Characterization of Phosphate Electrolytes For Use in Cu ECMP

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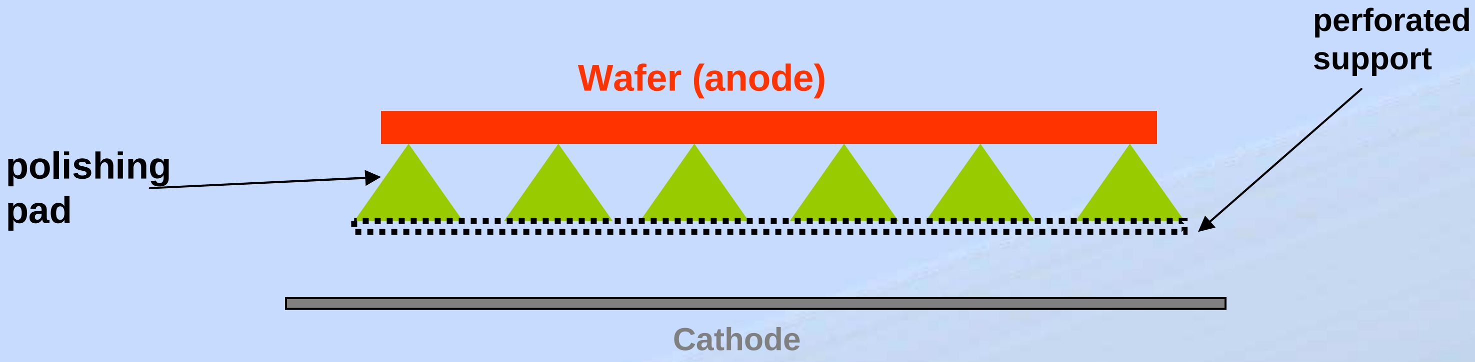
What is ECMP?

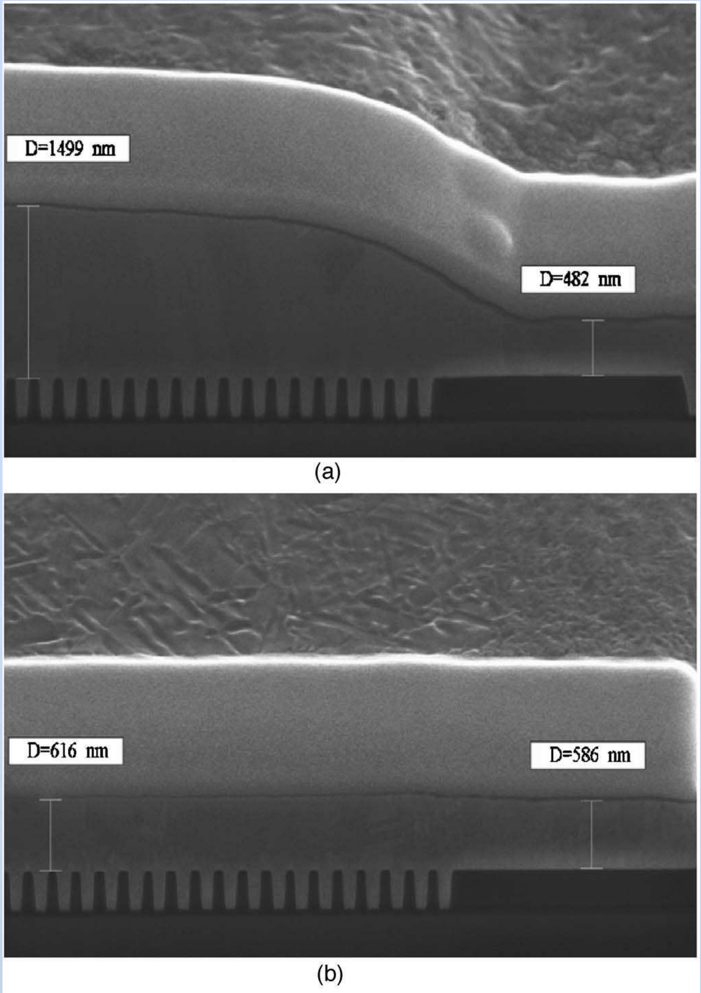


Potential Advantages

- **Potentially eliminates need for particles in slurry**
- **Reduce/eliminate use of strong oxidizers**
  - **electrons supplied by external circuit oxidize Cu**
- **Operate at low downforces (<0.3 psi)**

Planarization Challenges

(1)



(a)

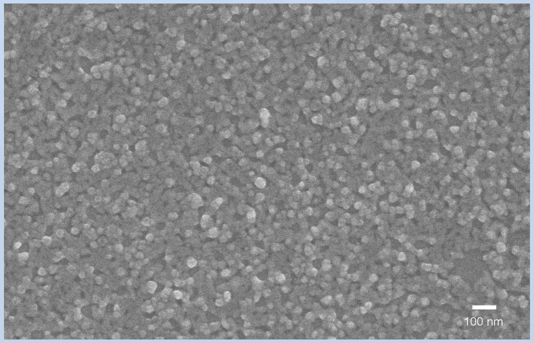
(b)

- Cu Challenges:
  - **Rates**
  - **Wafer Scale Uniformity**
  - **Feature-scale planarization**
    - Low Aspect Ratios
- Liner materials
  - **Ta-based materials (Srini Raghavan)**
  - **Ru (West)**
    - **Current year focus**

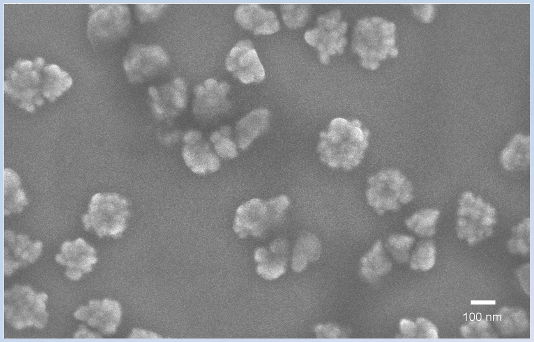
(1) Willey, M. J., J. Reid, A.C. West, Adsorption Kinetics of Polyvinylpyrrolidone during Cu Electrodeposition. *Electrochemical and Solid-State Letters,* **10** 4 D38-D41 2007

Other SRC Activities

- *Copper electrodeposition (SUNY Albany)*
  - *Material properties of smallest node lines (failure to achieve desired microstructure)*
  - *Direct metallization (Cu on Ru)*



Regular Pretreatment



No pretreatment

Cu: How to Choose an Electrolyte

- Screening process for ECMP electrolytes

  - **Parameters Examined (using RDE)**
    - pH
    - Salt concentration
    - BTA concentration
    - Mass transfer

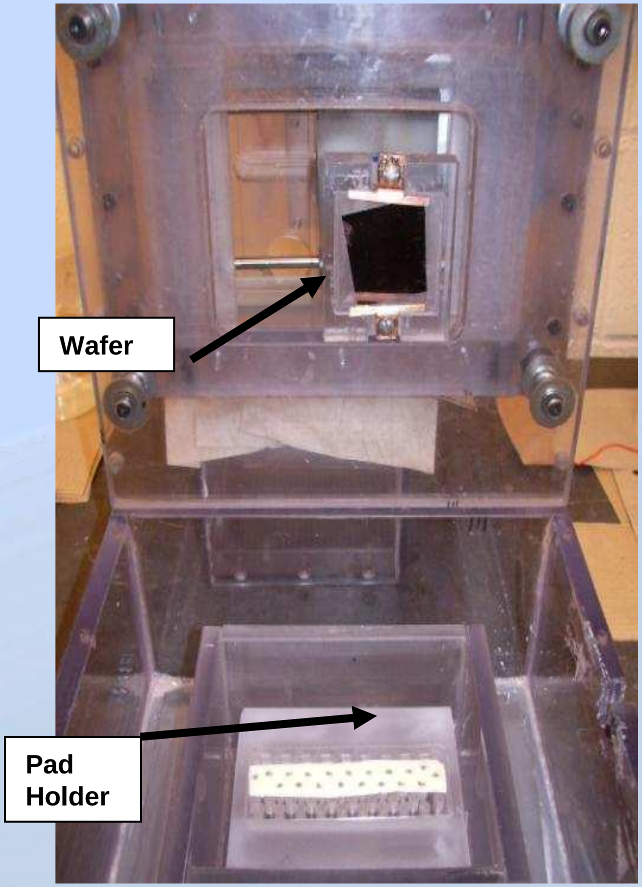
  - **Key Characteristics**
    - Metal-removal rates
    - Planarization efficiency

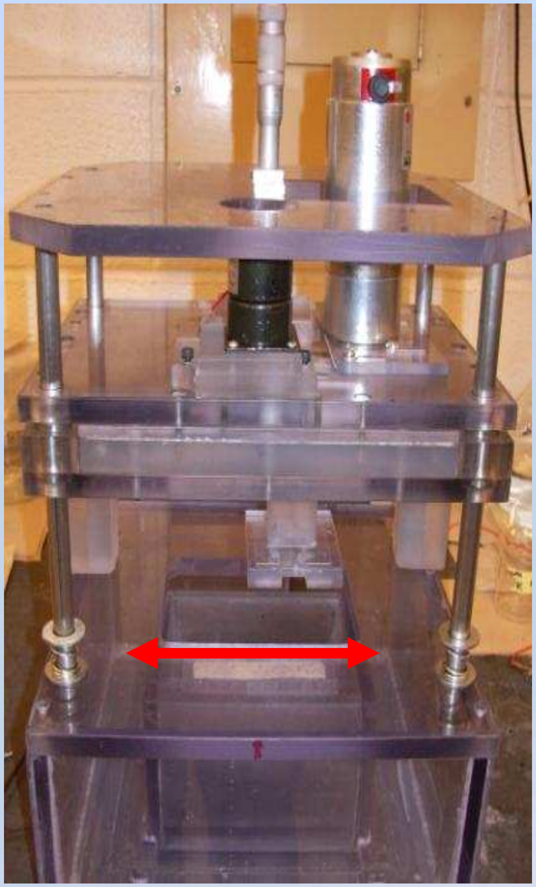
- Phosphate based electrolytes
- Benzotriazole (BTA) inhibitors

Method – ECMP Tool

Design features:

- 2D linear motion
- Apply and control low downforces (~1 psi)
- Ease of changing between various electrolytes and pads
- Operate in contact and non-contact modes

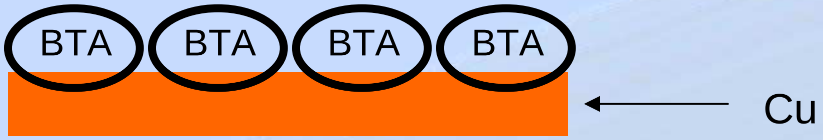




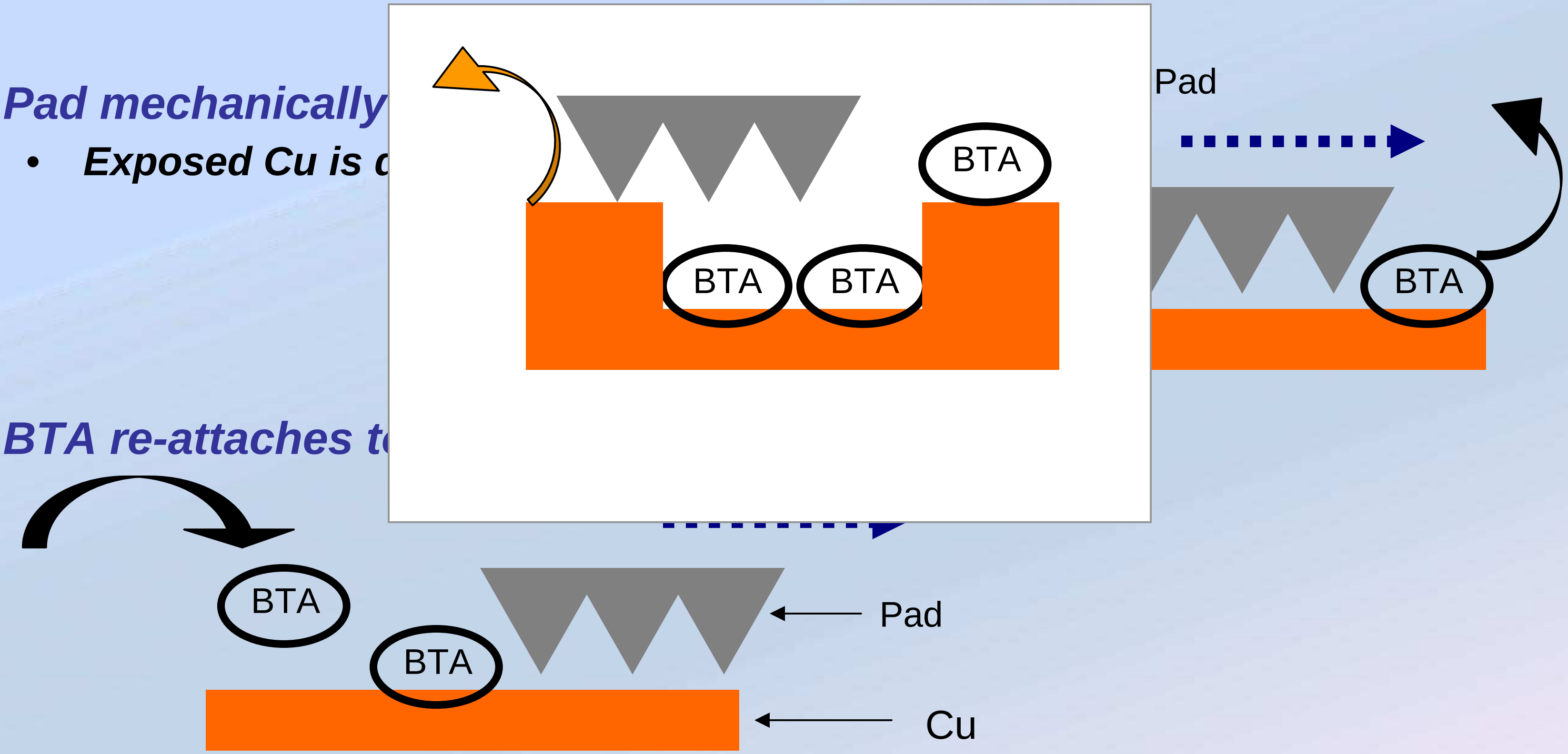
Removal Theory

Proposed BTA removal Mechanism

1. ***BTA adheres to surface***
   - ***Forms BTA-Cu complex***



2. ***Pad mechanically***
   - ***Exposed Cu is c***
3. ***BTA re-attaches t***



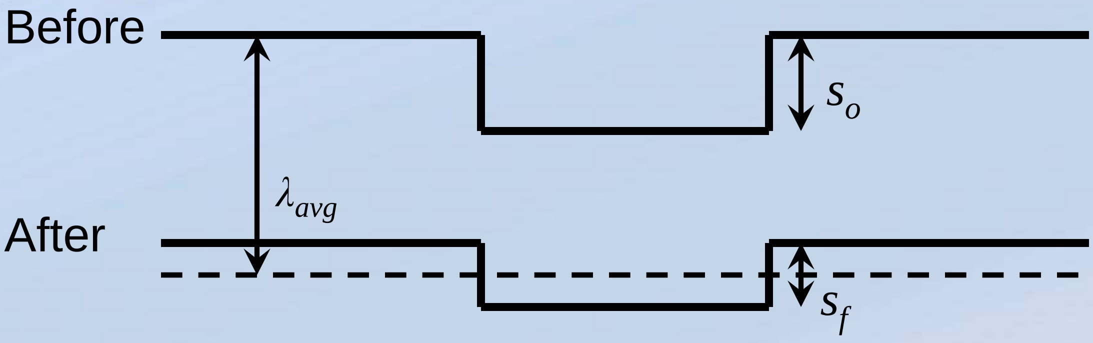
Theory

Quantifying Planarization

- Planarization is most challenging for low-aspect ratios

Can be theoretically characterized as:

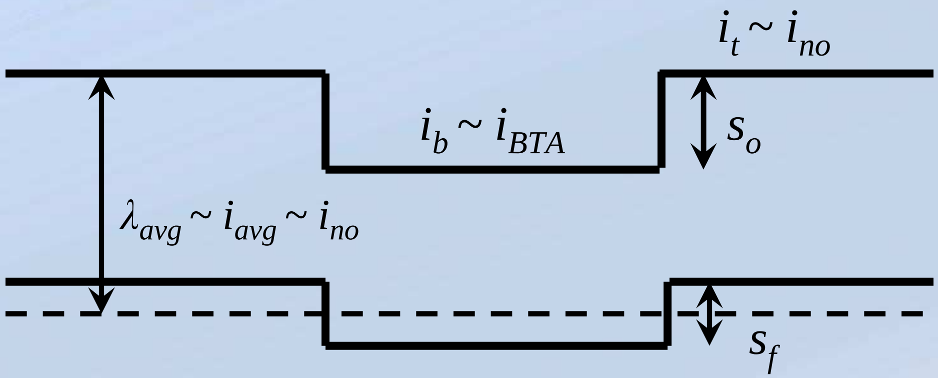
$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}}$$



Screening Approach

- Electrochemically screen potential ECMP electrolytes
  - Relate removal rate to current density
    - ***With and without inhibitor (BTA)***

$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \sim \frac{i_t - i_b}{i_{avg}}$$

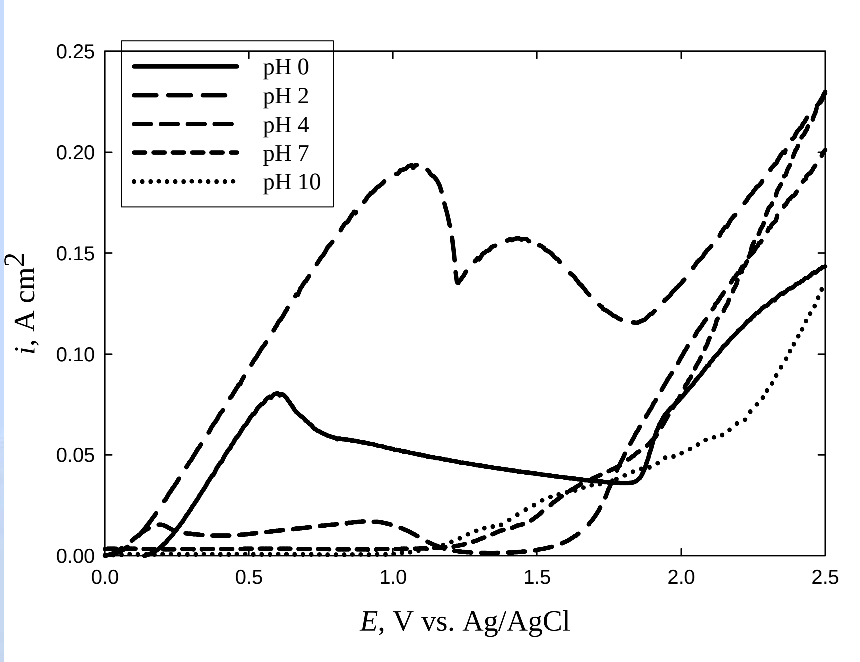


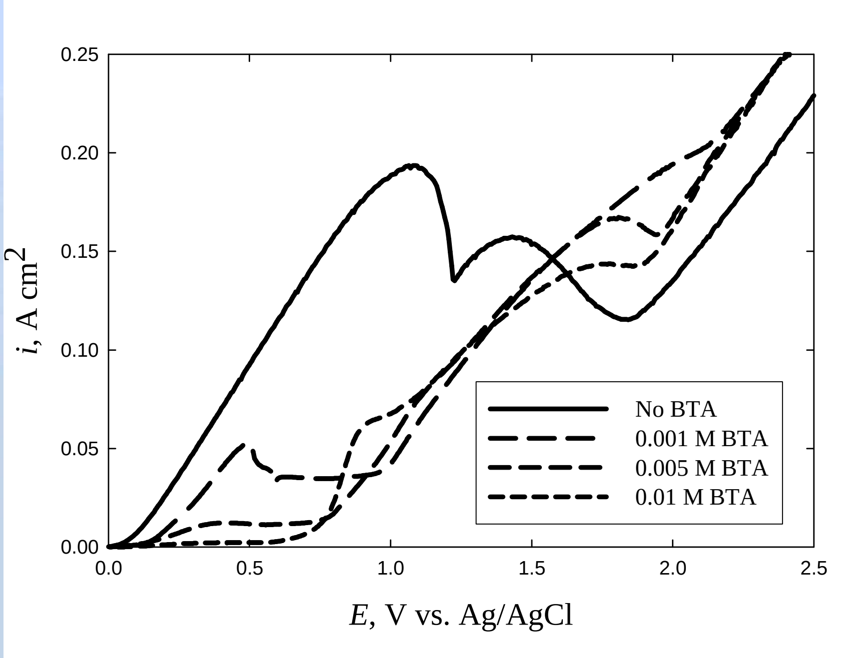
For Experiments Using <u>RDE</u>

$$\varepsilon_{RDE} = \frac{i_{no} - i_{BTA}}{i_{no}}$$

Results - RDE

- ***pH values 0 to 10***
  - *No BTA*
- ***pH 2***
  - *0 to 0.01 M BTA*





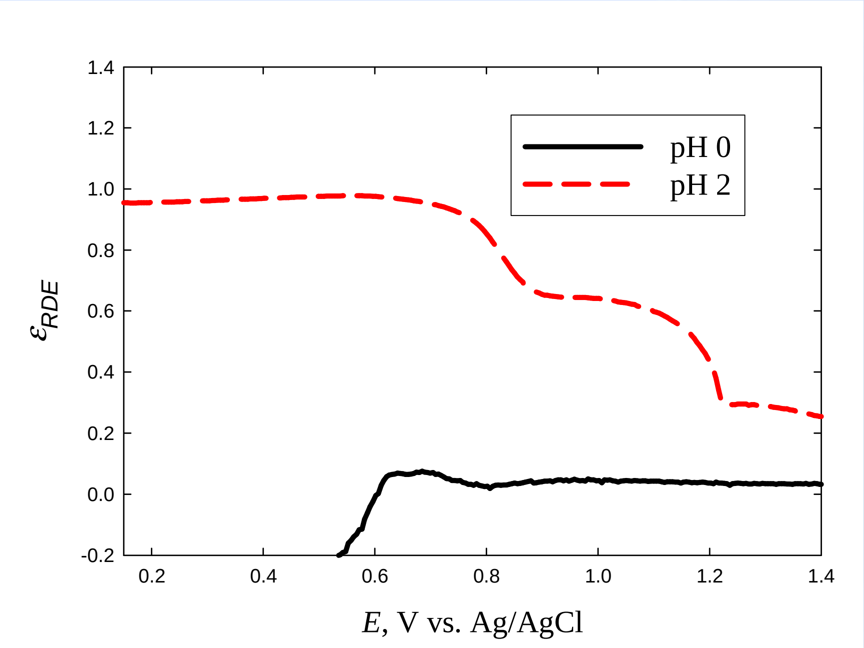
RDE results used to correlate current density to removal rate

Results - RDE

Theoretical Planarization Factor

RDE

- pH 0 & pH 2
    - 0.01 M BTA

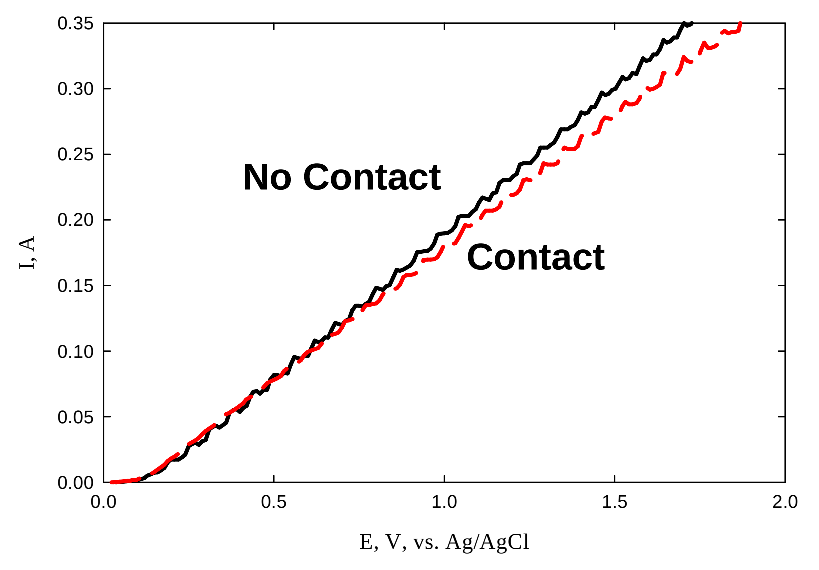


Using pH 2 → Good planarization is likely at potentials < 0.8 V

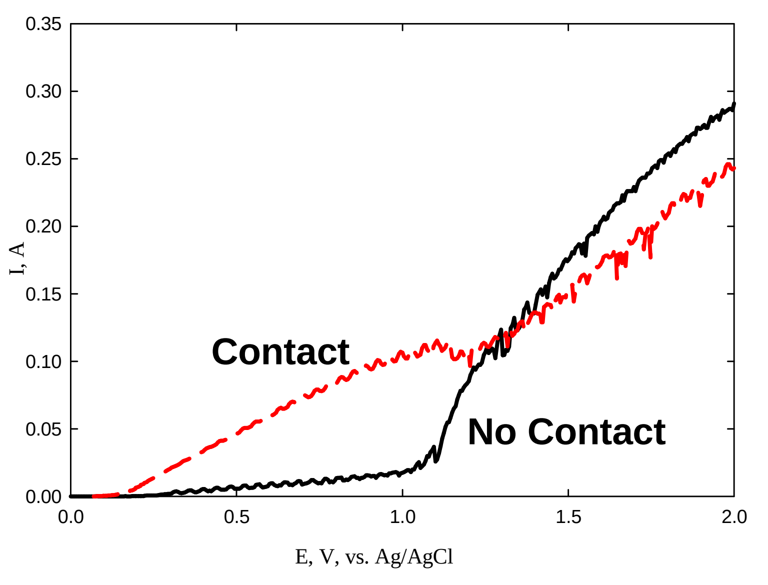
Results – ECMP Tool

Experiments using ECMP Tool with Blanket Wafers

pH 2, No BTA



pH 2, 0.001 M BTA



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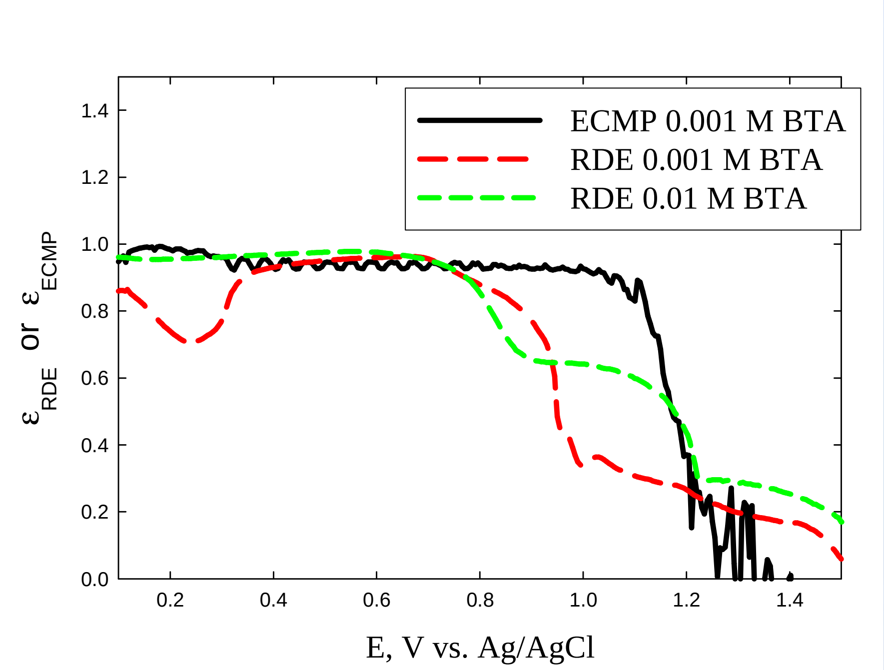
Results

Theoretical Planarization Factor

RDE & ECMP

- pH 2
    - 0.001 or 0.01 M BTA



Good planarization likely under conditions:

- Potential window **~ 0.4 to 0.8 V**
- Minimum BTA concentration **~ 0.001 M**

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Results

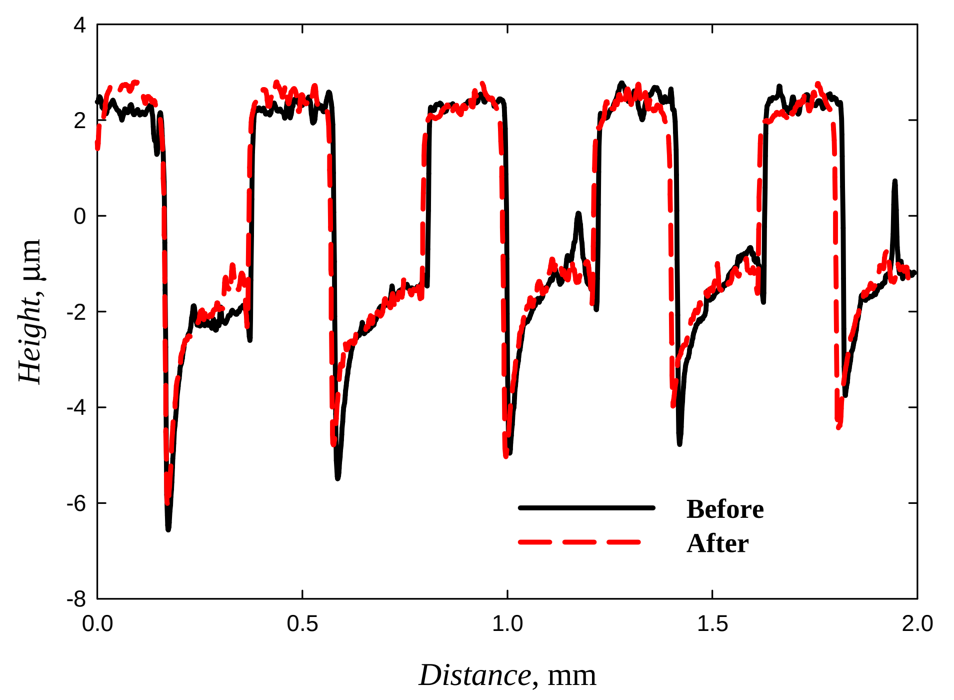
Summary Electrolyte Screening

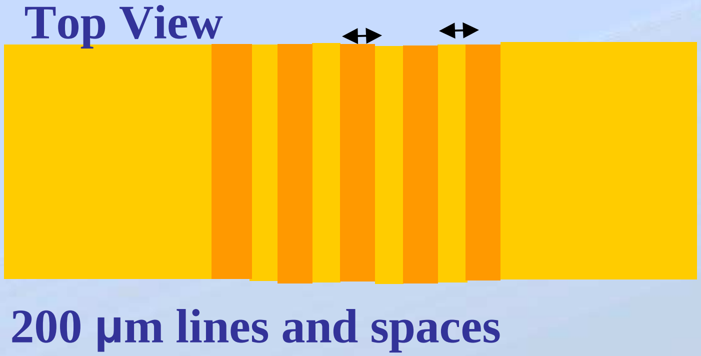
- Operating Conditions
  - pH ~ 2
  - Operating Potential → 0.5 V
  - BTA concentration → from 1 mM
  - Salt Concentration → 1 M
- Patterned structures tested to support screening process

Planarization Results

Pad Type: Suba

No BTA





500 nm of Material Removed

- No Step Height Reduction

No Planarization Achieved

- All planarization experiments were performed at:
  - 0.5 V vs. Ag/AgCl
  - Downforce ~ 1 psi

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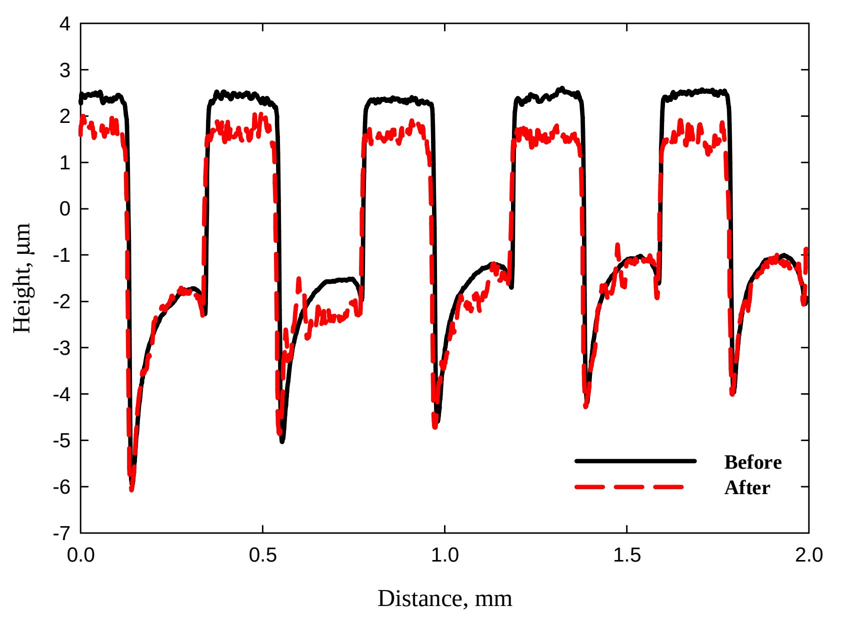
Planarization Results

0.001 M BTA

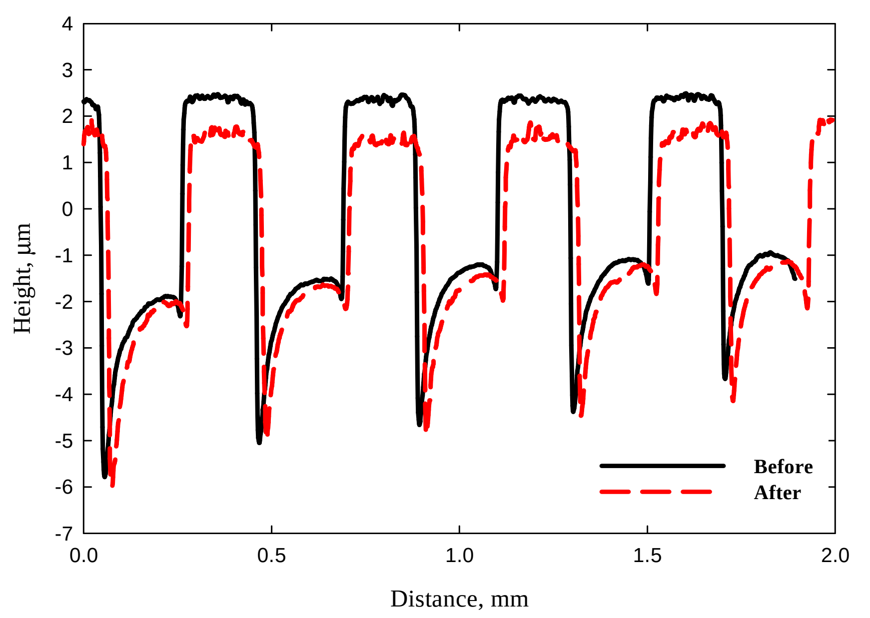
Pad Type: Suba



390 nm of Material Removed

- Step Height Reduction
  - ~ 780 nm

Pad Type: IC1000



340 nm of Material Removed

- Step Height Reduction
  - ~ 740 nm

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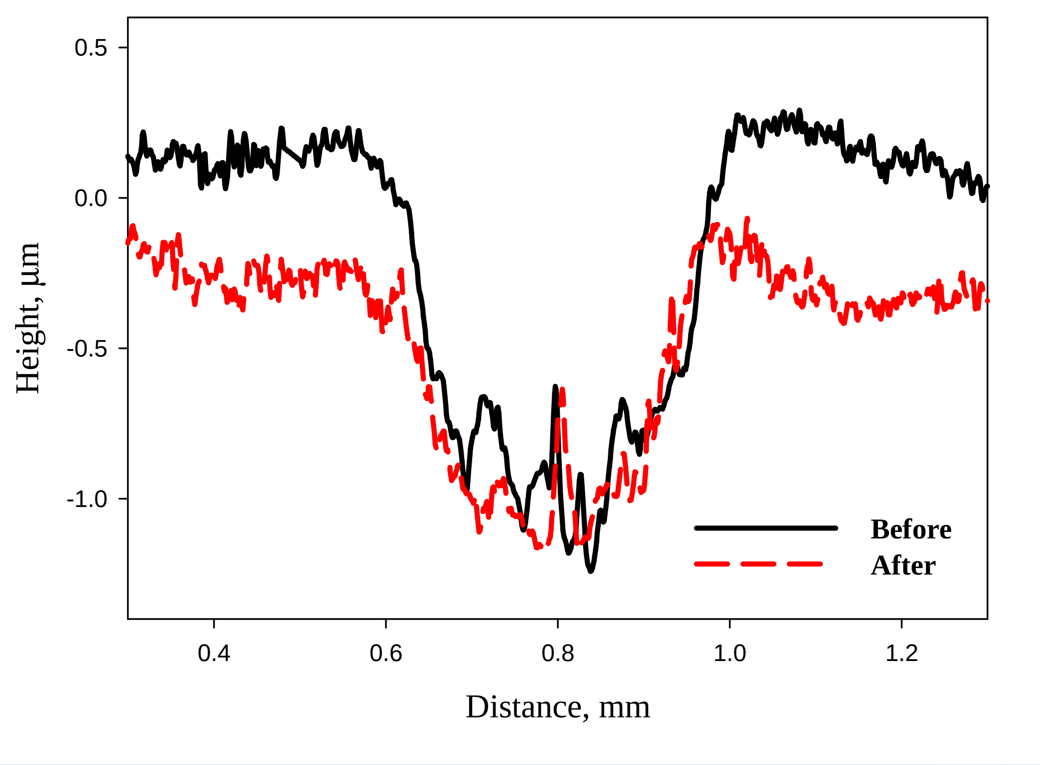
Planarization Results

✓ *Low aspect ratio polishing achieved*

Pad Type: D100



320 nm of Material Removed

- Step Height Reduction
  - ~ 400 nm

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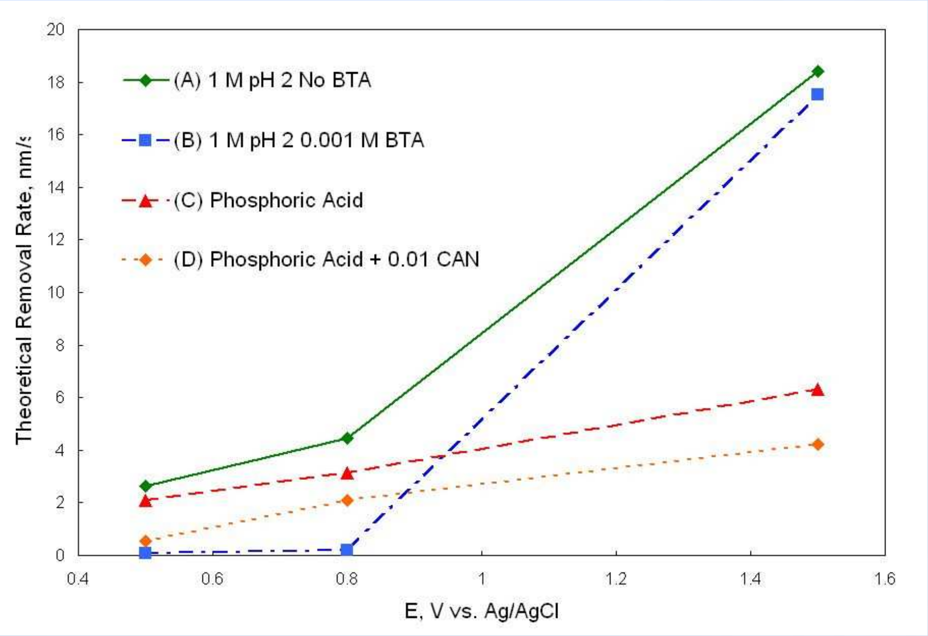
Cu ECMP: Future Work

- *Improved test structures*
    - *Feature size*
    - *Pattern effects*
    - *Roughening studies*
- *Alternative pads*
- *Other E-CMP Tools with better mechanics*

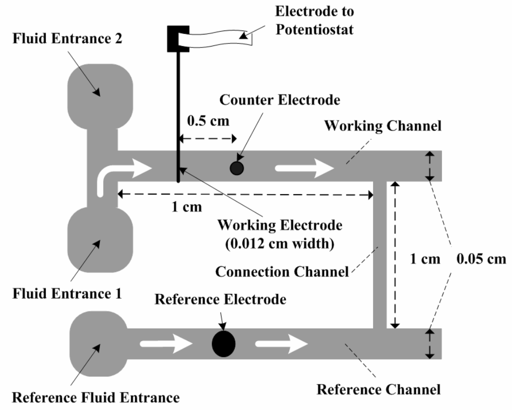
Ru ECMP

- *Phosphate based electrolytes*
- *Influence of BTA*
- *Apparent Selectivity*

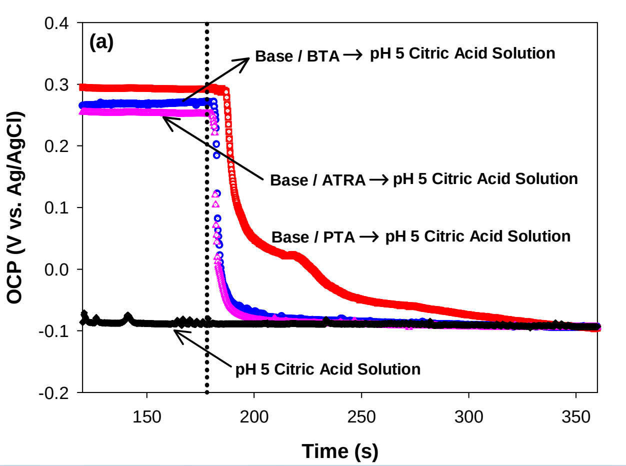


- *What can be learned from electrodeposition?*
    - *Oxide can be easily reduced*

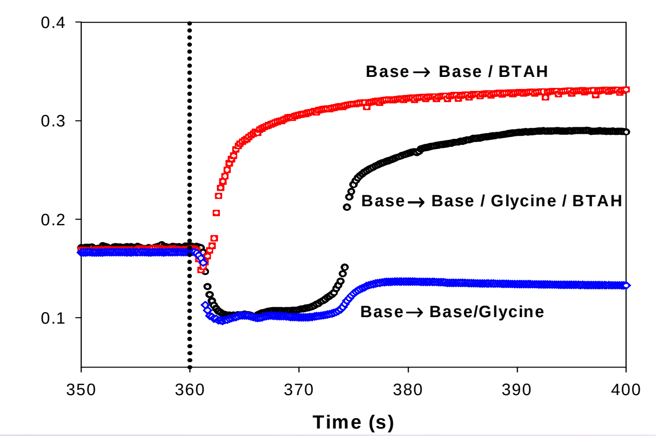
Other Relevant Studies



- Microfluidic Device originally developed to study adsorption/desorption kinetics of additives in plating



- Evaluation of Post-Cu CMP Cleaning of Organic Residues Using Microfluidic Device



- Adsorption and Desorption Studies of Glycine and Benzotriazole during Cu Oxidation in a Chemical Mechanical Polishing Bath

Conclusions

- ✓Electrolyte screening process was successful
- ✓Planarization was observed using phosphate based electrolyte

- Industrial partner needed for further testing

Acknowledgments

- SRC/Sematech
- Columbia University

- Neha Solanki

- Novellus
- Cabot
- Rohm & Haas