SLURRY FORMULATION OPTIONS

CHALLENGES FOR DEFECT REDUCTION IN CU,Ta/TaN AND Ru PLANARIZATION

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- My colleague Prof. Dip Roy
- Don Canaperi and his IBM team

Outline

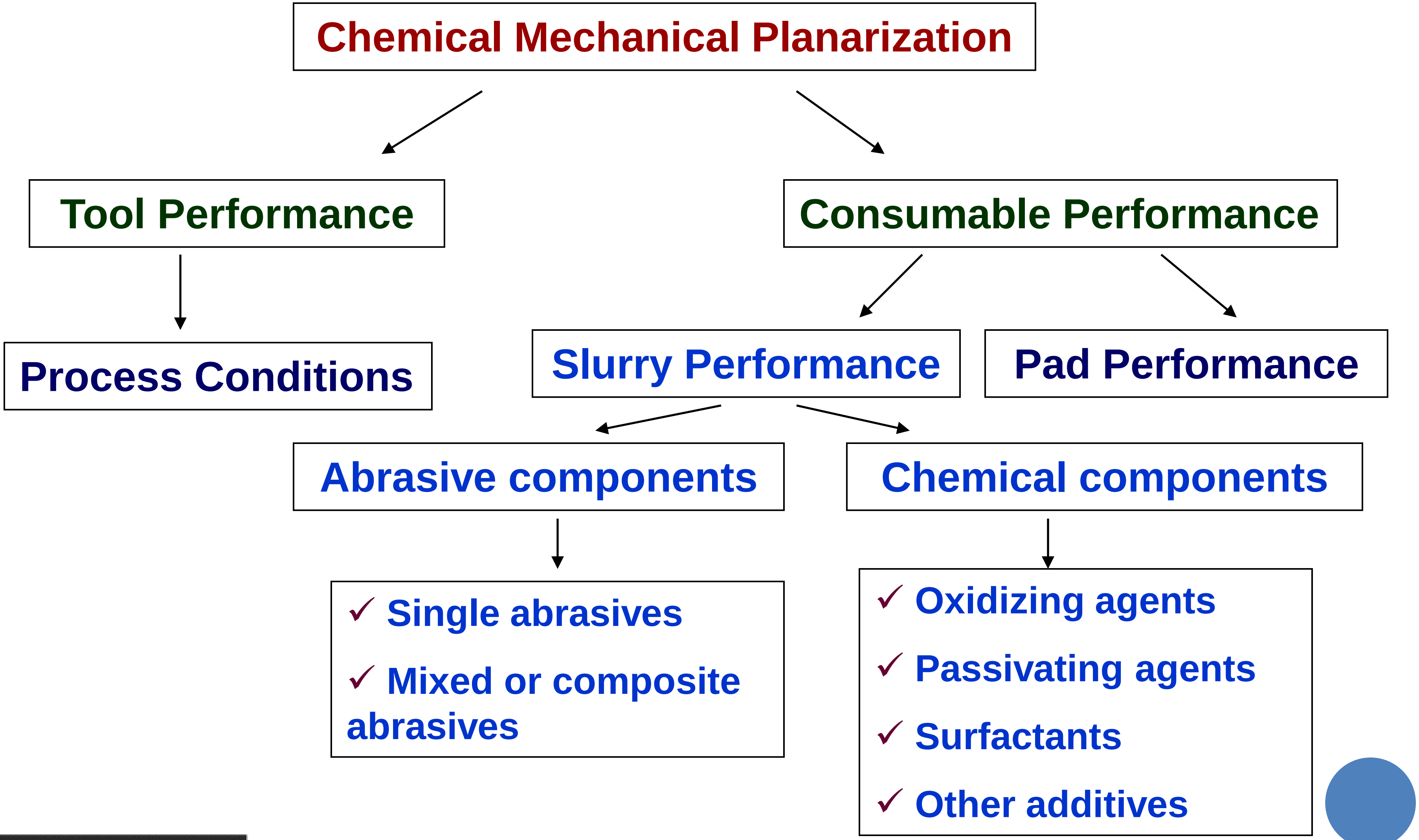
- Introduction

- New Slurry options for Cu and Ta CMP
  - Defects during Cu/barrier polishing
  - Patterned wafer polish results
  - Post-polish surface analysis

- New barrier materials (Ru-based)
  - Slurry options
  - Galvanic corrosion

- Conclusions

Factors Affecting CMP



Chemical Mechanical Planarization

Tool Performance

Process Conditions

Consumable Performance

Slurry Performance

Pad Performance

Abrasive components

- ✓ Single abrasives
- ✓ Mixed or composite abrasives

Chemical components

- ✓ Oxidizing agents
- ✓ Passivating agents
- ✓ Surfactants
- ✓ Other additives

Slurry impact on Defects

- Particles → scratches and related defects, residues, etc.
- Chemicals → corrosion, etching, nonplanarity, non- or inadequate selectivity, residues, etc.
- Combined → Dishing (pad also plays a role), erosion, etc.

Defectivity vs. Slurry Design

More mechanical slurries

Higher Defects

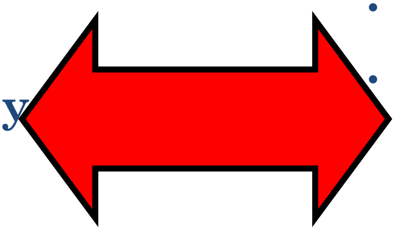
- ***scratches***
- ***slurry residues***

Higher planarity

Higher friction

Higher down force to

Maintain removal



More chemical slurries

- ***slurry residuals and precipitates***
- ***chemically driven scratches***
- ***clearing issues***

Cu surface protection

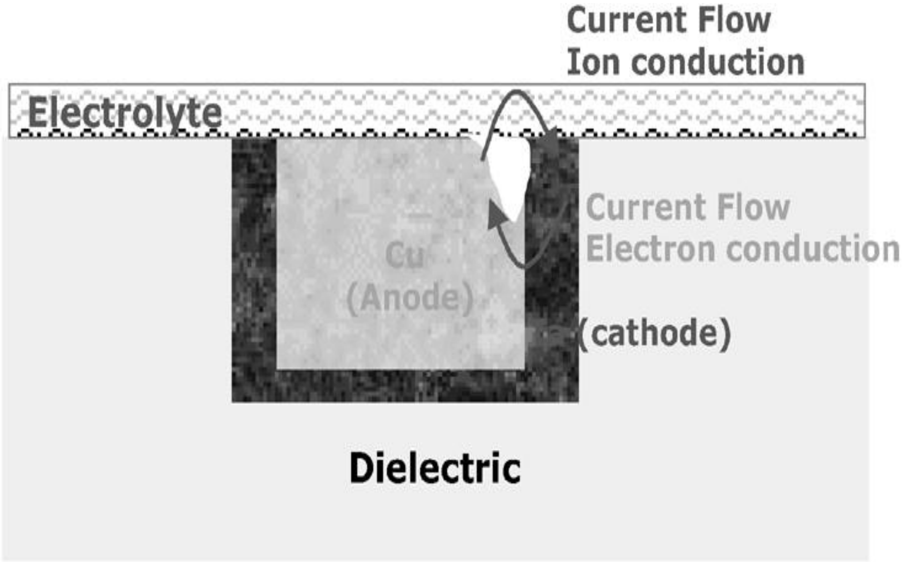
more critical

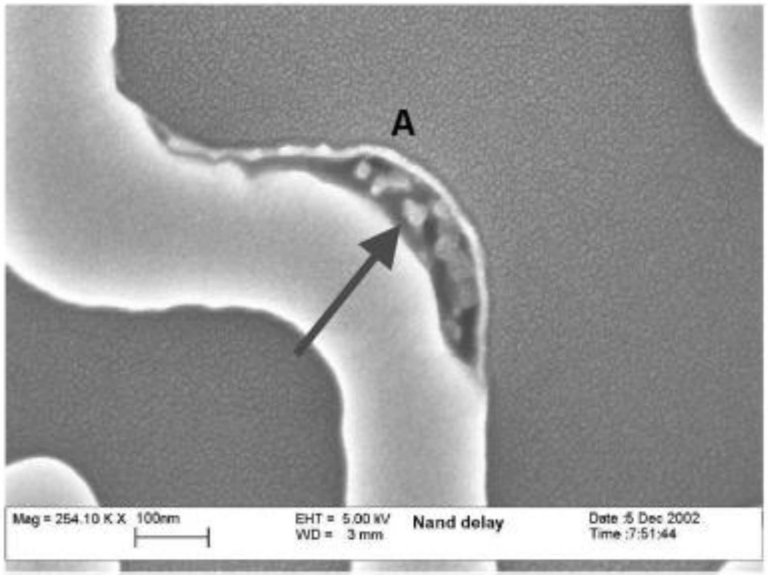
- ***corrosion risk***
- ***Dendrties***
- ***unstable process***
- ***copper etching/corrosion pits, etc/***

Barrier Slurry Requirements

- Barrier thickness is quite small → Rate not important
- Need to remove all the stop layer and perhaps some of the underlying dielectric
- Appropriate selectivity and achieving uniformity are critical
- Controlled dishing and erosion
- No galvanic corrosion
- Of course, no "damage" to the dielectric layer – pH has a strong influence
- ??

Cu loss due to galvanic corrosion





Ref: Zhigang song et al., IEEE transaction on device and materials reliability, Vol 5, (2005)

Barrier Slurry Selection

- C. Surisetty, P. Goonetilleke , D. Roy and S.V. Babu, J. Electrochem. Soc. 155, H971 (2008)
- C. Surisetty, B.C. Peethala, D. Roy and S.V. Babu, Electrochem. & Solid State Lett. 13 H244 (2010)
- C. Surisetty, PhD thesis, 2009 (Clarkson University)
- Sathish Janjam, PhD Thesis 2008 (Clarkson University)

Selection of slurry systems

Cu Slurries

- **0.021M Oxalic acid + 5wt% H_2O_2 + 4mM DBSA + 3wt% SiO_2 @ pH – 3 (Cu - I)**
- **1wt% glycine + 0.021M Oxalic acid + 5wt% H_2O_2 + 3.5mM DBSA + 3wt% SiO_2 @ pH – 3 (Cu - II)**

Barrier Slurries

- **0.065M K_2SO_4 + 1wt% H_2O_2 + 8wt% SiO_2 @ pH – 4 (Ta - I)**
- **0.065M K_2SO_4 + 8wt% SiO_2 @ pH – 4 (Ta - II)**

Dishing – ITRS requirements vs results

Year of Production	2007	2008	2009	2010	2011	2012	2013	2014	2015
Technology Node	hp 65			hp 45			hp 32		
Cu thinning of global wiring due to dishing (nm), **100 µm wide** feature	24	20	19	**16**	14	14	12	11	10

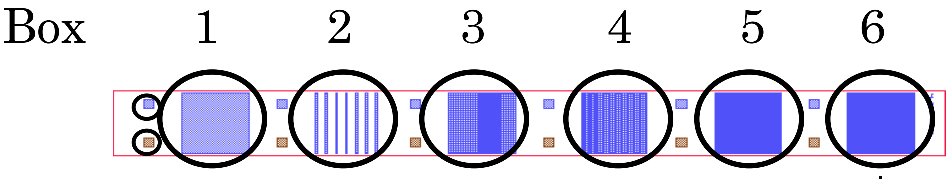
Dishing Performance	**Commercially available Slurries**	**Obtained in this work**
200 µm wide features	30-50 nm	**10-15 nm**

POLISHING CONDITIONS

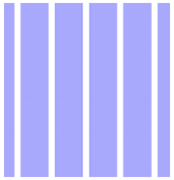
Wafer size	**300mm (12”)**
Tool	AMAT LK-Chamber
Slurry flow rate	300 ml/min
Pressure	2.2 psi
Platen / Head speed	102 / 100 rpm
Silica	Colloidal silica (~ 35nm)
Pad	Hard / Soft
Hard pad Conditioning type	In-situ with 5lbf and head speed of 108 rpm
Soft pad Conditioning type	Ex-situ with 2lbf and platen/head speed of 101/108 rpm

PATTERN DESCRIPTION

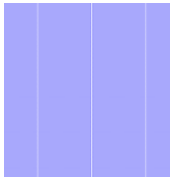
Box 1:
Cu Plate
100% pattern factor



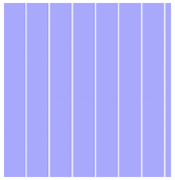
Box 2:
1 um line, 10 um space
9% pattern factor



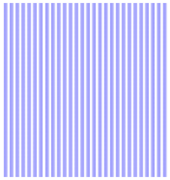
Box 3:
0.8 um line, 0.2 um space
80% pattern factor



Box 4:
0.1 um line, 0.2 um space
33% pattern factor

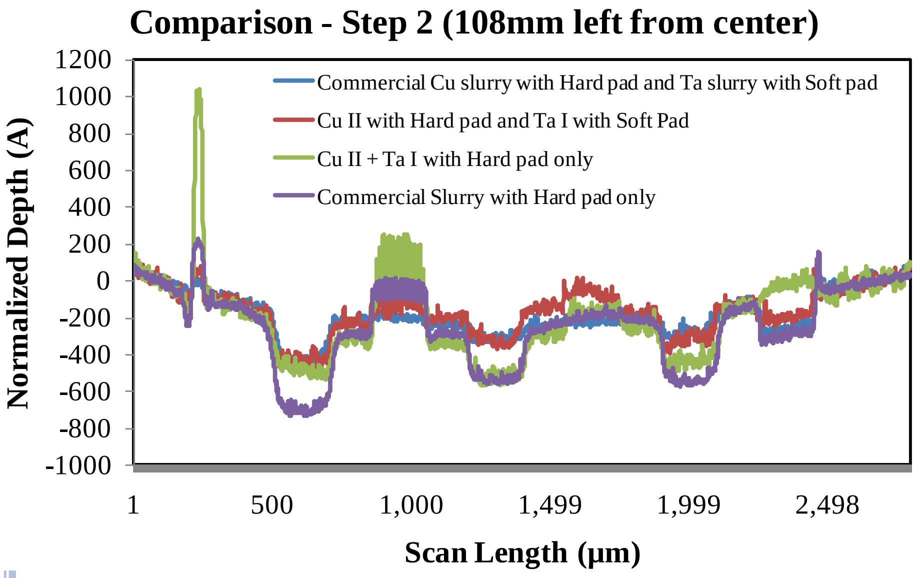


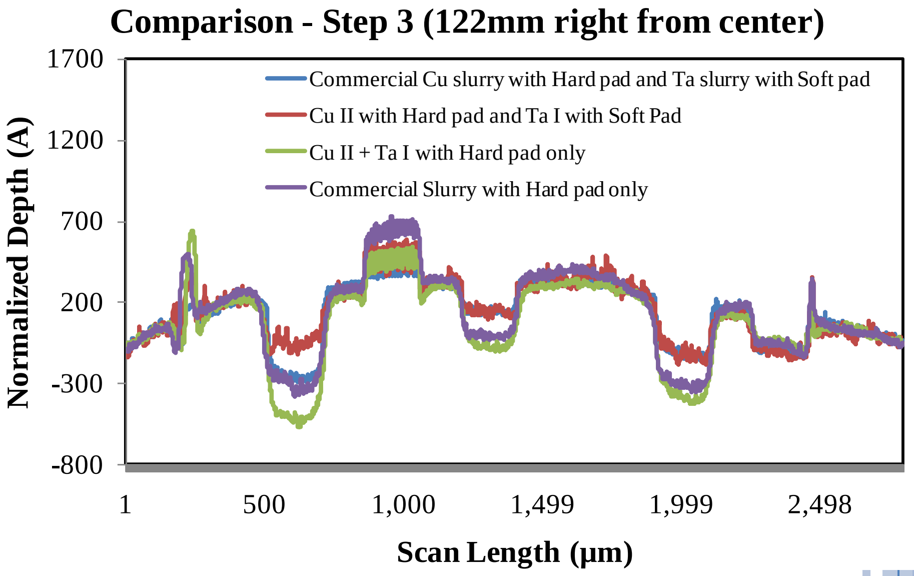
Box 5:
1.8 um line, 0.2 um space
90% pattern factor

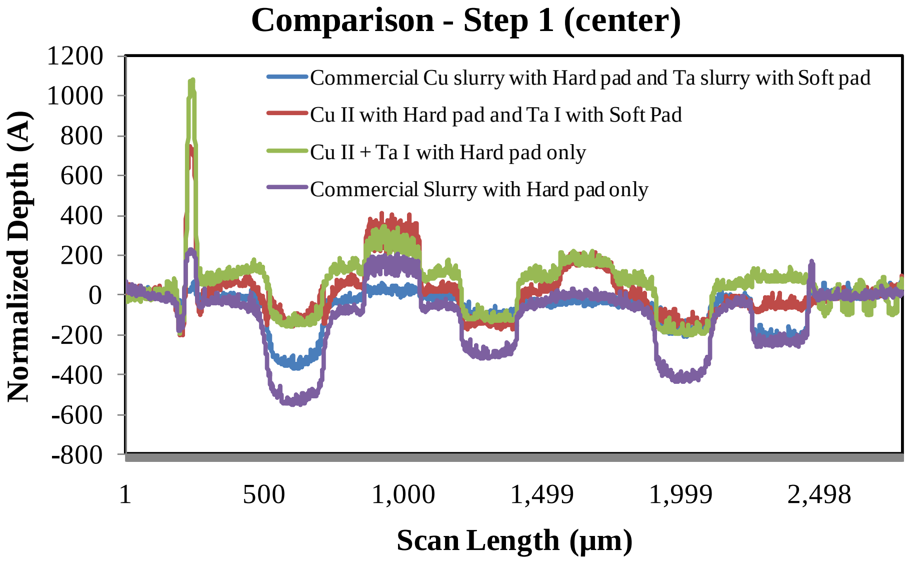


Box 6:
Minimum line, minimum space
50nm line/space; 50% pattern factor

Dishing comparison – Profilometry

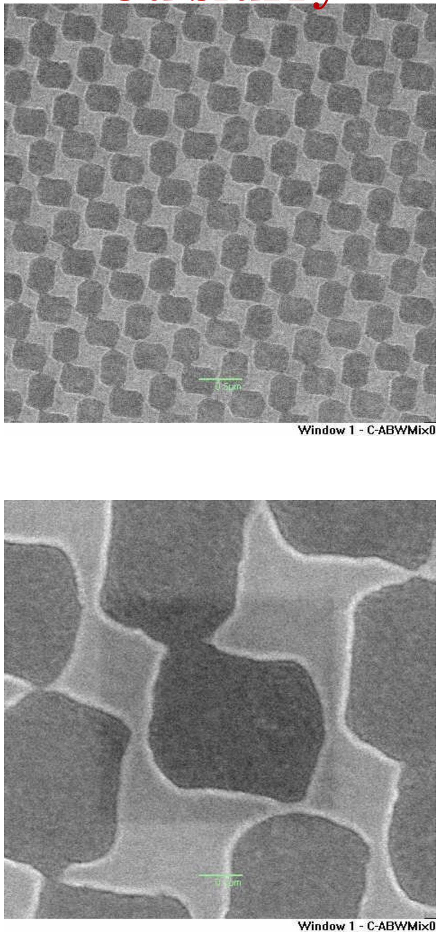




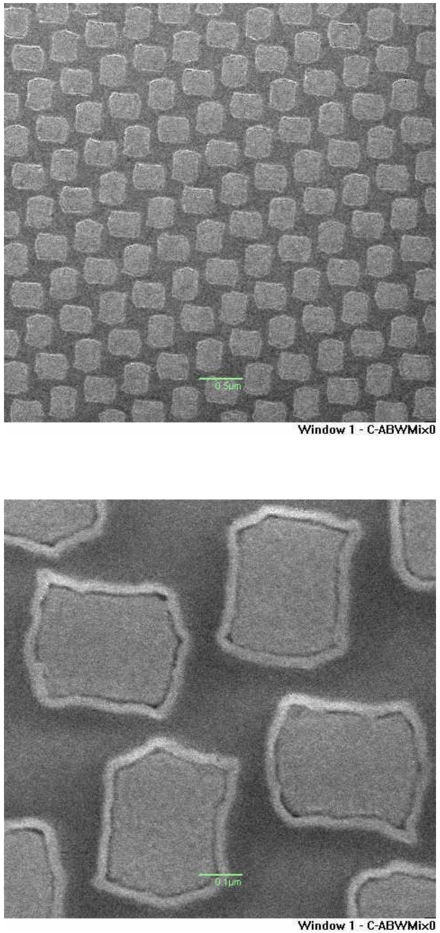


SEM Inspection of wafers polished with various slurries

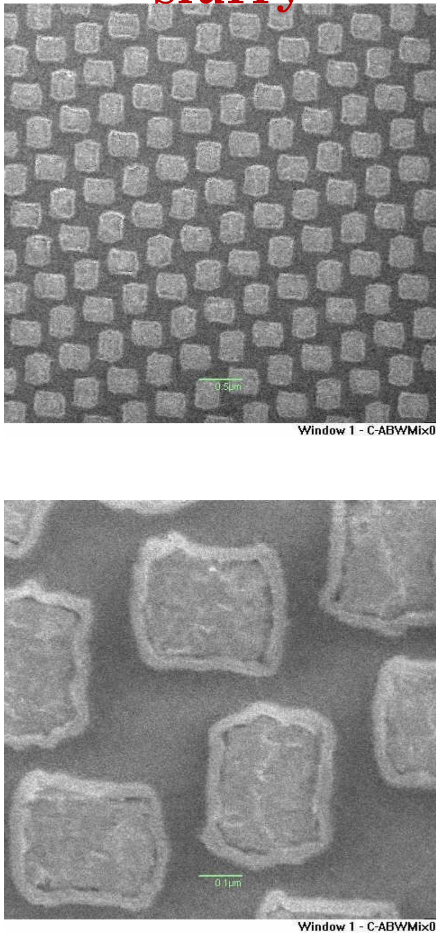
Commercial Cu slurry



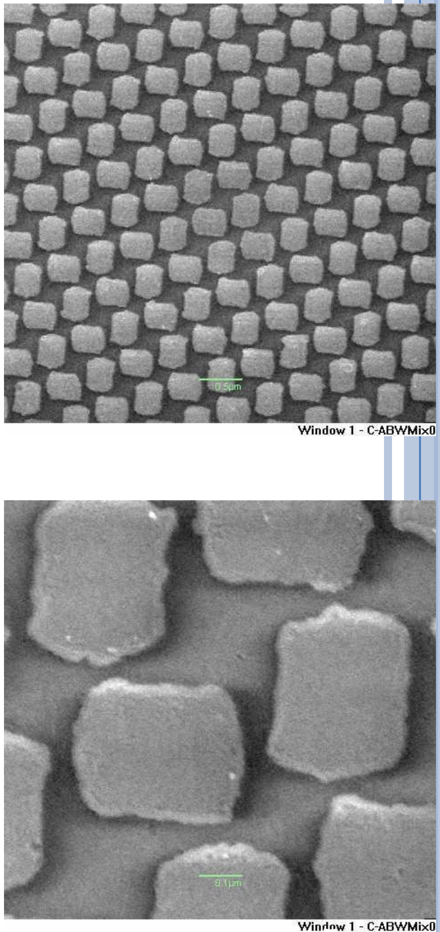
Cu – I slurry



Cu – II slurry



Ta – I slurry



Tool: Brightfield Defect Detector

Performance comparison of 2nd step slurries

Parameter	**Ta – I slurry (K_2SO_4-H_2O_2)**	**Ta – II slurry (K_2SO_4)**
Dishing Improvement for 200 x 200 µm features	20 – 30 nm	Not measurable
Optical Profilometry	Good	Cu was damaged
SEM Inspection	Lower defects compared to commercial slurry	N/A

Bulk Cu for these wafers was polished with commercial Cu slurry.

New Barrier materials (Ru-based)
-Slurry options

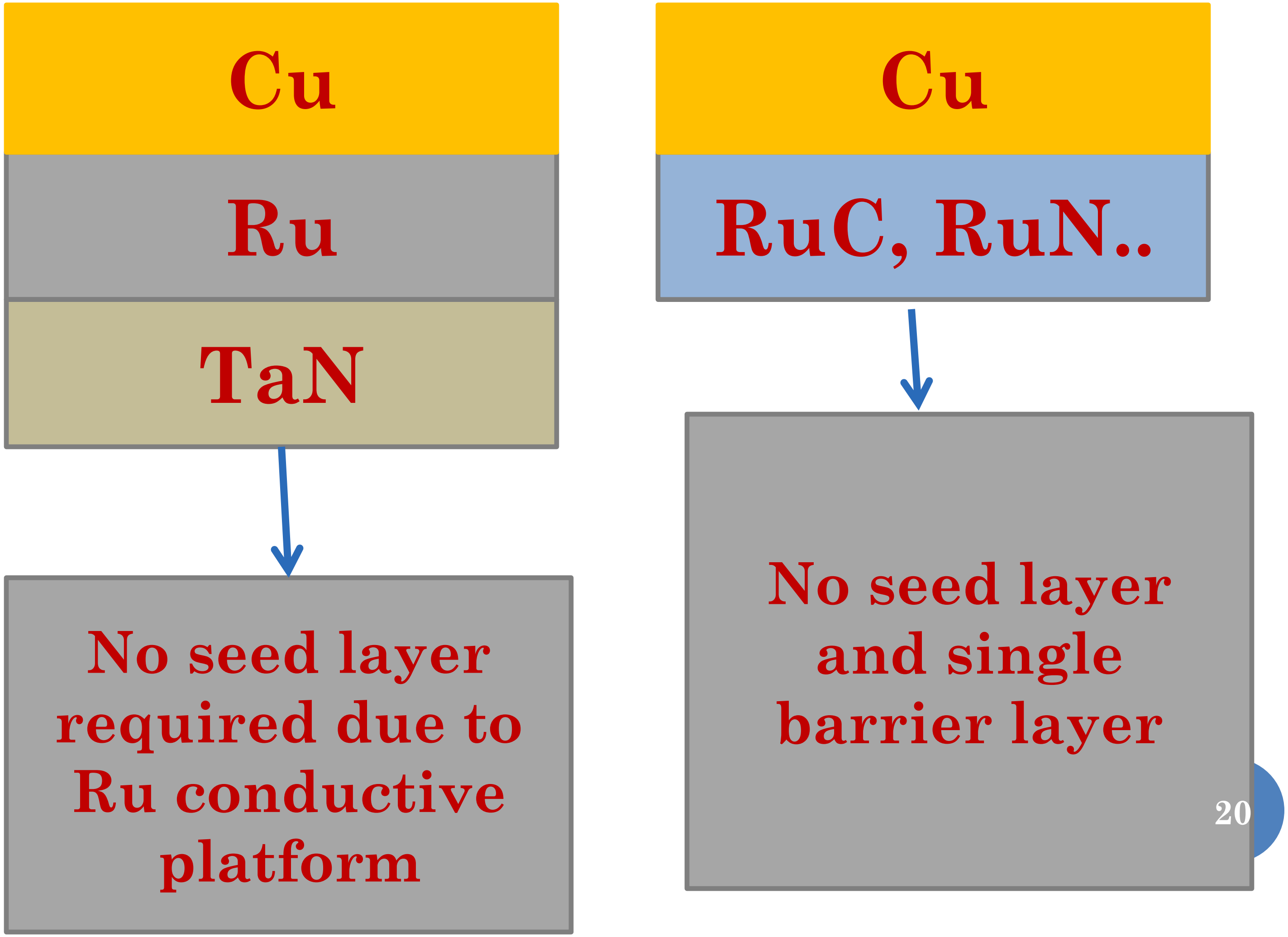
Challenges with Ta/TaN

- Barrier thickness is **~ 5 nm or less** for < 45 nm technology node
- Higher resistivity
- A Cu seed layer is required for electroplating Cu on Ta/TaN
- It is increasingly difficult to deposit Cu seed/Ta/TaN trilayer within the spatial limits

Alternative barrier requirements

- Need diffusion barriers with stability over wide (300 – 700 C) temperature range
- Conductive platform for direct electroplating of Cu, eliminating the need for a seed layer
- Single layer to decrease the complexity in the process

Alternative to Ta/TaN



Stack

Cu

Ru

TaN

Cu

RuC, RuN..

Advantage

No seed layer required due to Ru conductive platform

No seed layer and single barrier layer

Some Advantages of Ruthenium

- Lower (~7 µΩ cm) resistivity compared to Ta (~14 µΩ cm) and TaN (~200µΩ cm)
- Good adhesion to Cu – improves electromigration resistance
- High thermal stability
- Direct electrodeposition of Cu

Ru barrier

Drawback with only Ru barrier

- Ru due to its columnar structure, may not be a good diffusion barrier below 10 nm thickness

Incorporation of materials into Ru or Ru stack

- Ru/TaN was shown to have improved barrier properties
- Carbon incorporation into Ru stabilizes the amorphous structure and thereby improves barrier properties
- Similarly N, P, B.. incorporations have been investigated for improving barrier performance

Replacement of W contacts with Cu

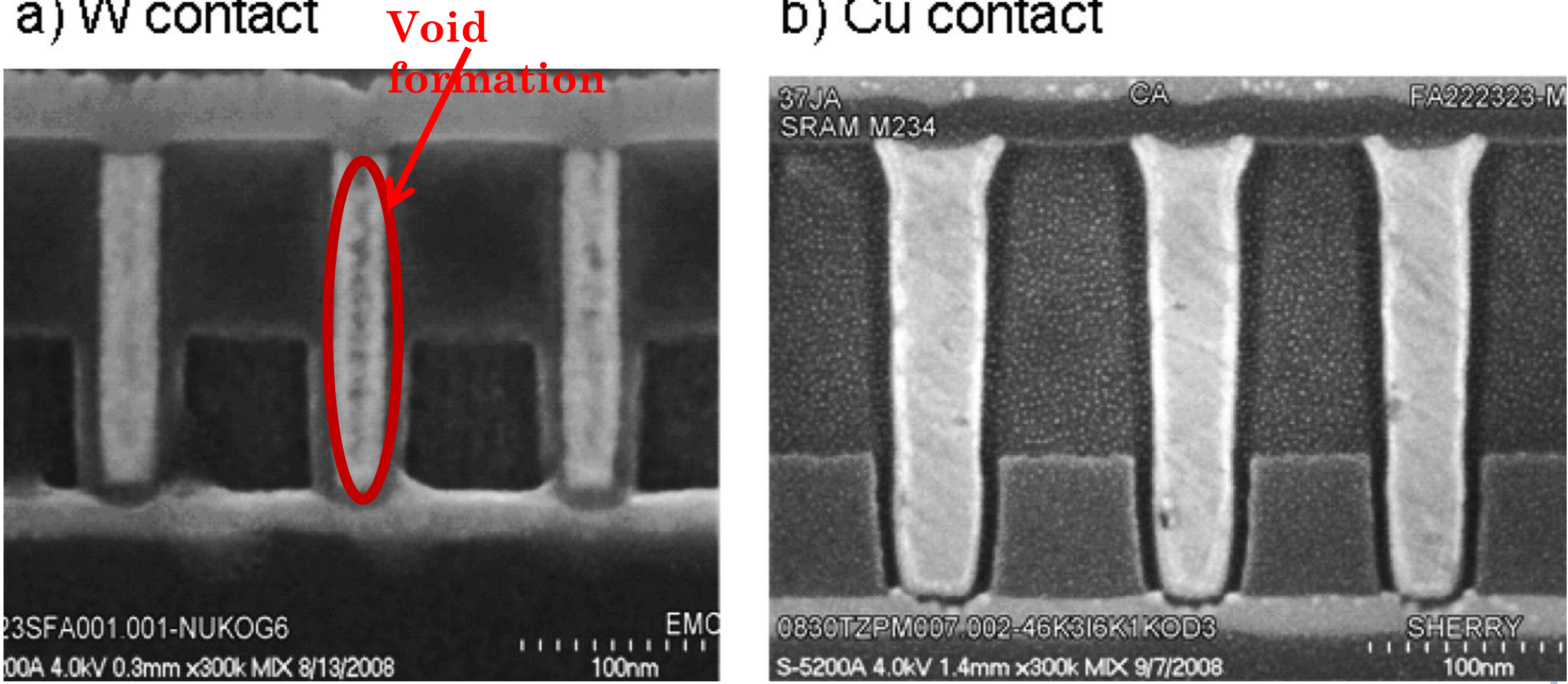
Problems for < 32 nm technology node with W:

- Large resistance of W(5.28 μΩ cm)
- Large resistance due to poor gap fill

Alternative:

- Cu (1.6 μΩ cm); but needs a robust diffusion barrier to block Cu diffusion
- Possible options for barrier: Ru/TaN, RuC, RuN…..

Comparison of W and Cu contacts



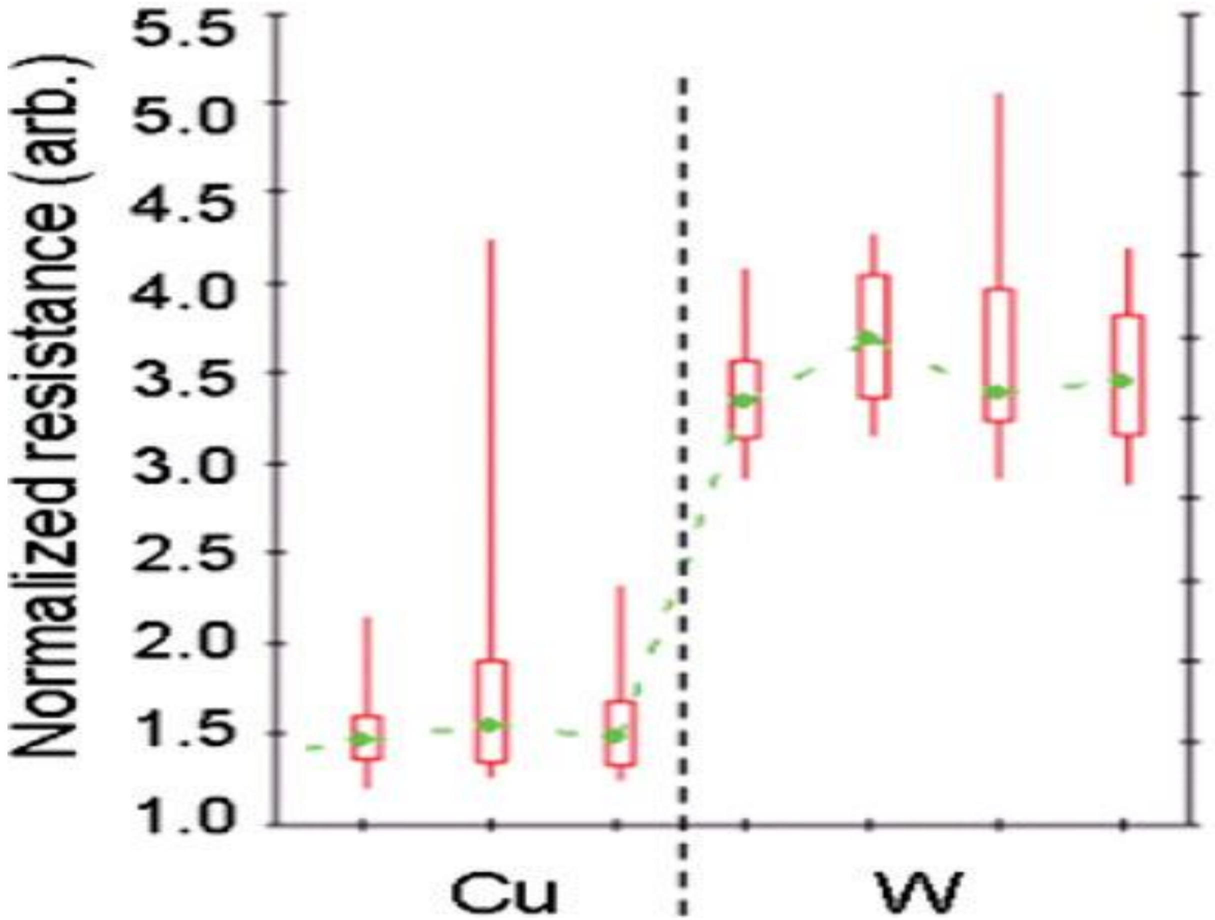
a) W contact

b) Cu contact

Line -200 nm depth and width of 35 nm, Cu contact on CVD Ru/TaN

Ref: S. C. Seo et al., Electrochemical and Solid-State Letters, 14 (5) H187-H190 (2011)

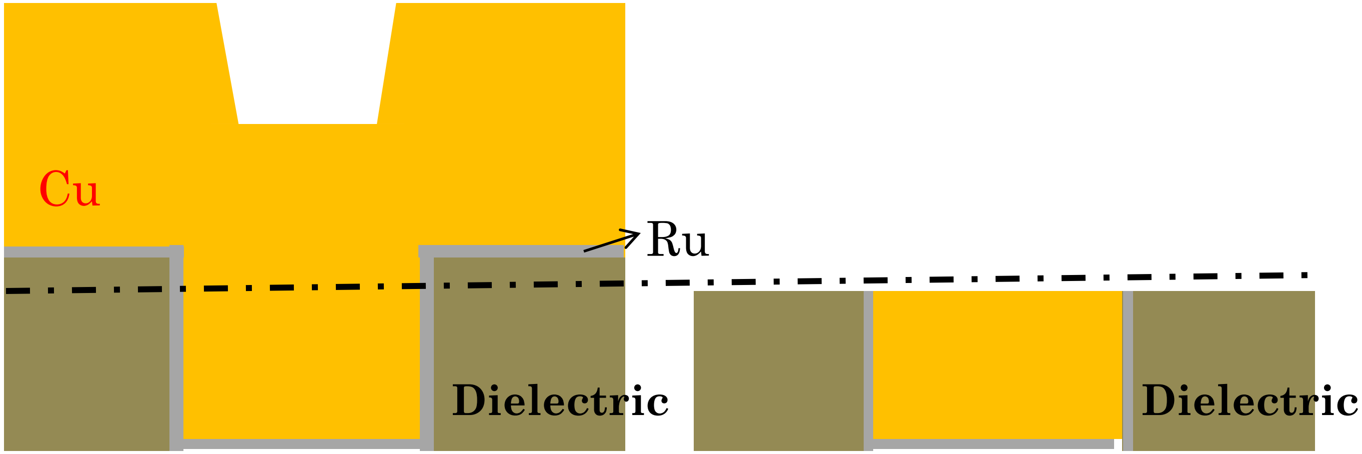
Comparison of resistance



Ref: S. C. Seo et al., Electrochemical and Solid-State Letters, 14 (5) H187-H190 (2011)

Challenges for Ru CMP

- Ru, a noble metal, has a very low polish rate in typical barrier slurries (needs oxidizer for higher RRs)
- Can induce galvanic corrosion in Cu due to difference in corrosion potentials
- Selective removal of Cu, hardmask (SiO2), and low-k (SiCOH) is required



Ru CMP - Early Work

Oxidizer	pH	RR (nm/min)	Pressure (psi)	Problem	Ref
Ceric ammonium nitrate (CAN) + HNO_3	1	40	1	Formation of RuO_4 and insolubility of CAN above pH 2	Lee et al (2004)
Hydrogen peroxide	3 -10	10	3	High silica wt% (30)	Vishwas (2005)
Sodium periodate	4 -10	130 (pH 6)	4	Na contamination	Park et al (2009)

New KIO_4-based slurry for Ru CMP

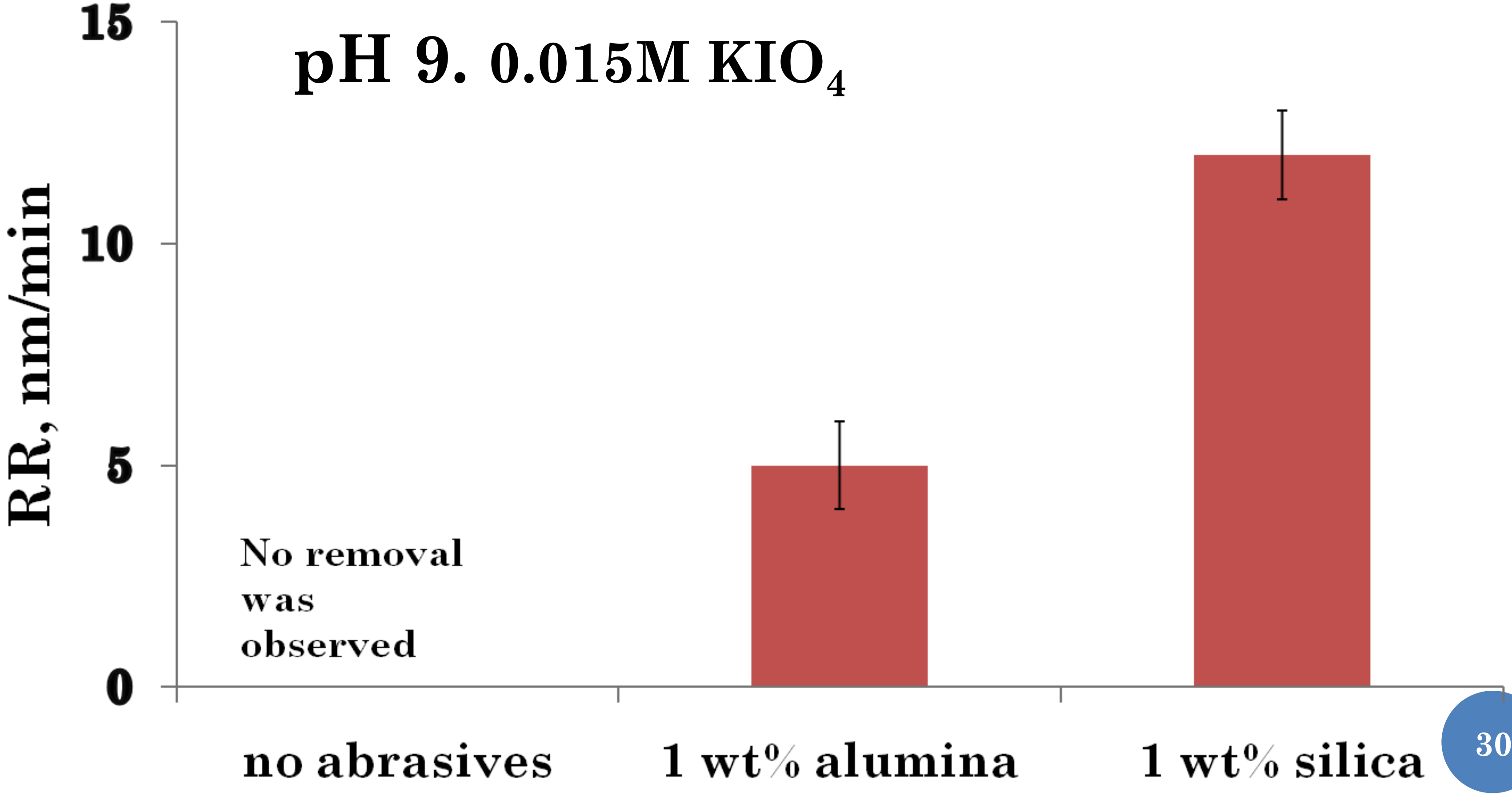
- **Some targets**
  - Ru Removal rate > 50 nm/min
  - Eliminate formation of RuO_4 (toxic)
  - Adequate removal rate selectivities over Cu and SiO_2
  - Minimize defects and galvanic corrosion

***B. C. Peethala and S. V. Babu, J. Electrochem. Soc* 158, H271 (2011)**

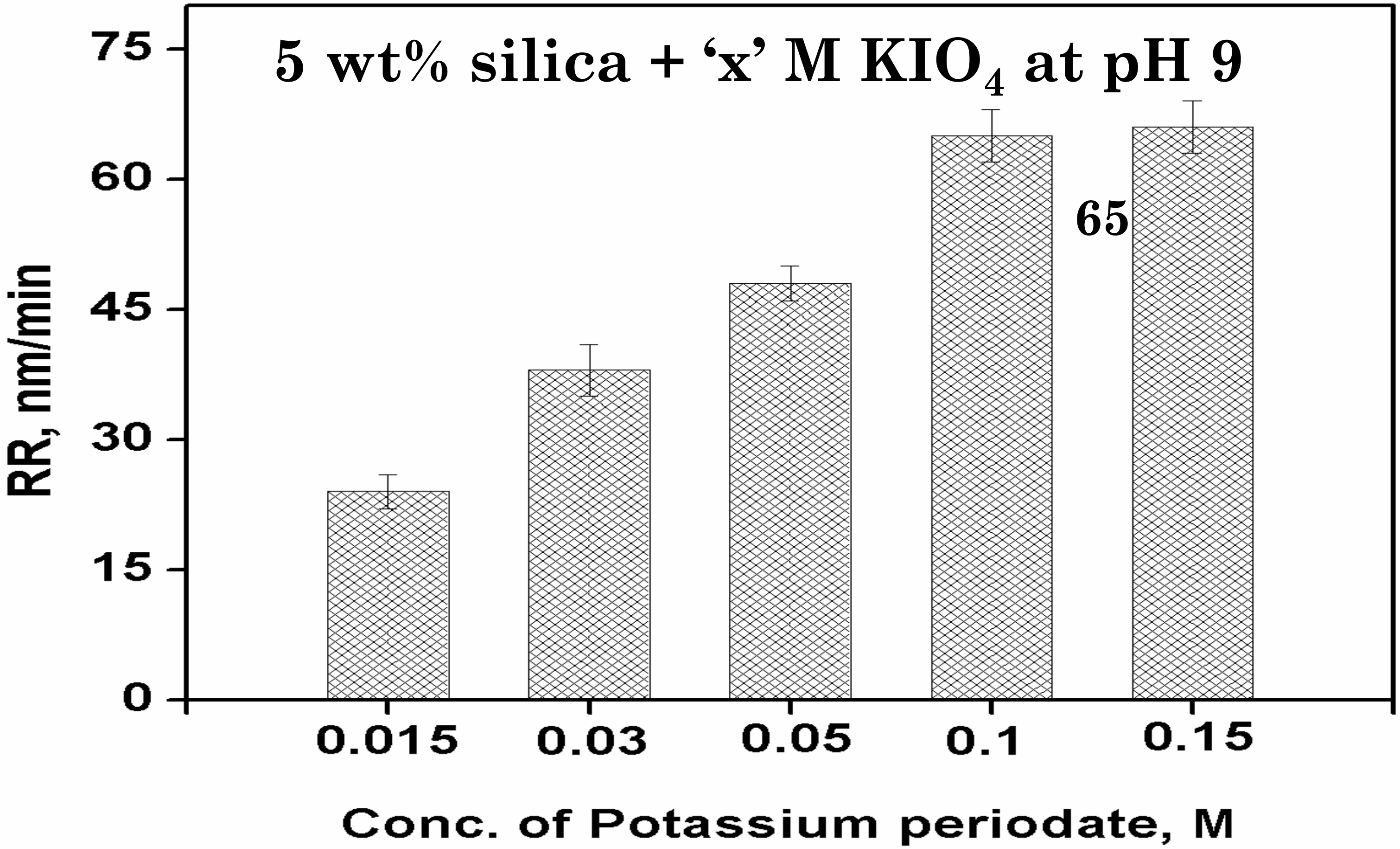
Concentration and pH of KIO_4

- Solubility at 20°C is 0.018 M, increased by adding KOH
- 0.015 M concentration was chosen for an initial study
- Toxic RuO_4 is reported to form in the acidic region ($pH \leq \sim 7$), therefore pH 9 was chosen

Effect of Abrasives

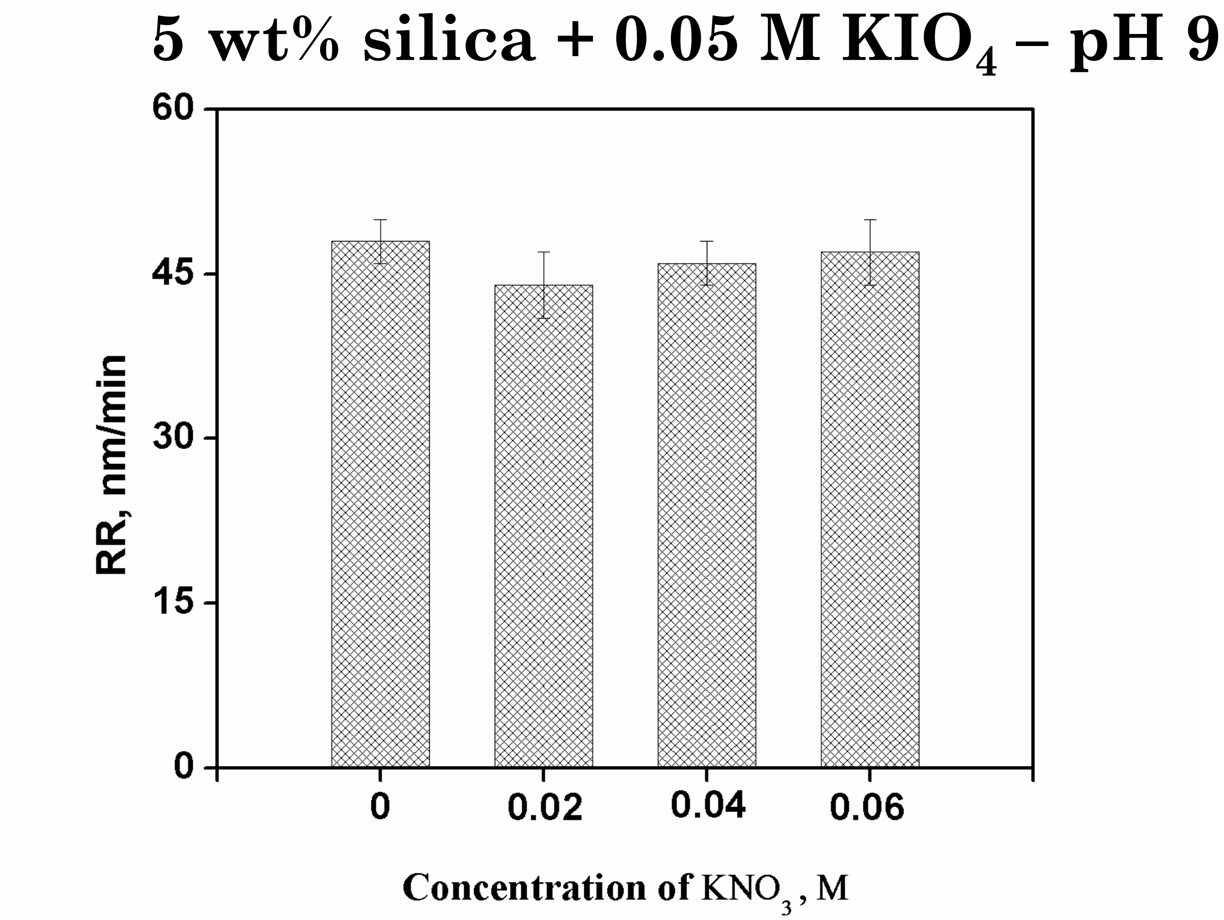


Enhancement in the Ru RRs



B. C. Peethala and S. V. Babu, J. Electrochem. Soc (2011)

Effect of ionic strength



5 wt% silica + 0.05 M KIO_4 – pH 9

Proposed reaction mechanism

- pH ≤ 7

$$Ru + KIO_4 \rightarrow RuO_4(toxic) + I^- + K^+$$

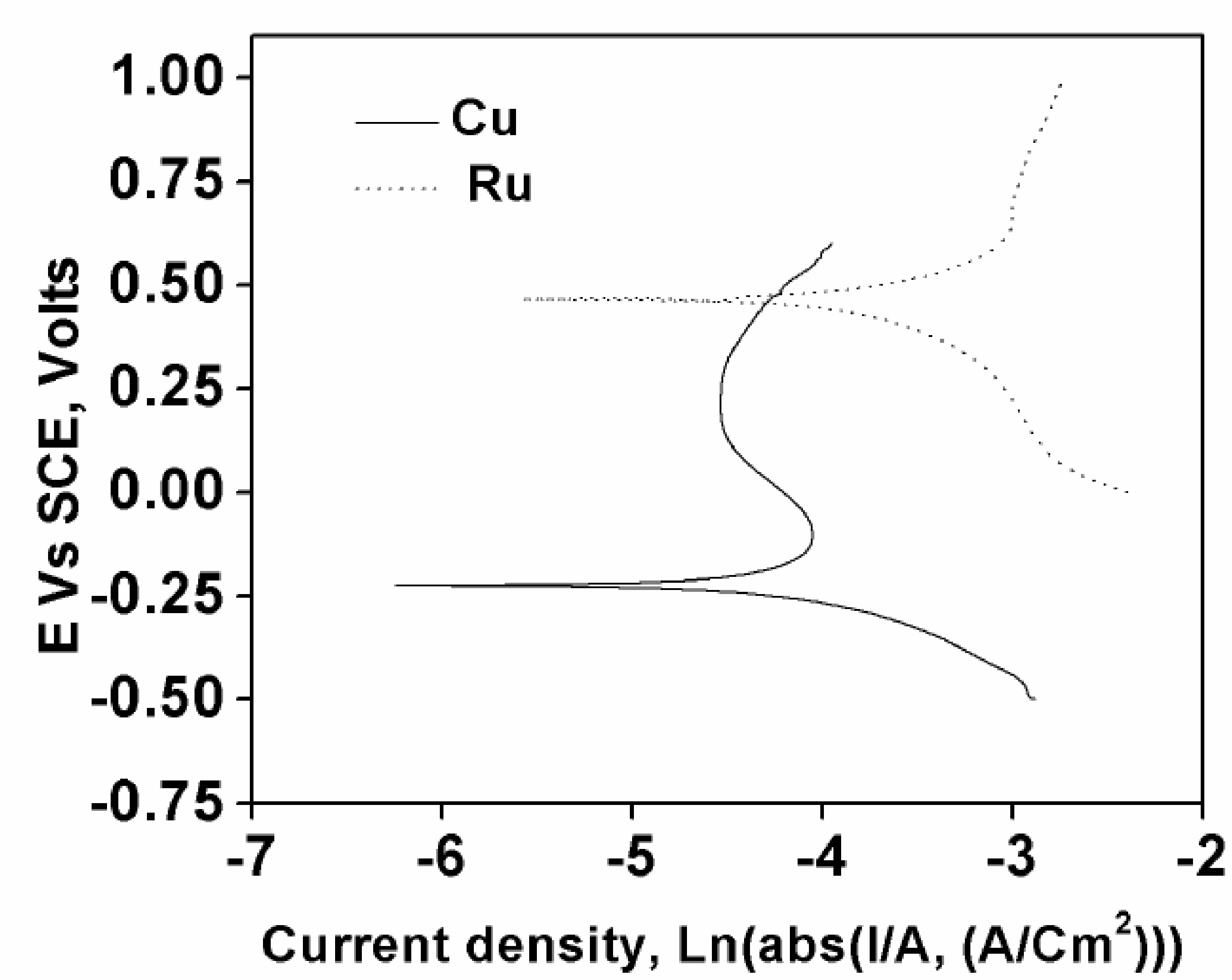
- pH ≥ 8

$$Ru + KIO_4 + 2OH^- \rightarrow RuO_4^- + H_2O + \frac{1}{2}O_2 + I^- + K^+$$

$$4RuO_4^- + 4OH^- \rightarrow 4RuO_4^{2-} + 2H_2O + O_2$$

Galvanic Corrosion Analysis

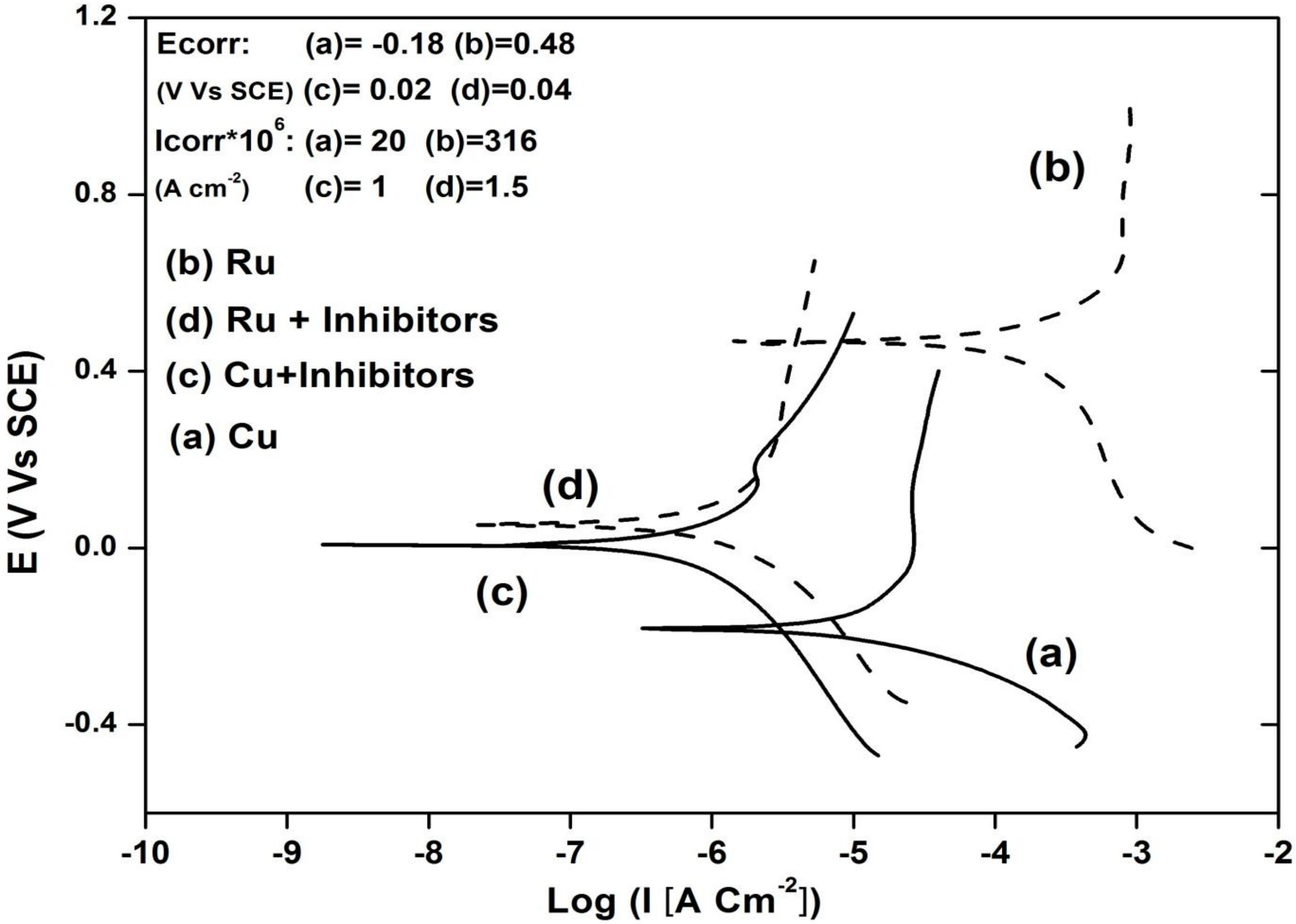
Galvanic corrosion issue with Cu



Solution:
0.03 M KIO4 at pH 9

Observation:
Corrosion potential difference of ~600 mV

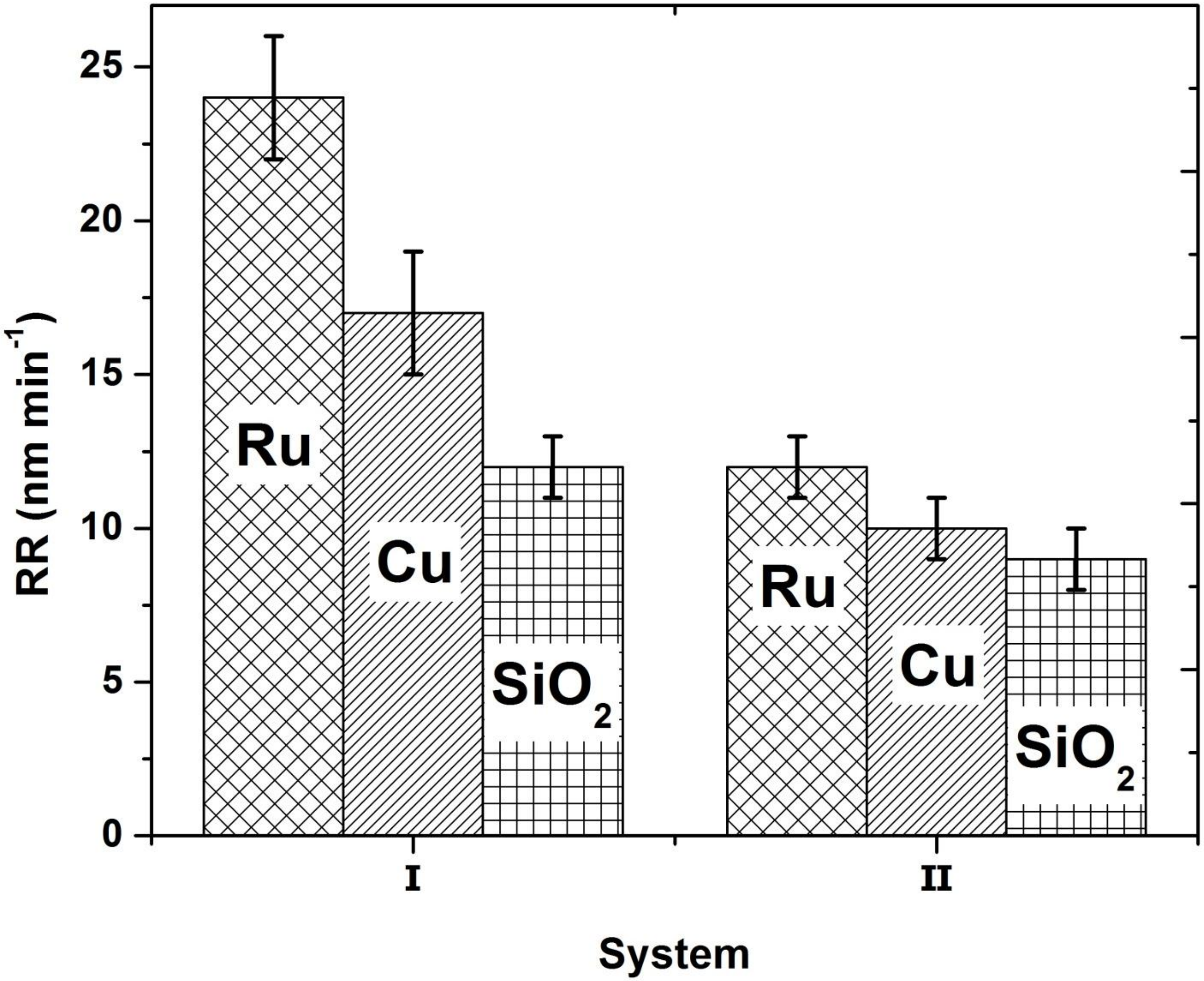
Combination of inhibitors (7 mM AA + 5 mM BTA)



Combination of inhibitors decreased the corrosion potential significantly to a value of ~20 mV

B. C. Peethala et al.,Electrochem. Solid-State Lett. July 2011(**DOI: 10.1149/1.3589308)**

RRs with and without inhibitors



System I:
0.015 KIO_4 +
5% Silica

System II:
0.015 M KIO_4
+ inhibitors

Ref: B. C. Peethala et al., Electrochem. Solid-State Lett. July 2011

Summary

- Slurry selection can severely impact defect control
- Barrier Slurry is becoming more critical
- New barrier materials (Ru and alloys) impose additional challenges
- Additives that can minimize the possibility of galvanic corrosion of Cu during Ru polishing have been identified.
- Mixed oxidizer slurries without BTA and sulfate-based barrier slurries are attractive