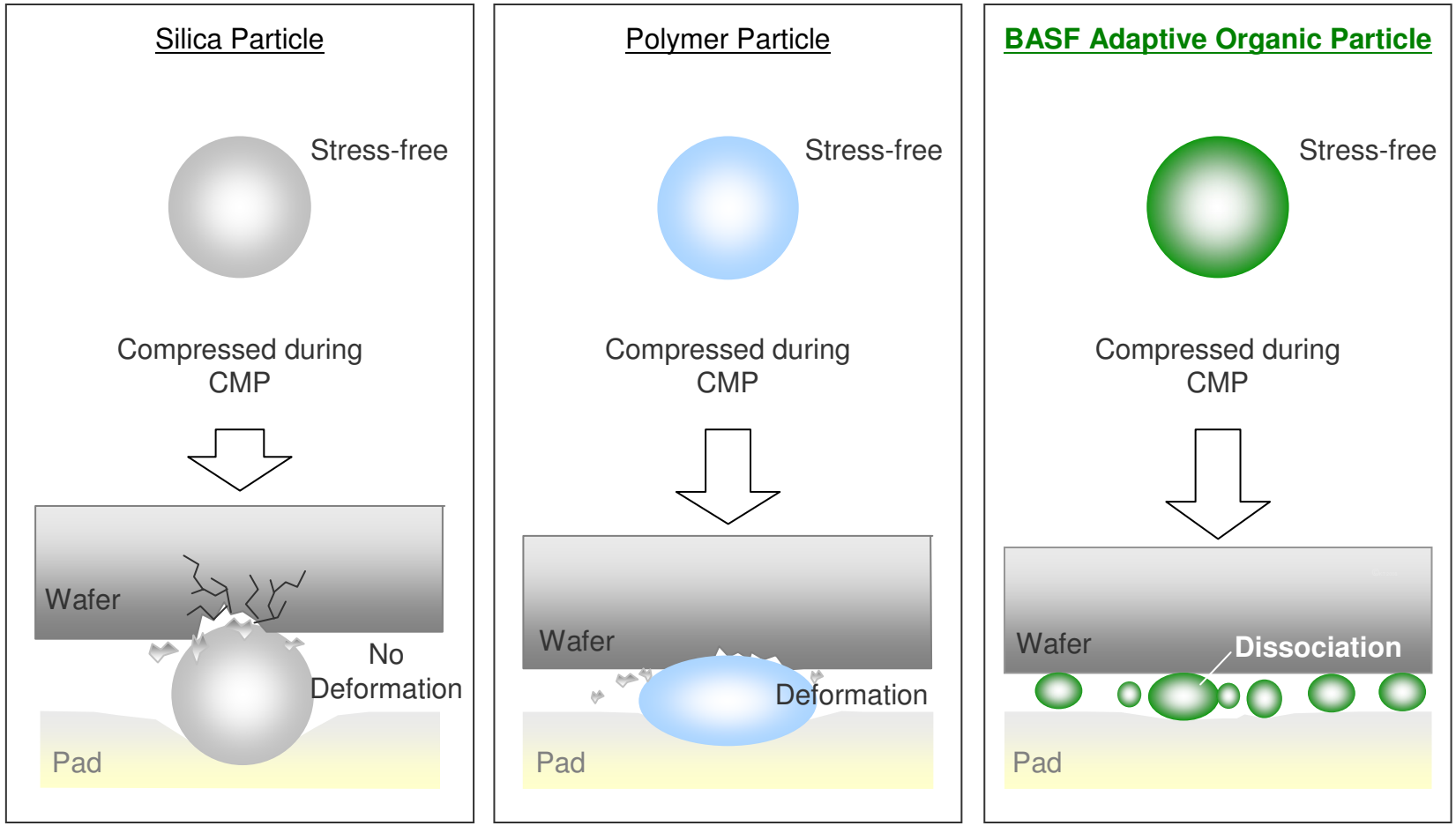


- Structured process checks chemical and applications viability
- Practical and focused approach accelerates commercialization

Chemistry Innovation in CMP

Adaptive Organic Particle

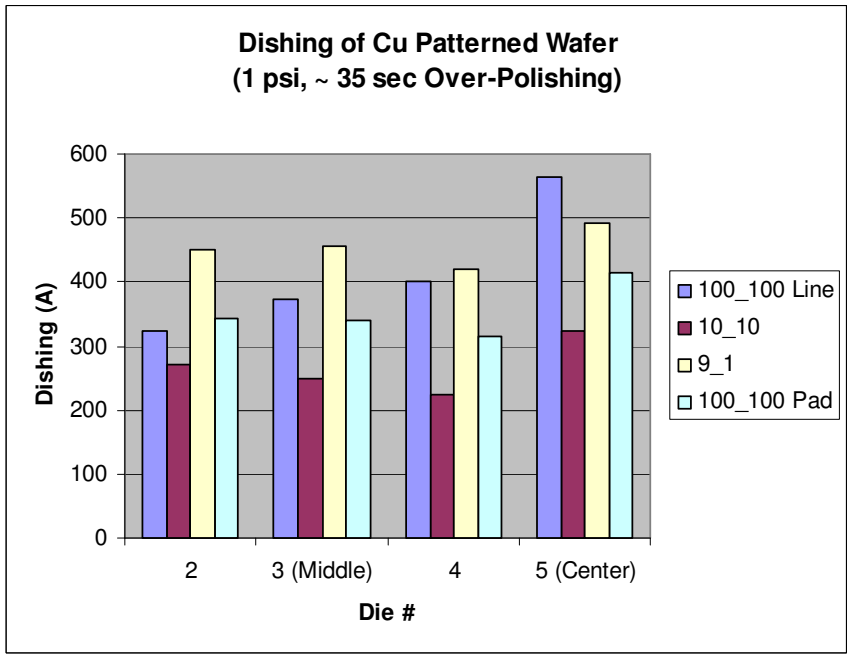
BASF
The Chemical Company



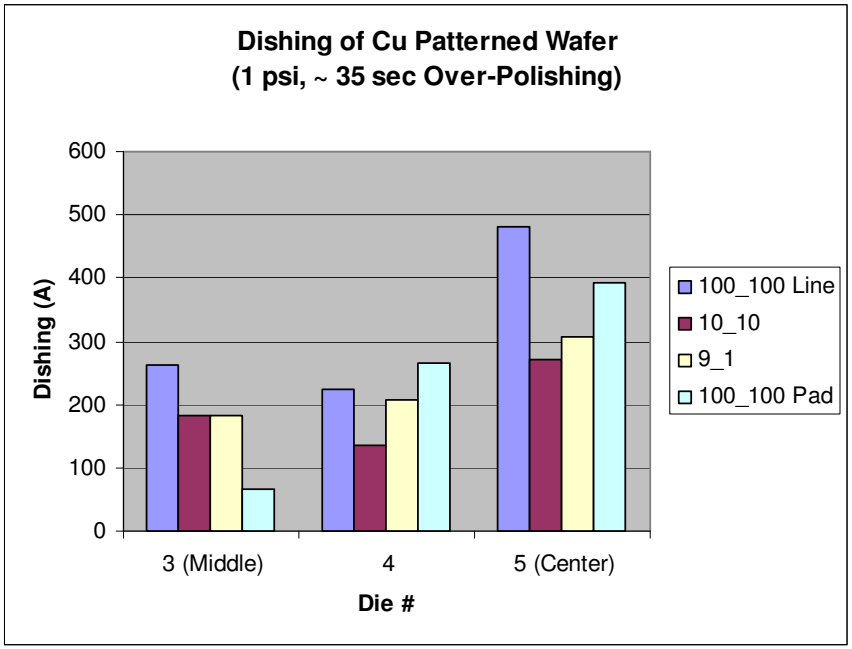
Typical Dishing Results for PC606 (100 um lines)

BASF
The Chemical Company

Baseline slurry PC606x21a



Baseline slurry PC606x21b

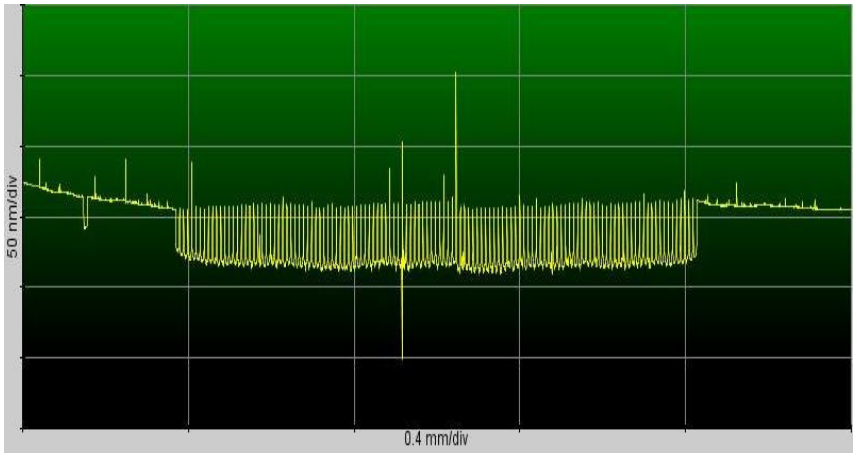


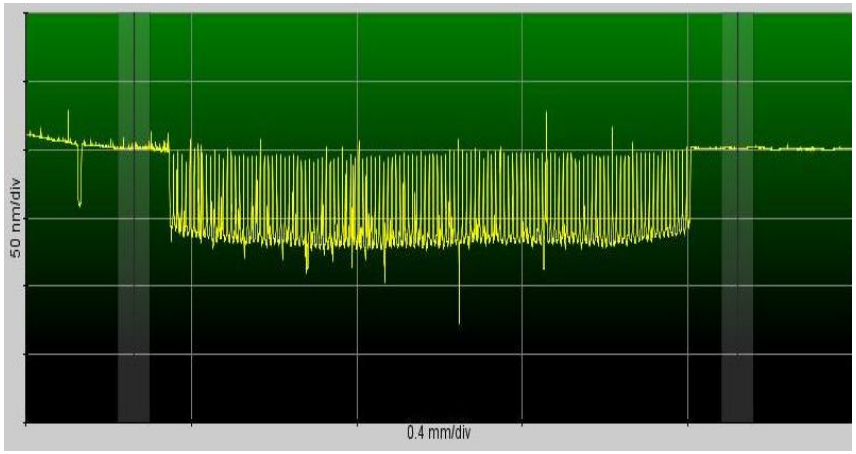
~ 35 sec over-polishing under 1 psi, 95/85 rpm, 200 ml/min polishing condition

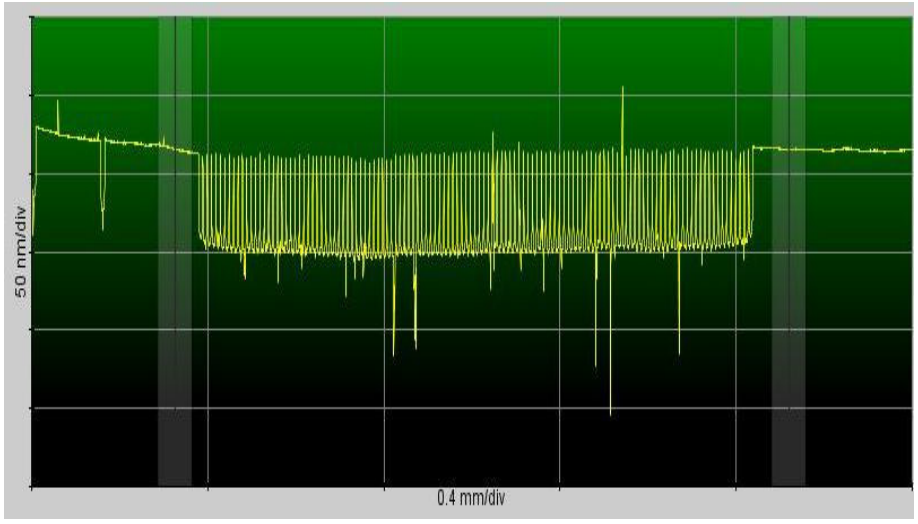
Low Erosion on 9x1 Features shown by Profilometry Traces

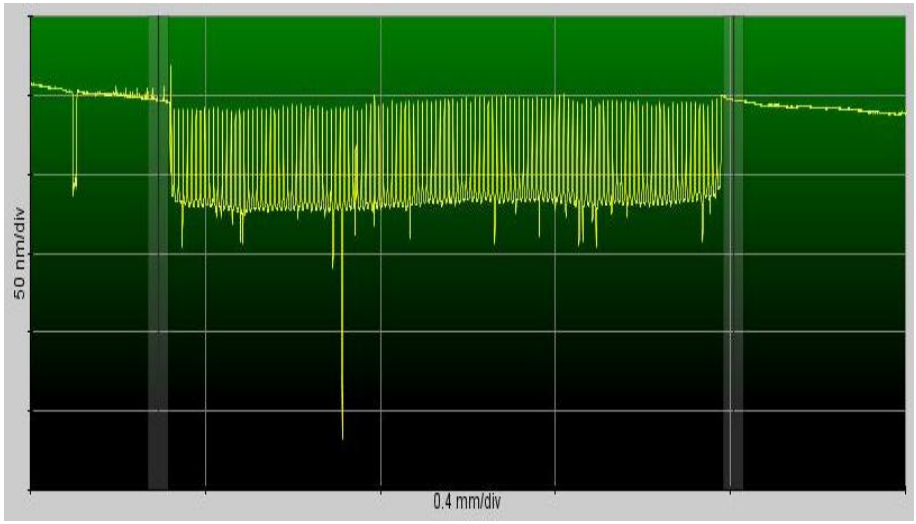
Park System AFM Profilometer Scan

BASF
The Chemical Company





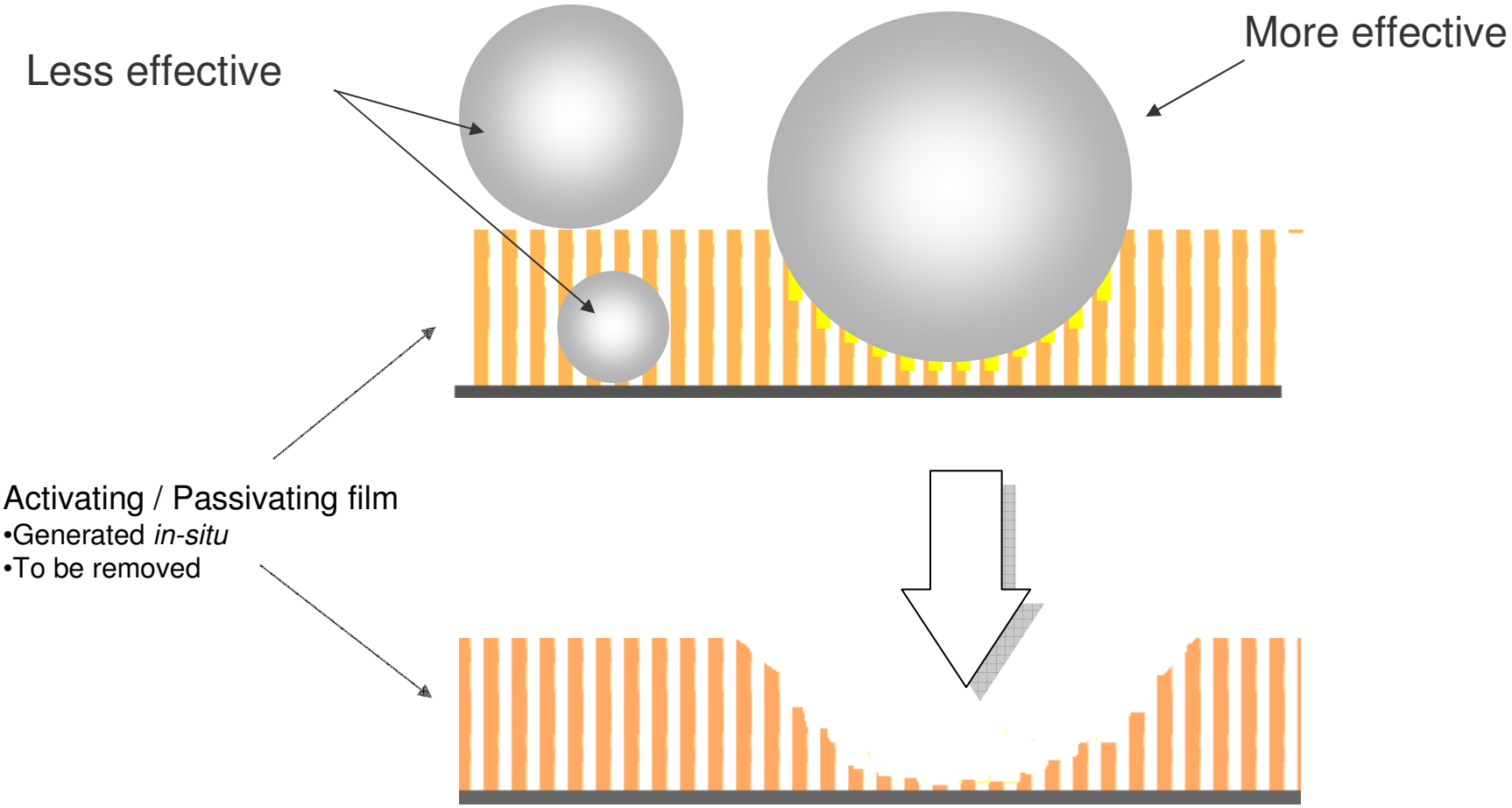




Matching Surface Chemistry

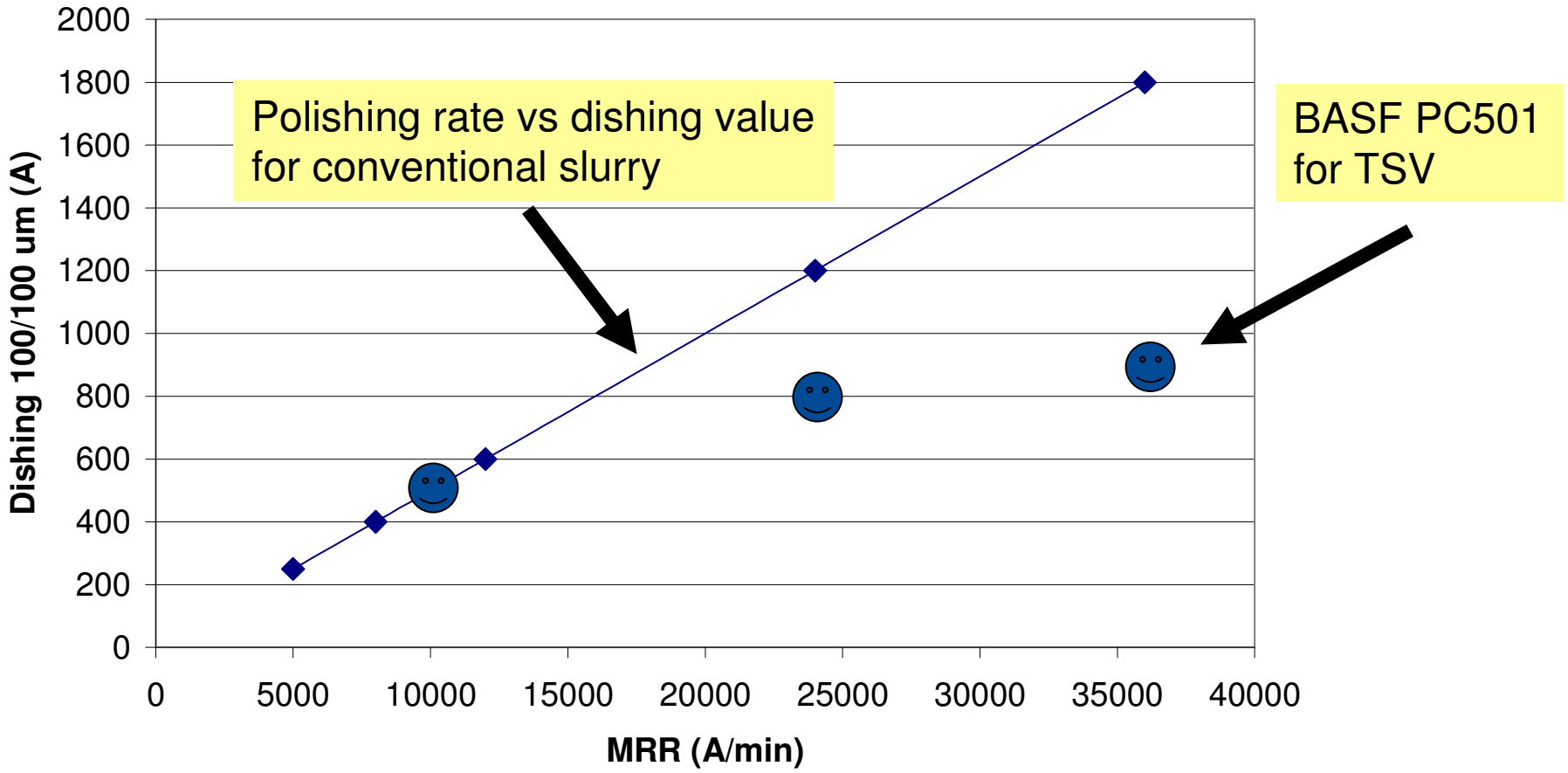
Increased efficiency of material removal

BASF
The Chemical Company



BASF TSV Cu CMP Slurry Defy Dishing Trend Predicted by Polishing Rates for Conventional Slurry

BASF
The Chemical Company

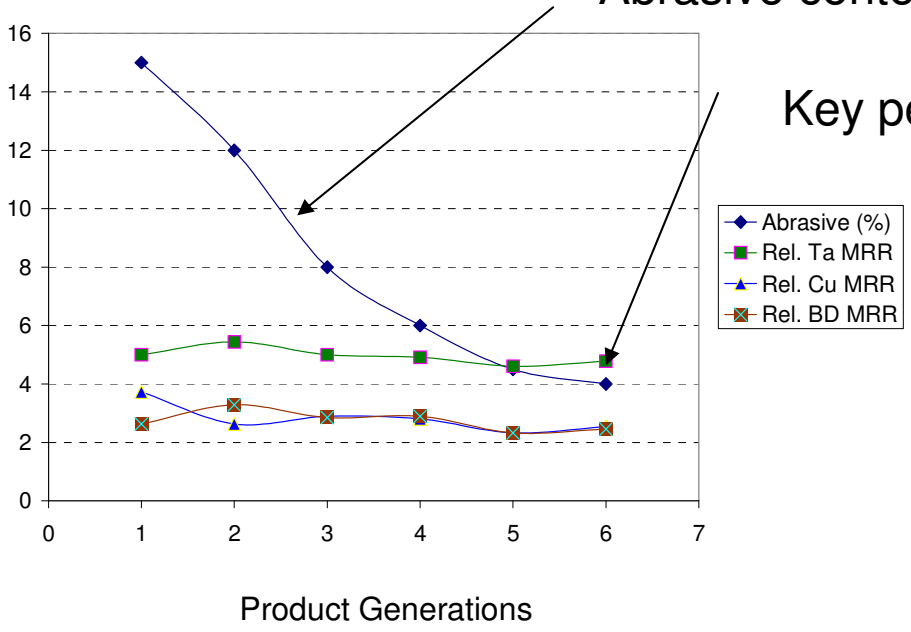


Advanced BASF Barrier Slurry

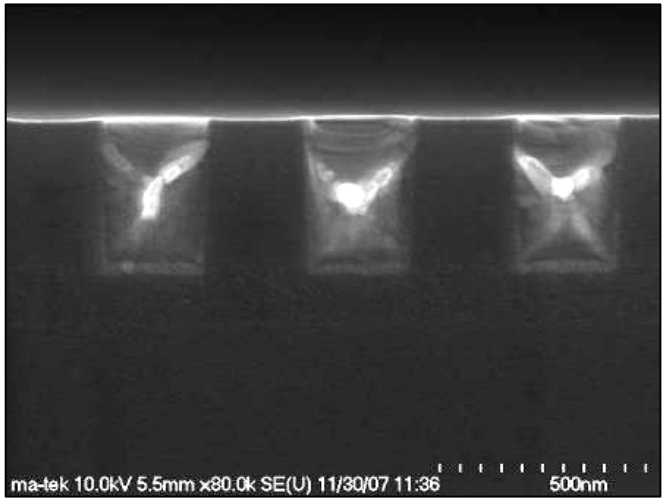
Maximize removal rate with minimal solids content

BASF
The Chemical Company

Abrasive content significantly reduced



Key performance characteristics retained



Benefits for the customers:

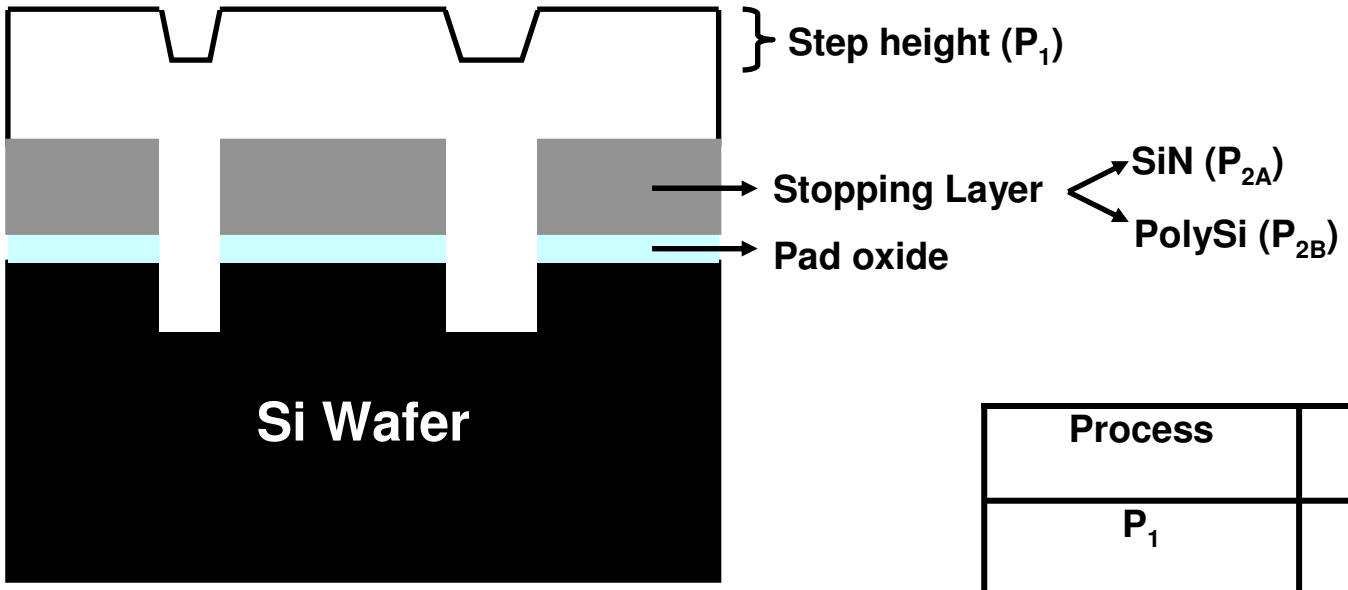
1. Lower defects
2. Lower COO
3. Lower burden on filters
4. Simpler waste treatment

0.25 micron line array after barrier polish

Minimal dishing and erosion

No EOE (“tiger teeth / fangs”)

BASF Planapur STI Products

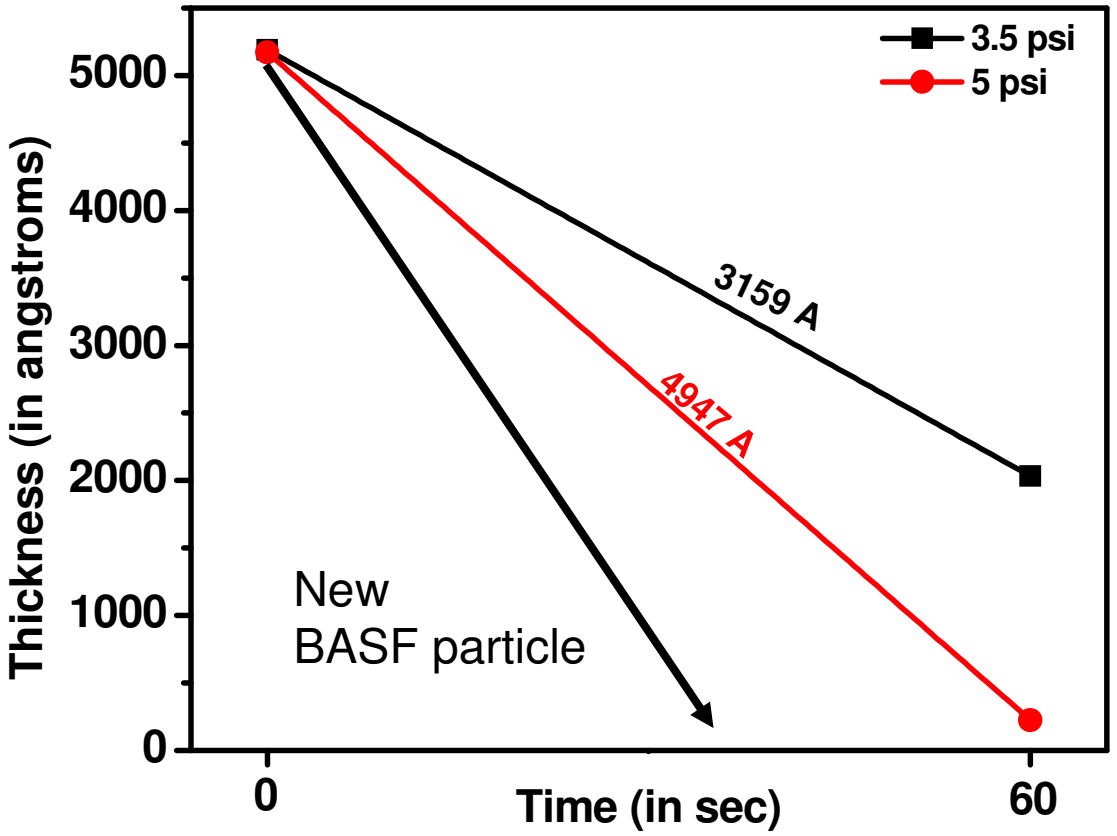


Process	Slurry Code
P_1	PS5600
P_{2A}	PS5010
P_{2B}	PS5545

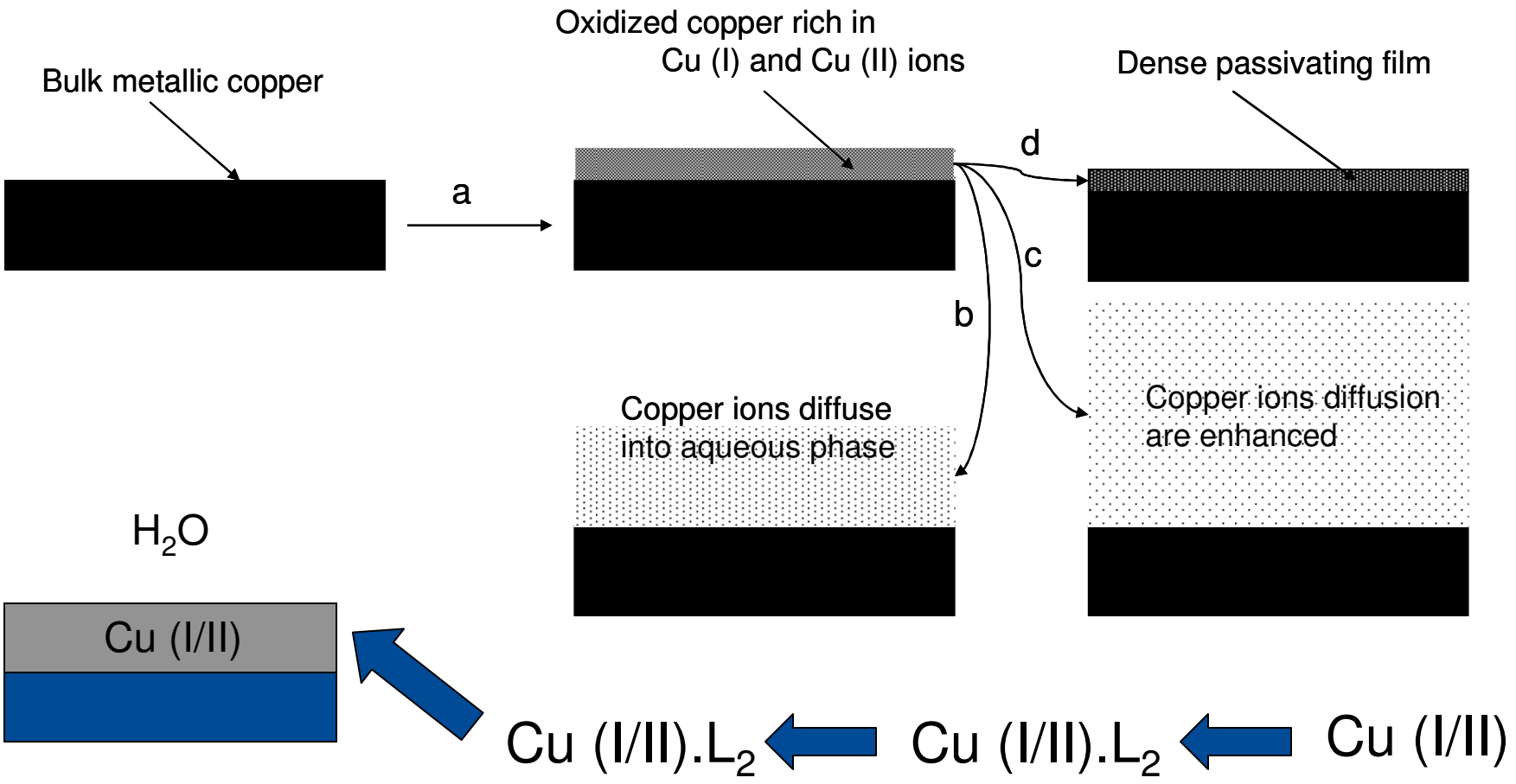
PS5600 (P_1) – High RR STI Bulk

100 x 100 line

BASF
The Chemical Company



Copper Surface Oxidization/Passivation



THE JOURNAL OF BIOLOGICAL CHEMISTRY
Vol. 249, No. 2, Issue of January 25, pp. 656–658, 1974

BASF
The Chemical Company

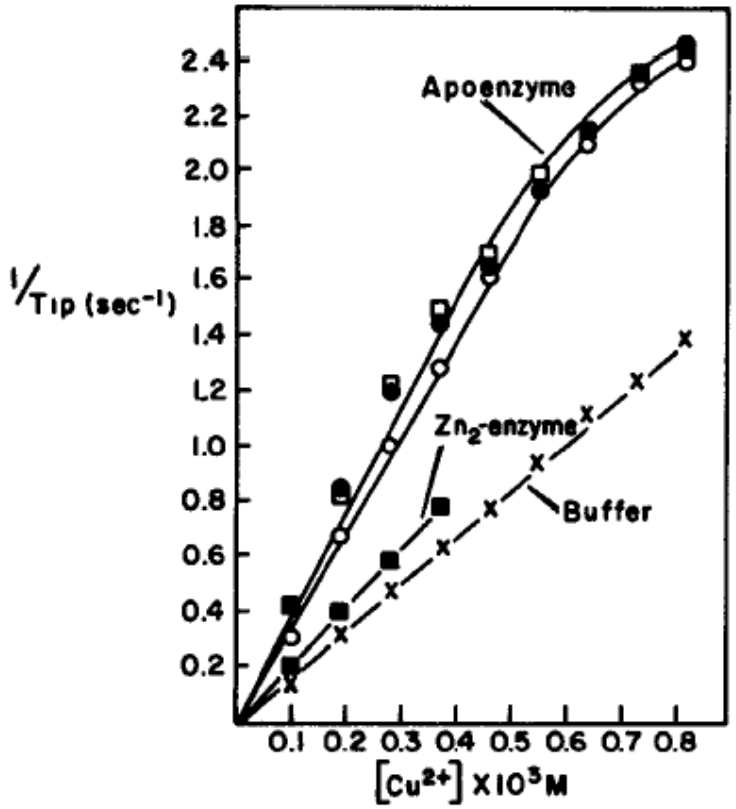
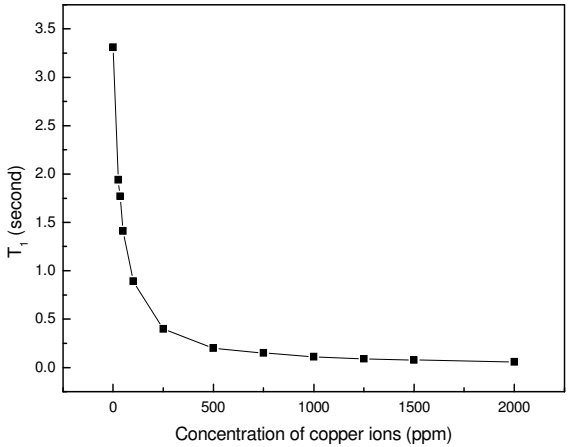
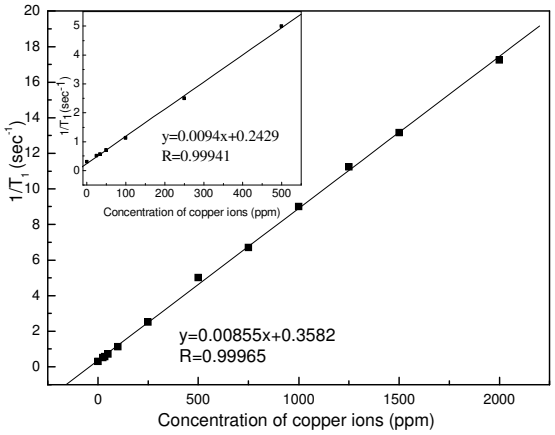
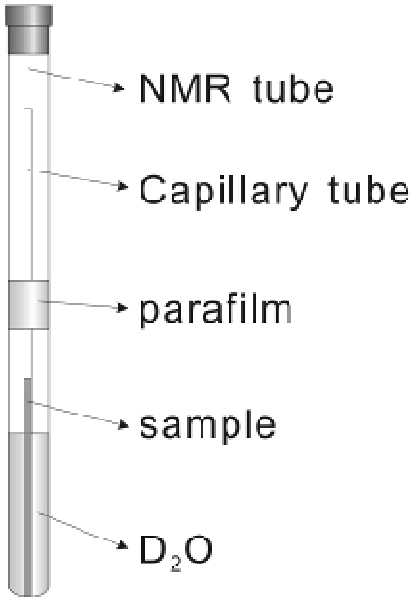


FIG. 1. Titration of 0.25 mM apoalkaline phosphatase with $CuSO_4$ (○), $CuCl_2$ (●), and $Cu(NO_3)_2$ (□) and titration of Zn_2-enzyme with $CuSO_4$ (■) in 10 mM Tris-Cl buffer, pH 7.0, at 3°. Water proton relaxation rates at 24.3 MHz are shown.

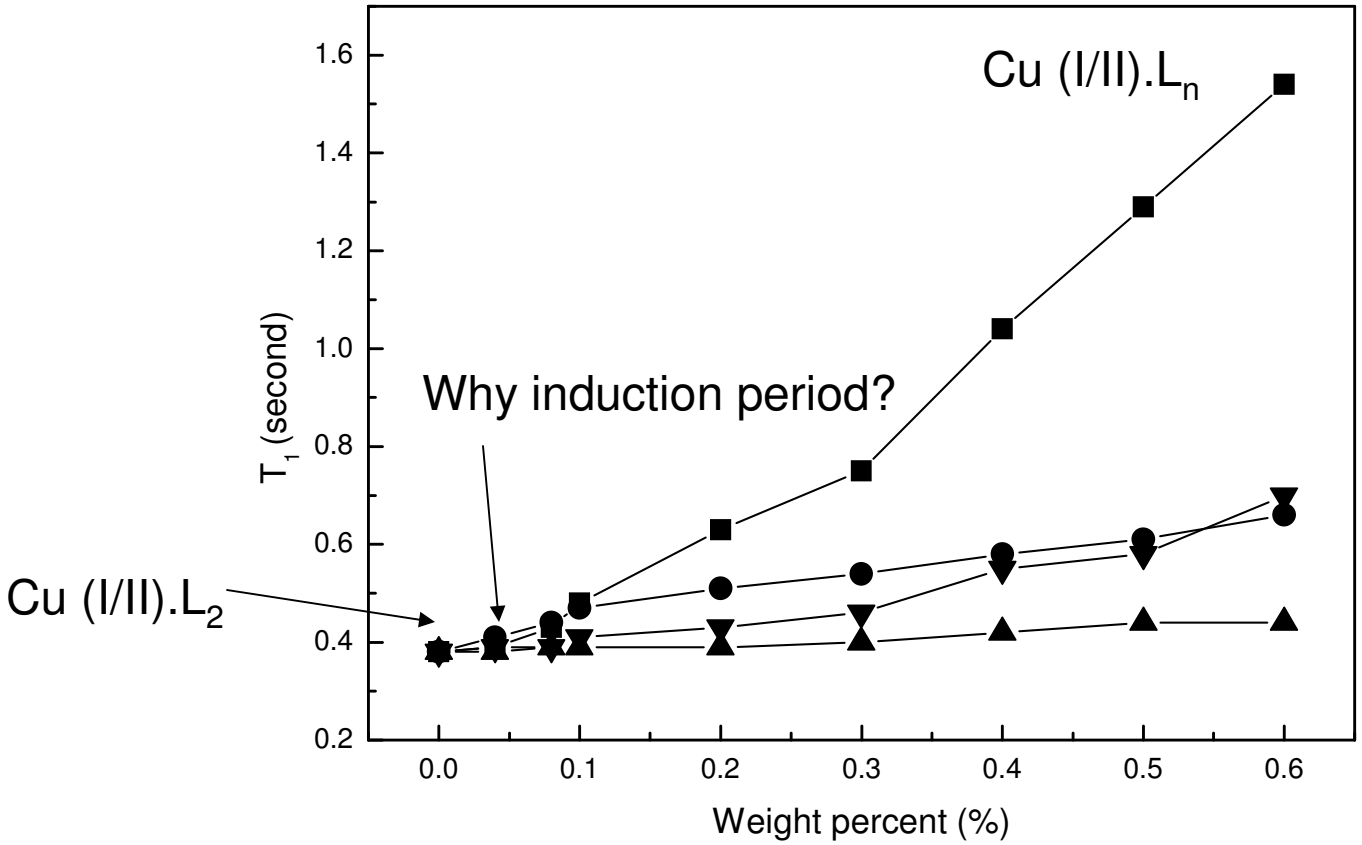
Effect of Cu Ion on Water T1







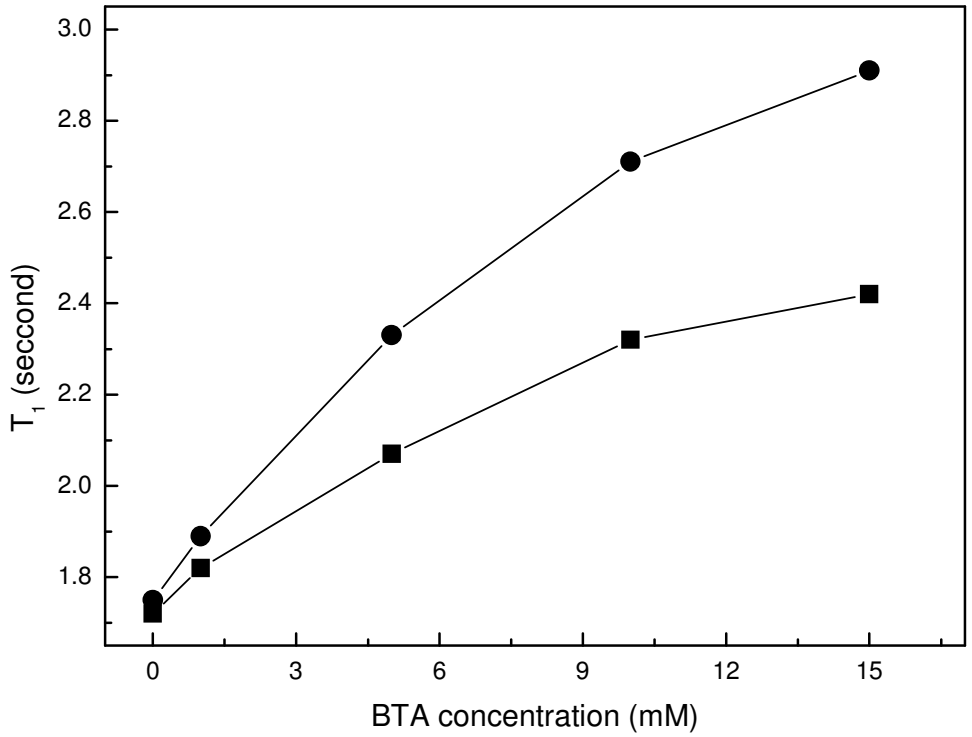
Classification of Complexing Agent



Film forming

None film forming

Effect of Silica on BTA-Cu Complex



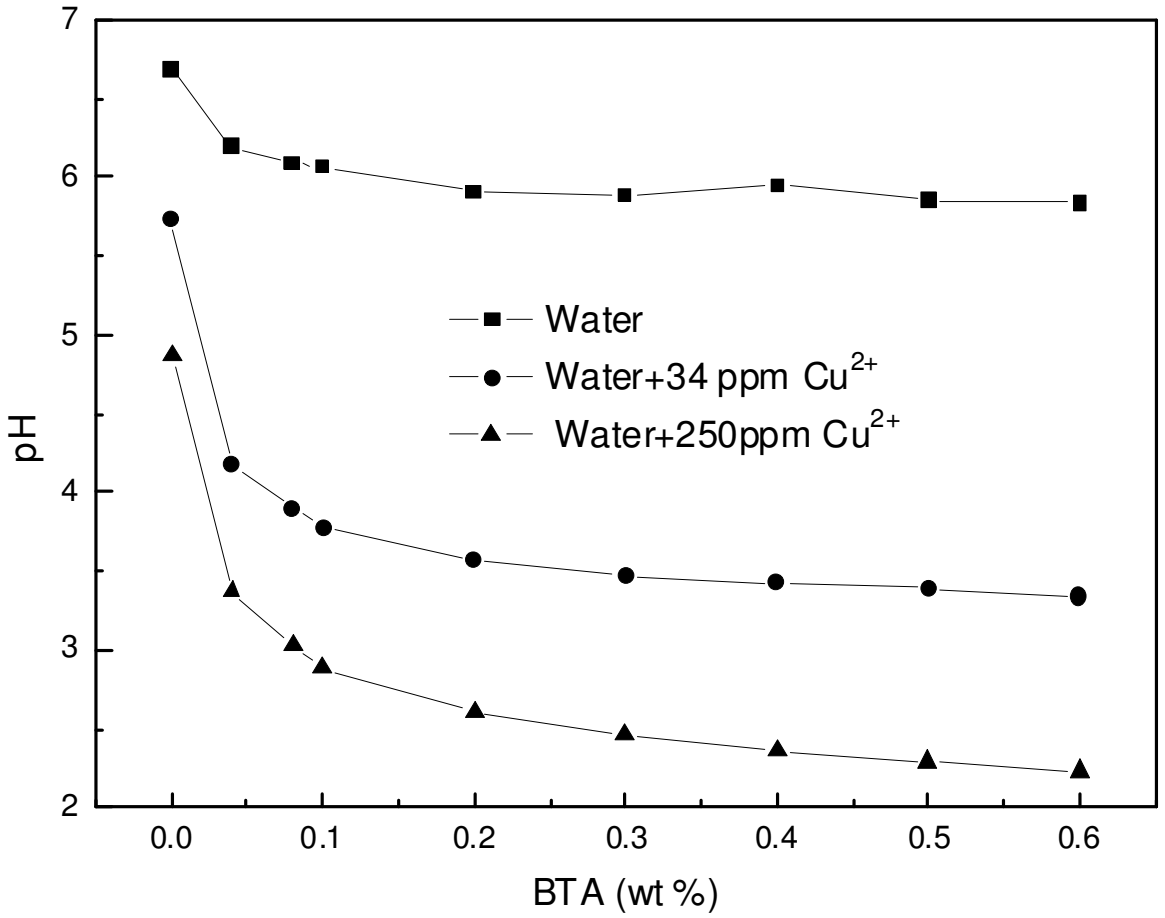
Without silica

With silica

T1 values for water proton of 34 ppm Copper ions dependence on BTA concentration: (■) in the presence of 0.2%N85 (●)without silica

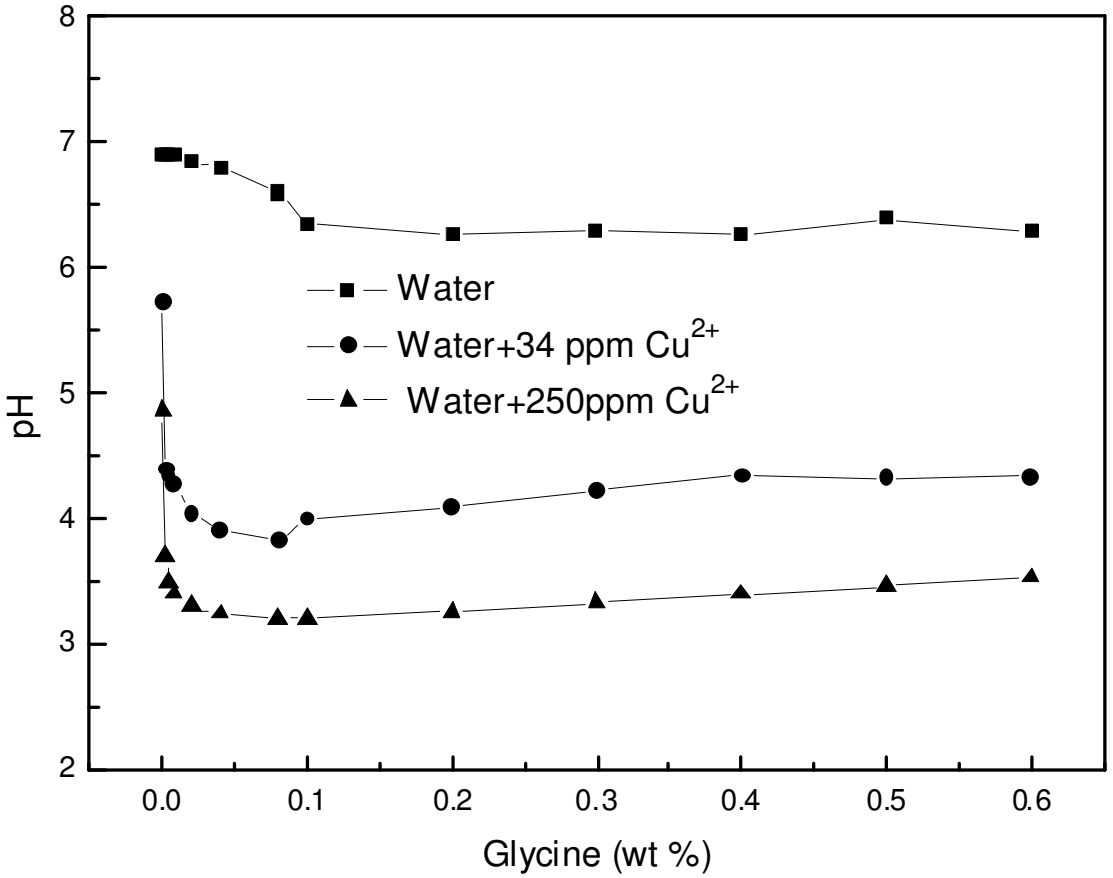
Reaction Between Cupric Ions and BTA

BASF
The Chemical Company



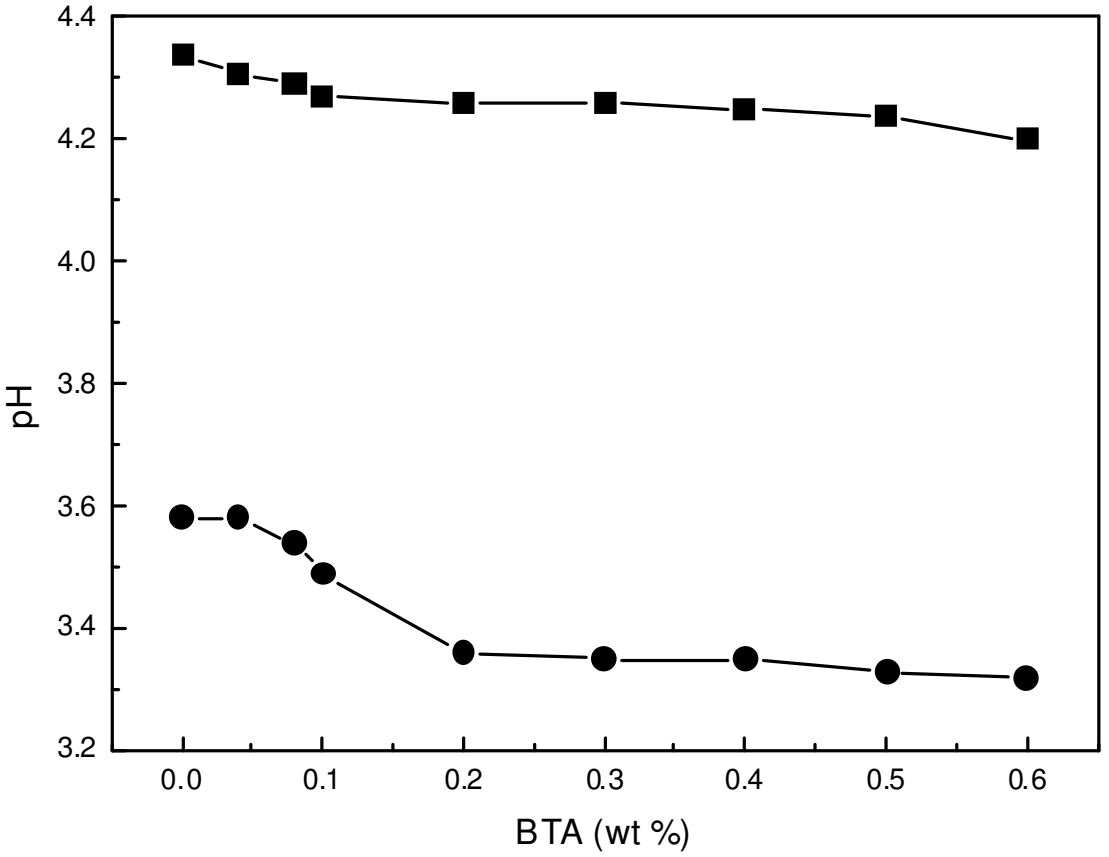
Reaction Between Glycine and BTA

BASF
The Chemical Company



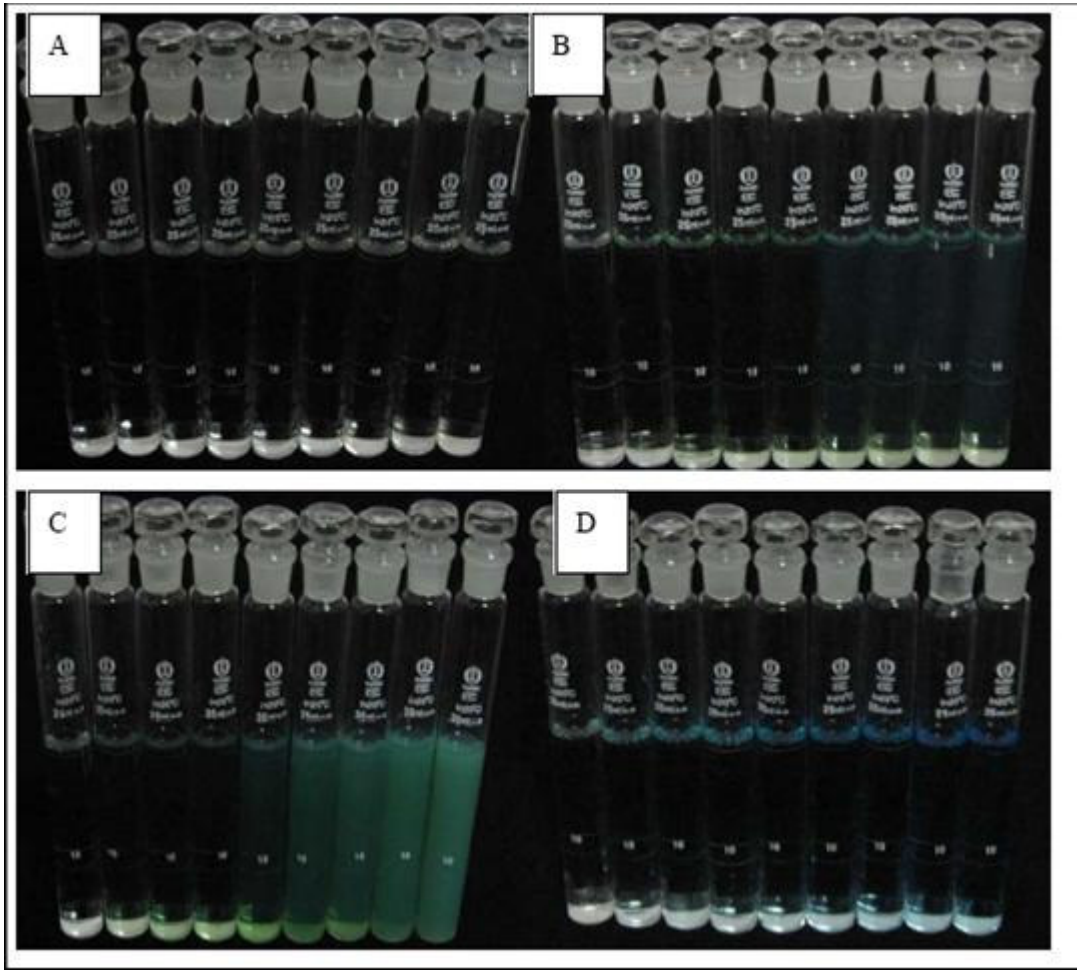
BTA Competes with Glycine for Cupric

Contains
0.6% Glycine



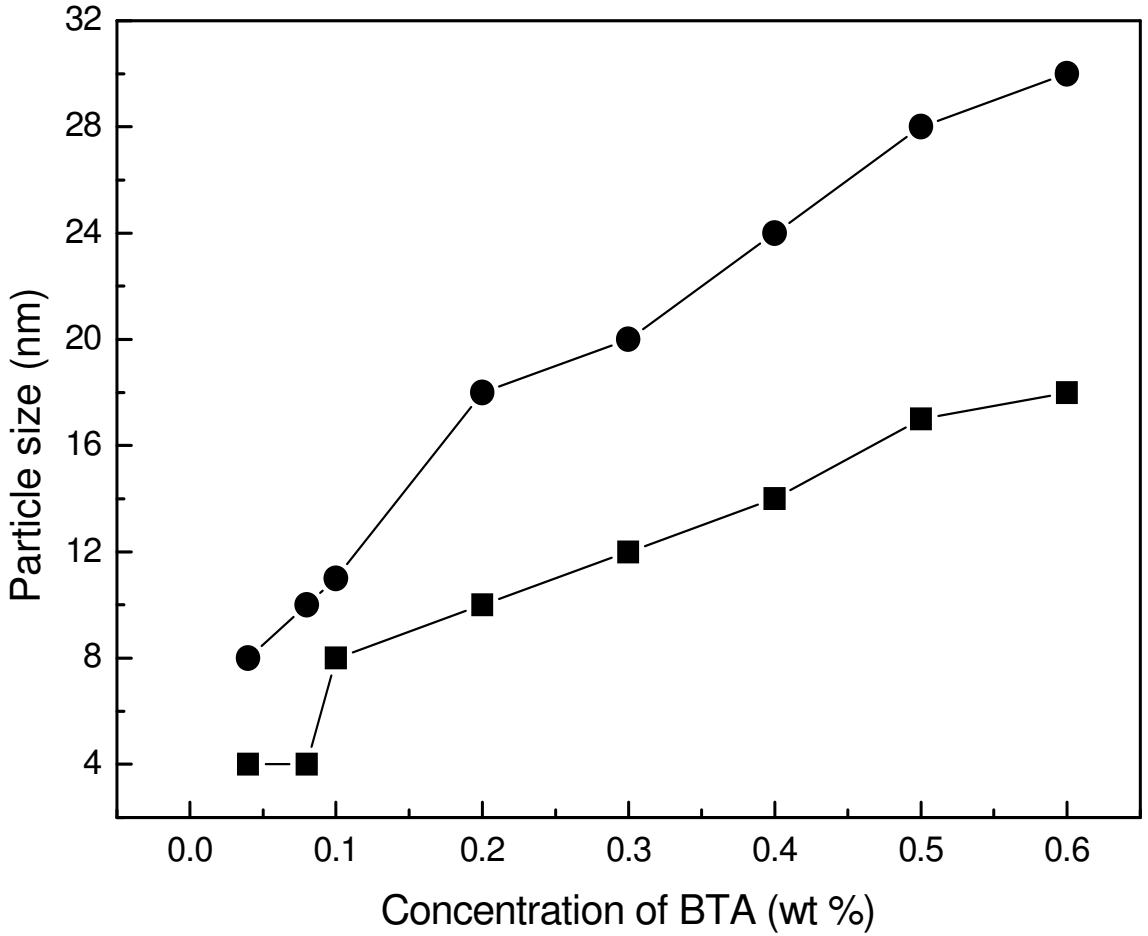
No Cu

With Cu


A
B
C
D

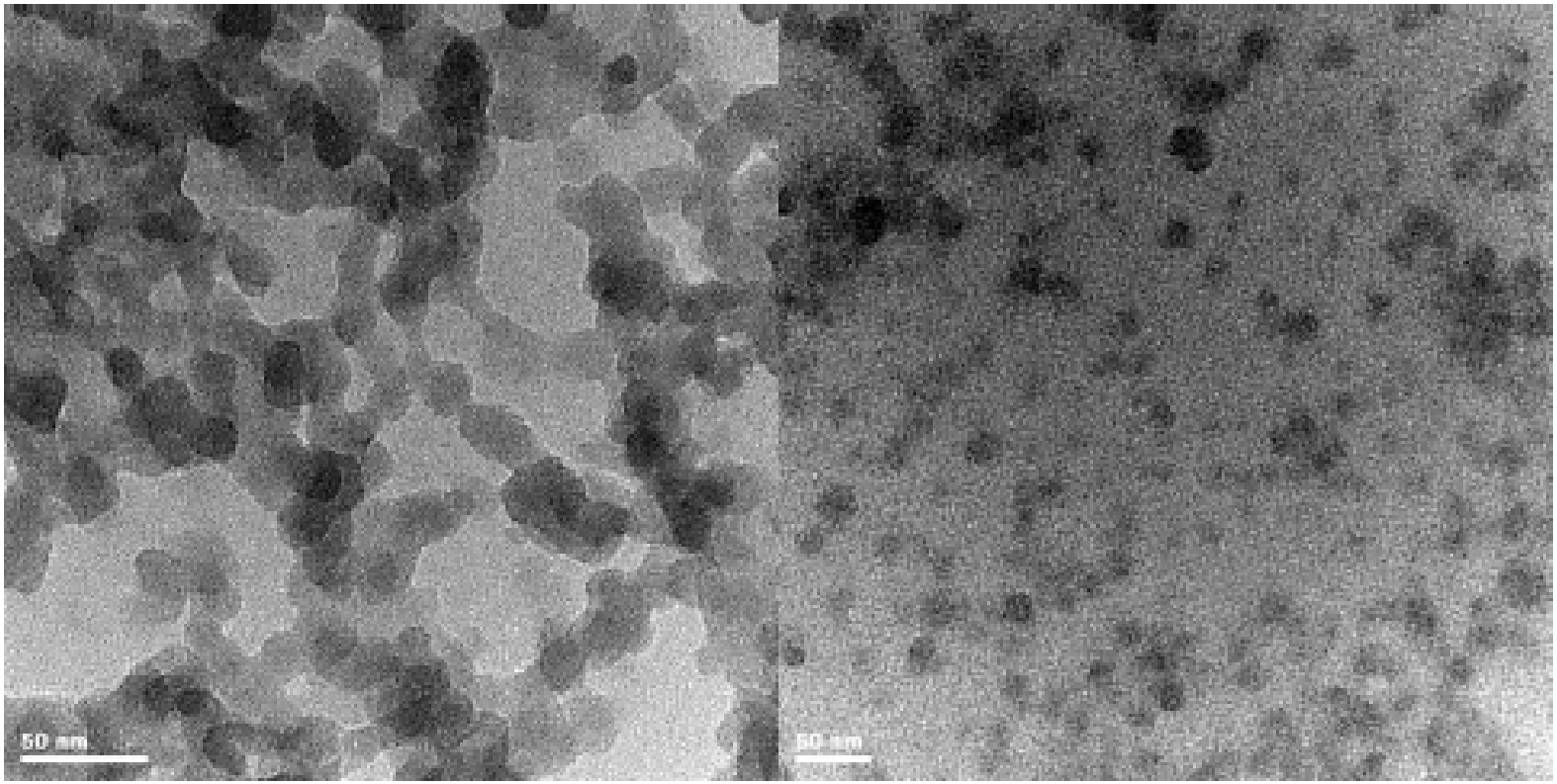
Particle size of samples containing varying amount of BTA and cupric ions (■ for 34 ppm and ● for 250 ppm)

BASF
The Chemical Company



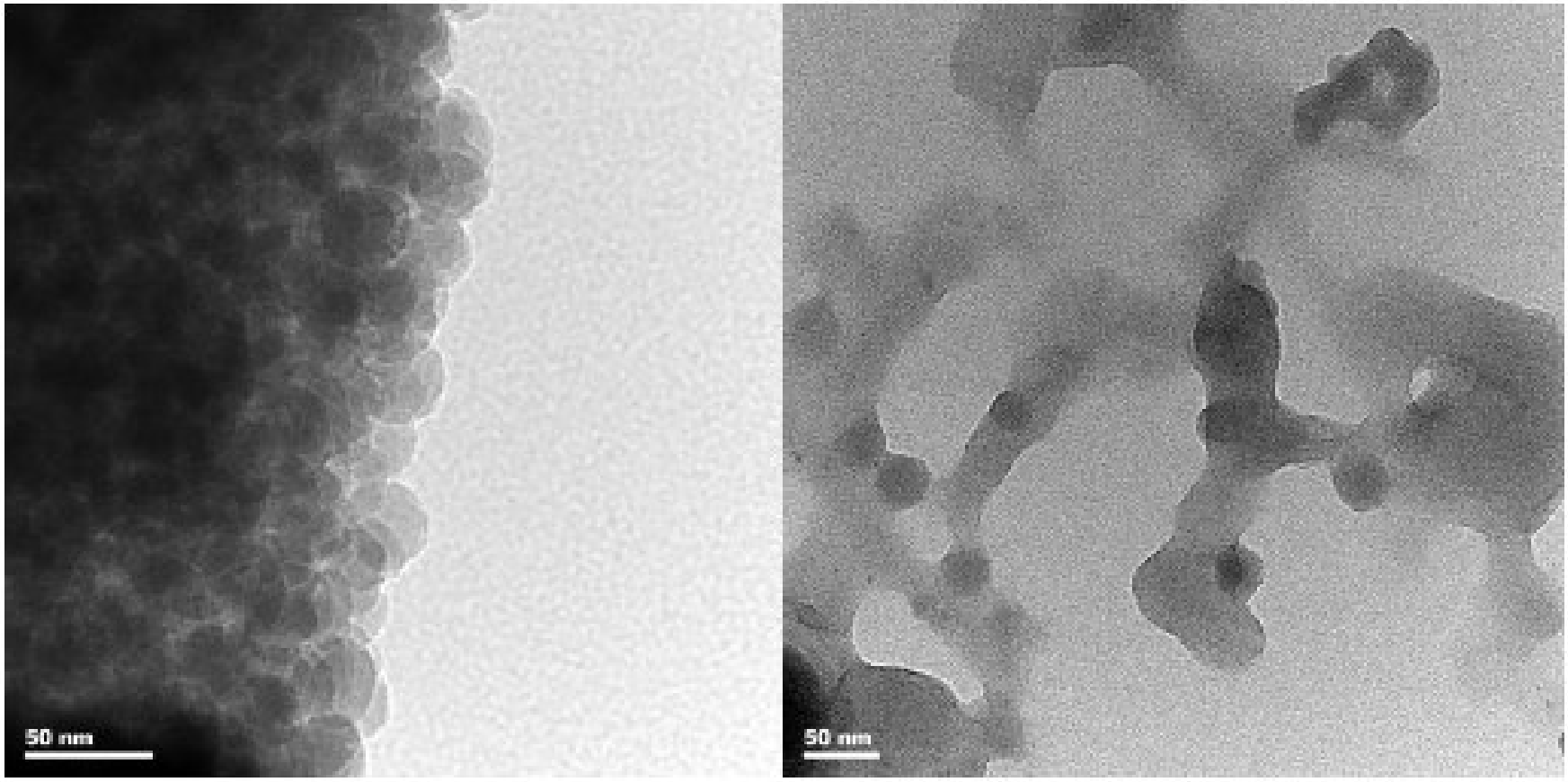
TEM images of samples containing 0.2% BTA and varying amount of cupric ions (left: 34 ppm and right: 250 ppm).

BASF
The Chemical Company



TEM images of samples collected from the wafer surfaces after the exposure to a solution containing hydrogen peroxide, glycine, and BTA (left) and a solution containing hydrogen peroxide and BTA (right).

BASF
The Chemical Company



Summary

BASF
The Chemical Company

- BASF CMP slurry development setup
  - Strong global R&D organization
  - Local presence to support our customers
- Significant progress made in 2008/2009
  - Innovative particles for copper slurries
    - Functionality and morphology design
  - Progress in barrier slurries
    - Lower COO and defect level
  - Polishing debris management for STI
    - Lower defect
  - Fundamental understanding of CMP
    - Important component in slurry and R&D team development

Acknowledgment

- BASF (Germany)
  - Dr. Klemens Mathauer
  - Dr. Michael Lauter
  - Dr. Mario Brands
  - Dr. Vijay Raman
  - Dr. Claus Poppe
  - Mr. Yongqing Lan
  - Mr. Roland Lange
  - Ms. Elisabeth Seltzer
  - Mr. Kennith Rushing
- BASF (Asia)
  - Dr. Charles Lin
  - Mr. Kevin Teo (USA)
  - Mr. JJ Chu
  - Mr. William Chiu
  - Mr. Daniel Shen
  - Mr. Robert Lo
- STLN/Clarkson University (USA)
  - Dr. Changxue Wang
  - Professor S.V. Babu
  - Mr. Shyam Venkataraman
  - Mr. Paul Vendadi
  - Mr. Ke Wang
  - Mr. Harvey Pinder
  - Dr. Valli Ramji
  - Mr. Jeff Yu
- ISIT (Germany)
  - Professor G. Zwicker
- Sun Yat-sen University (China)
  - Professor Menglian Gong
  - Ms. Yan Li