INVESTIGATION OF PHOSPHATE BASED ELECTROLYTES FOR USE DURING Cu-ECMP

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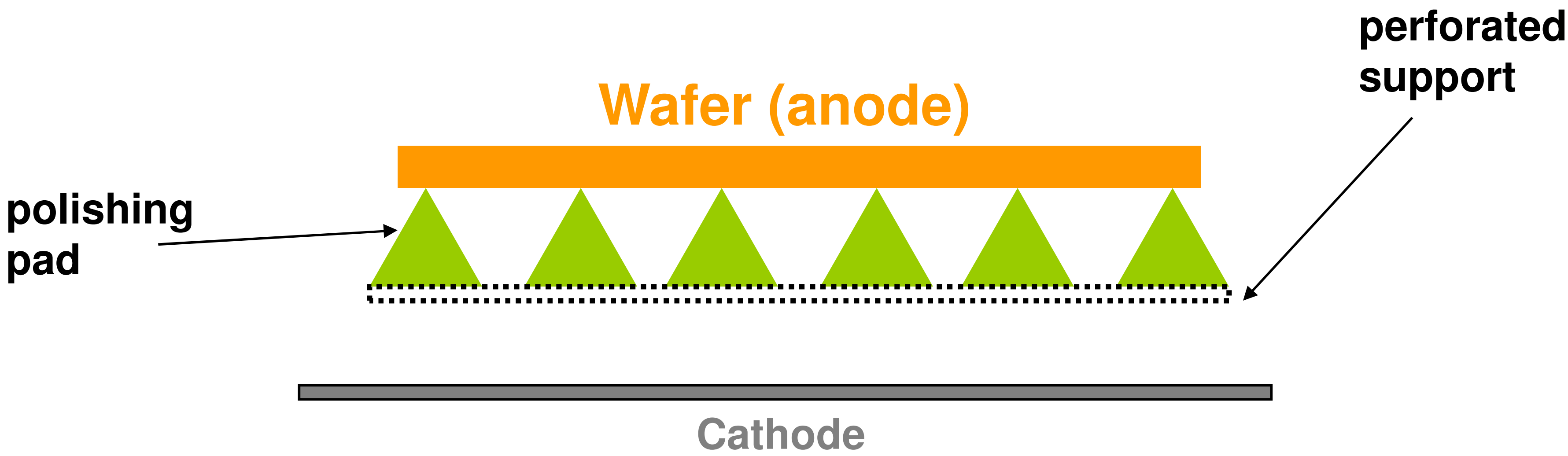
What is ECMP?



- **Potentially eliminates need for particles in slurry**
- **Reduce/eliminate use of strong oxidizers**
  - **electrons supplied by external circuit oxidize Cu**

Recent Objectives

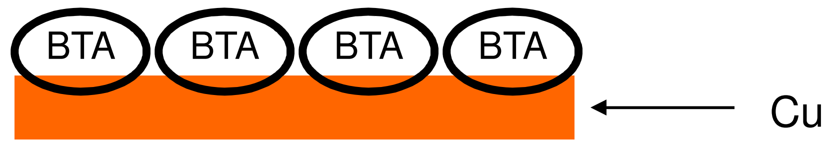
- **Current Studies Focus on:**
  - **Studying ECMP using:**
    - **$KPO_3 – H_3PO_4$ / BTA electrolyte**
    - **ECMP tool to determine:**
      - **Removal rates**
      - **Planarization capabilities**
  - **Using microfluidics to study BTA adsorption/desorption**
- **Experimental Parameters**
  - **pH**
    - **Range 0 – 10**
  - **BTA Concentration**
    - **Range 0- 0.01 M**
  - **Mass Transfer**
- **Characterization**
  - **Electrochemical Impedance Spectroscopy (EIS)**
  - **Linear Sweep Voltametry (LSV)**
  - **Cyclic Voltametry (CV)**
  - **Profilometry**

EHS Impact/ Metrics

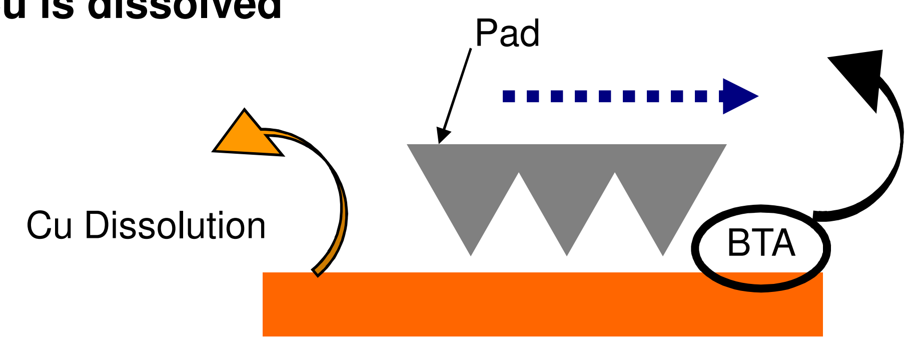
- Environmental Health and Safety (EHS) impact of Electrochemical Planarization Technologies
  - Eliminating need for abrasive particles in electrolyte
    - Particles make waste difficult to treat
  - Possibly eliminating the use of strong oxidizing agents in electrolytes
    - Electrolytes without these oxidizing are less toxic and easier to treat
  - Potential reduction in electrolyte volume
    - Reduce waste generation

Proposed eCMP Mechanism Utilizing BTA

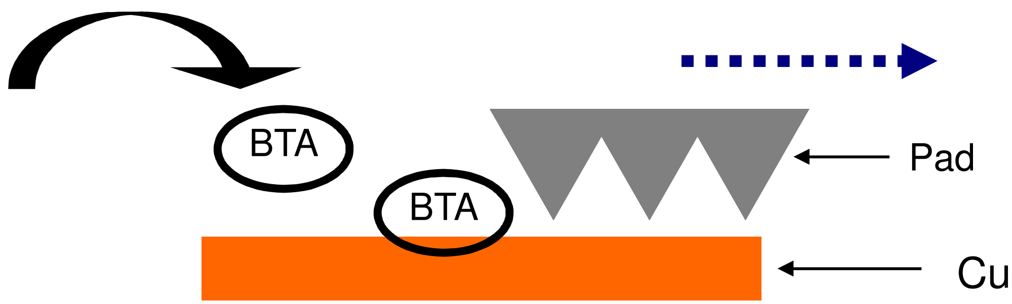
1. **BTA adheres to surface**
   – **Forms BTA-Cu complex**



2. **Pad mechanically removes Protective BTA layer**
   – **Exposed Cu is dissolved**



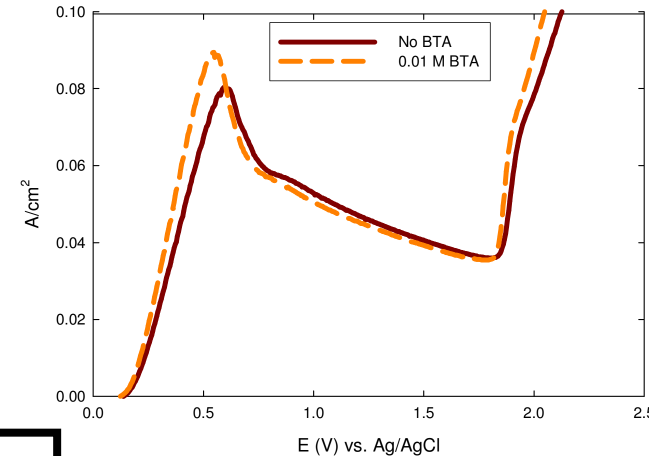
3. **BTA re-attaches to protect new CU surface**



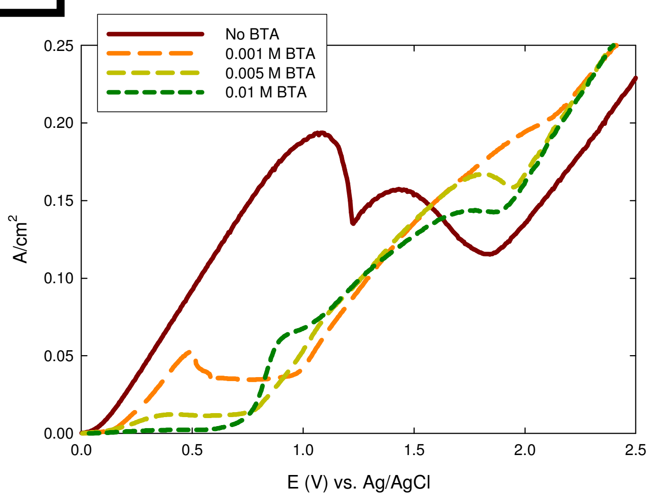
Results of BTA Inhibitor Study

- **Effect of pH and Concentration**
  - **Scan rate 5 mV/s – RT – 100 RPM**
    - **pH 0 –** BTA shows no passivation effect
    - **pH 2 –** Even at lowest concentration (0.001 M) , BTA demonstrates significant passivation
    - **pH 7 –** BTA has little effect compared to base solution due to the nature of oxide formation at high pH's

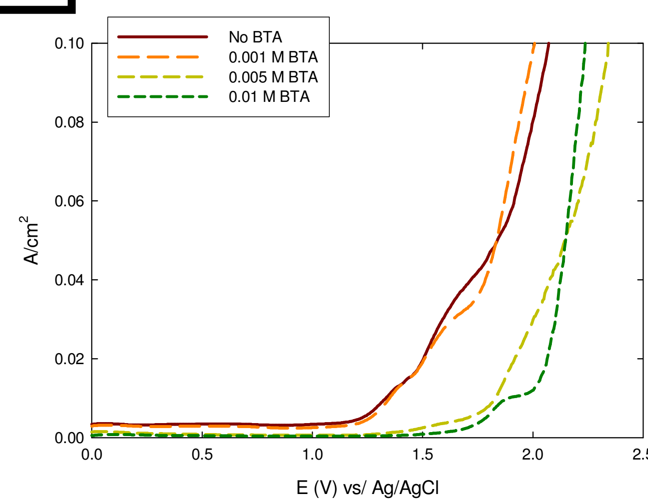
pH 0



pH 2



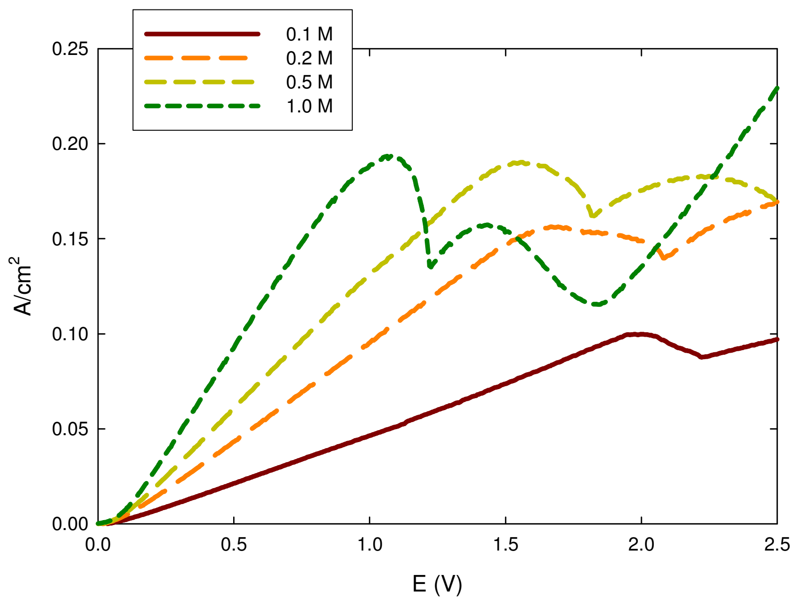
pH 7



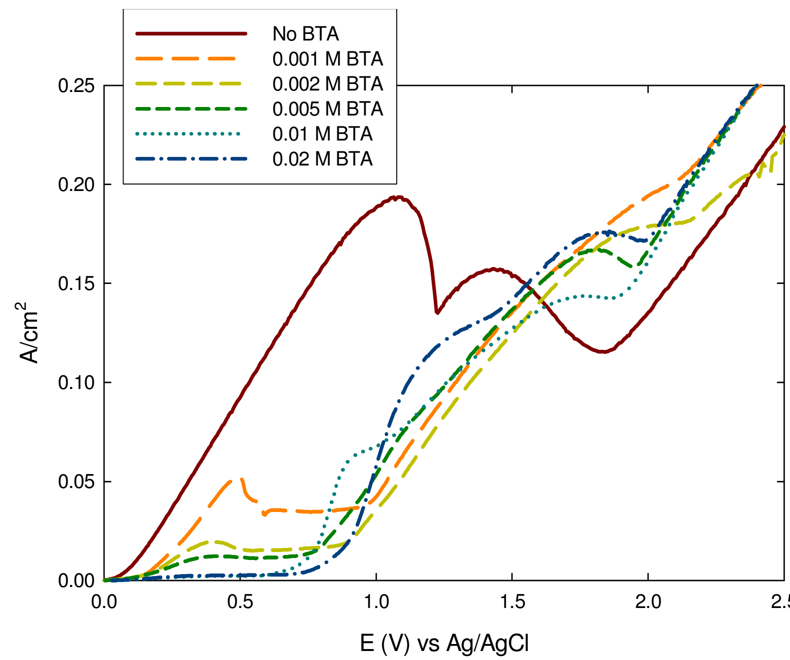
pH 2 Optimization

- Electrolyte molarity is important when considering IR drop
  - Above 1 M, no change in polarization curve
  - 1 M chosen as appropriate molarity for electrolyte
- Various BTA concentrations of 1 M pH 2
  - Good operating voltage between 0.5 – 1.0 V, before BTA loses passivation effect

pH 2 with different molarities: 0.1 M to 1.0 M



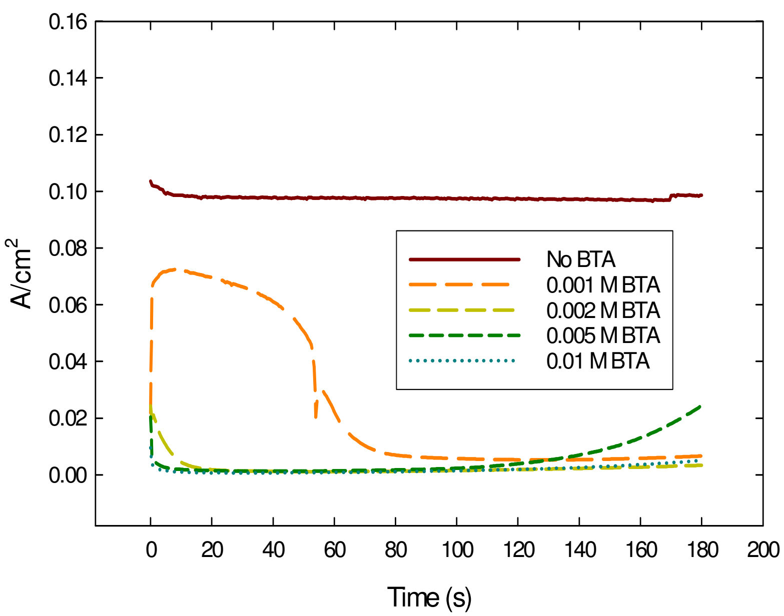
pH 2 with different BTA concentrations: 0.001 M to 0.02 M



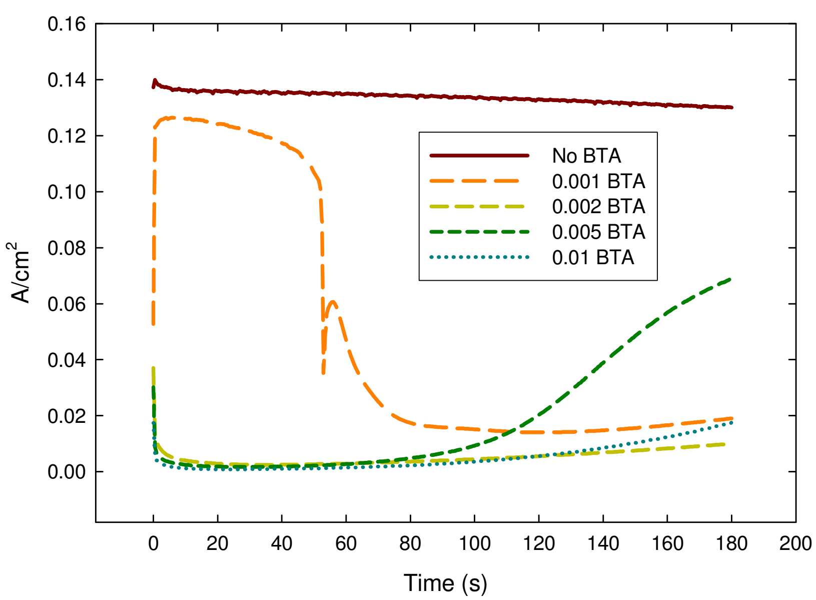
Chronoamperometry

- Gives insight into BTA film stability over time scales appropriate for ECMP
- Applied voltages are vs. Ag/AgCl reference performed on RDE

0.5 V for 180s



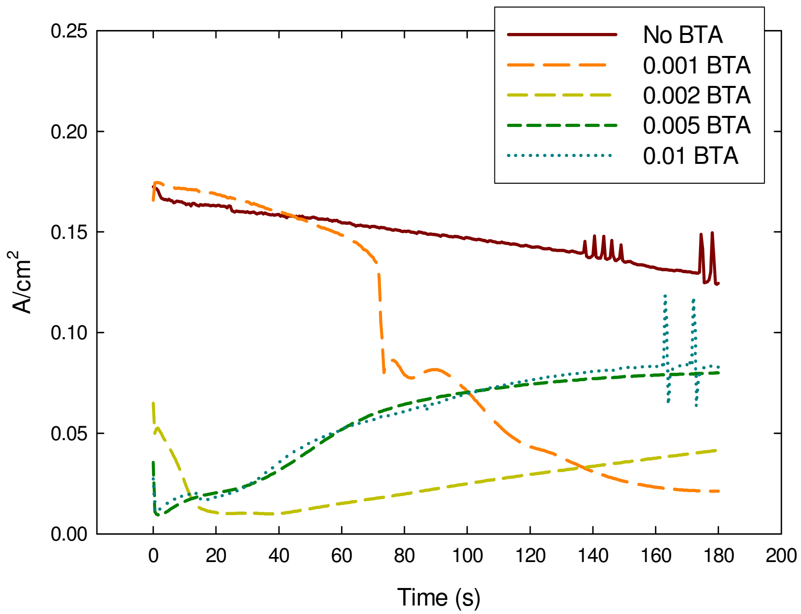
0.7 V for 180s



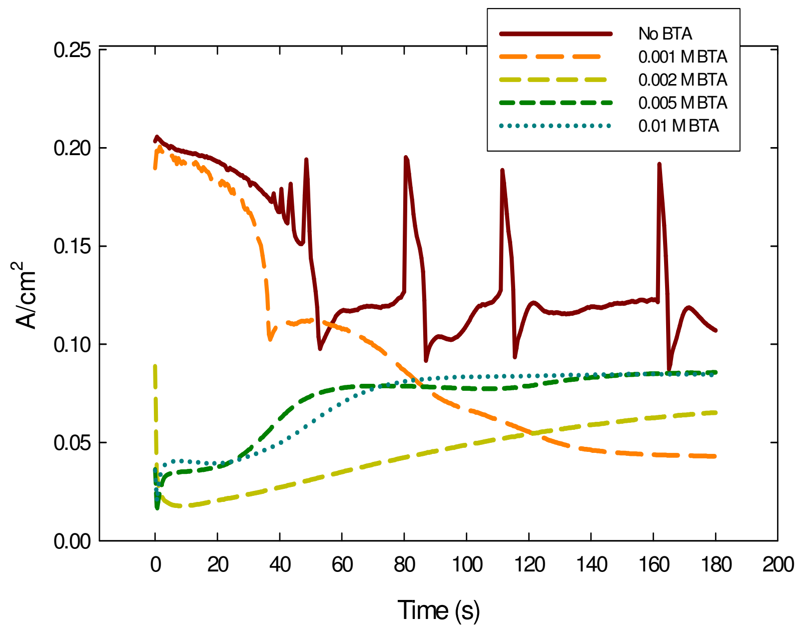
Chronoamperometry

- High applied voltages
  - base solution is not stable
  - BTA has less passivation effect
- Applied voltages are vs. Ag/AgCl reference performed on RDE

0.9 V for 180s



1.0 V for 180s

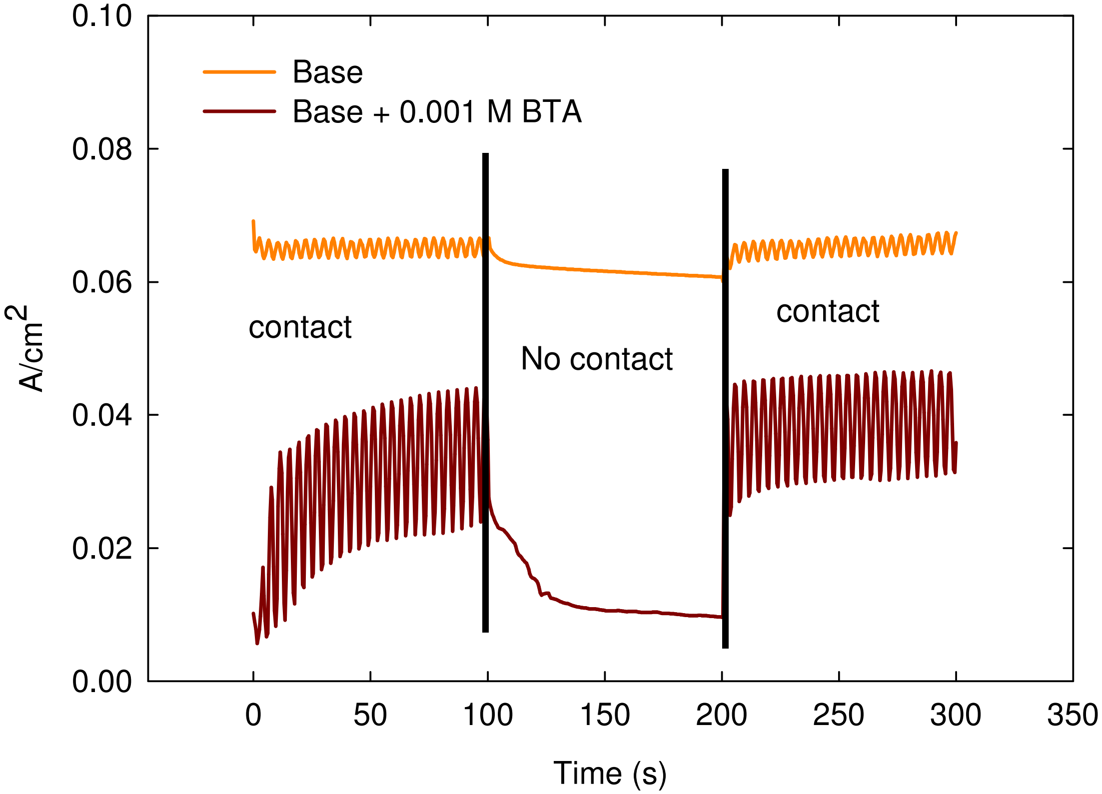


Contact vs. No Contact

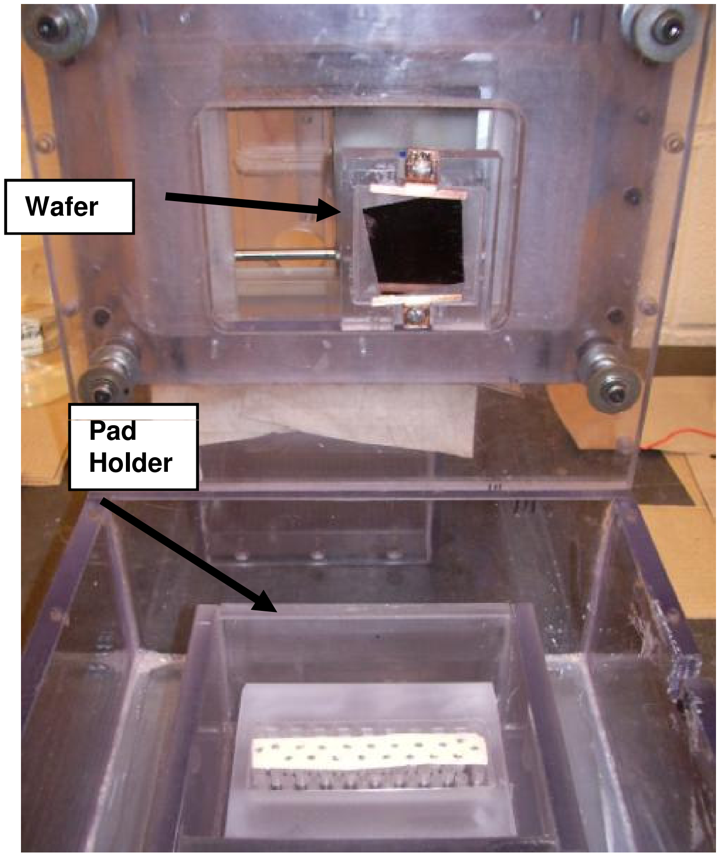
- **Using RDE setup with pad**
  - **0.5 V vs Ag/AgCl**

•Current density decreases as BTA passivation increases when contact is stopped

•Little to no change in current density when No BTA is present



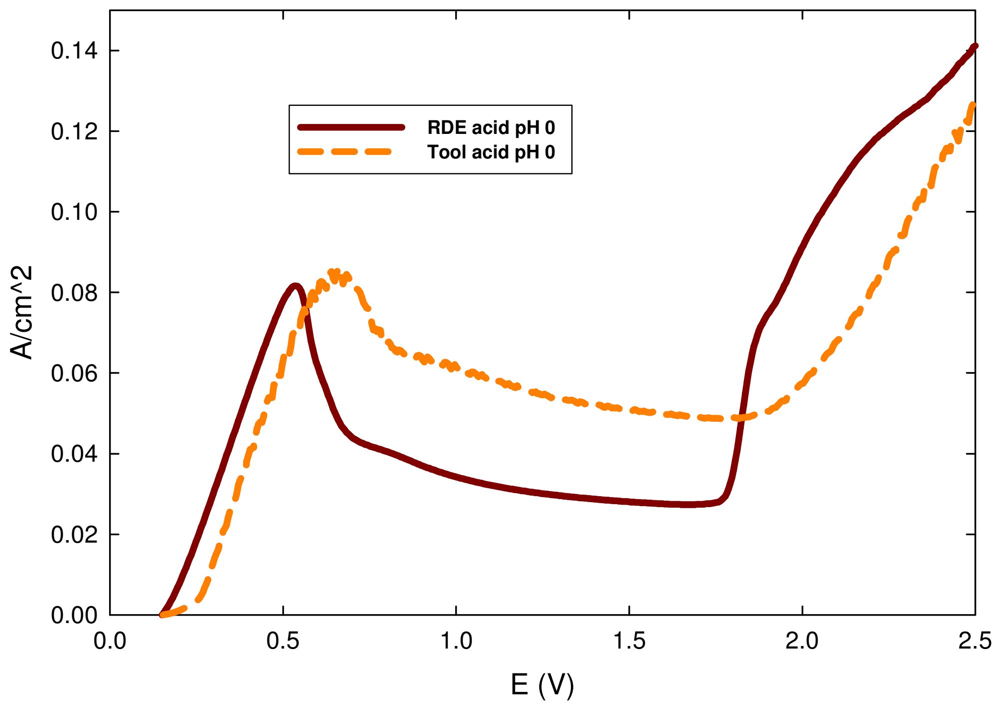
ECMP Tool



- **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
- **Major Characterization**
  - Metal-removal rates
  - Selectivity
  - Planarization efficiency

ECMP Tool

- **Good Agreement with RDE polarization curves**

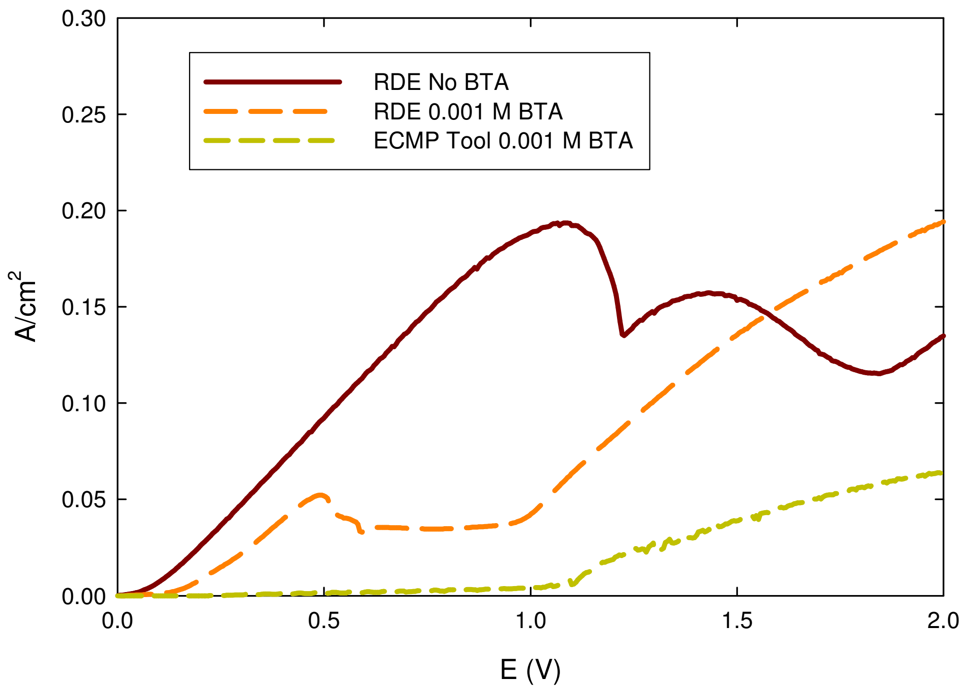


Anodic polarization curves of H_3PO_4 using e-CMP tool and RDE

ECMP Tool

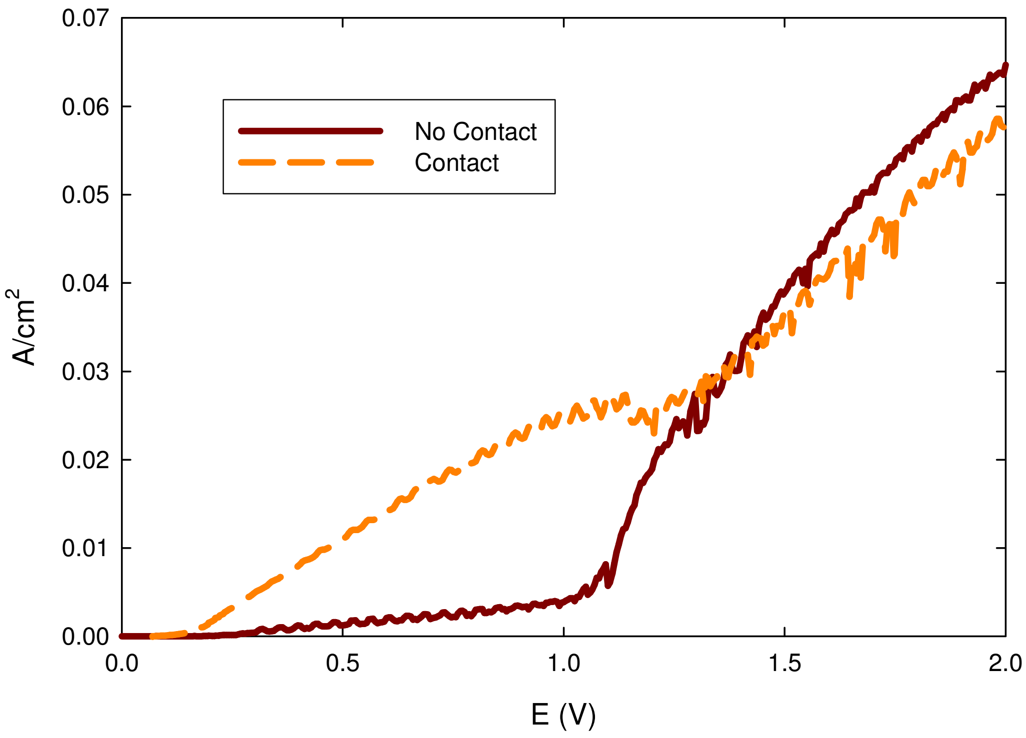
•**Polarization curves from RDE and ECMP Tool – pH 2**

- **0.001 M BTA both instruments**
- **RDE No BTA**



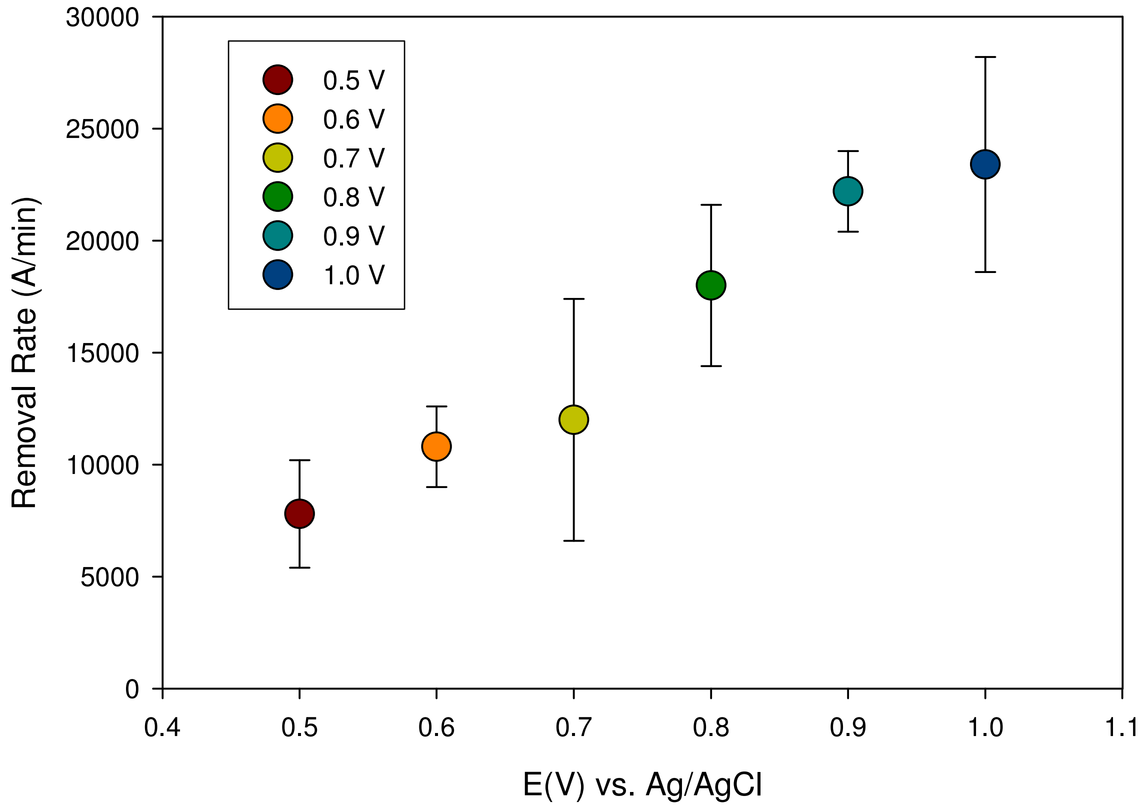
Polishing Results

- pH 2 - 0.001 M BTA → Pad Contact vs. No Pad Contact
  - **Suba™ 500 Pad**



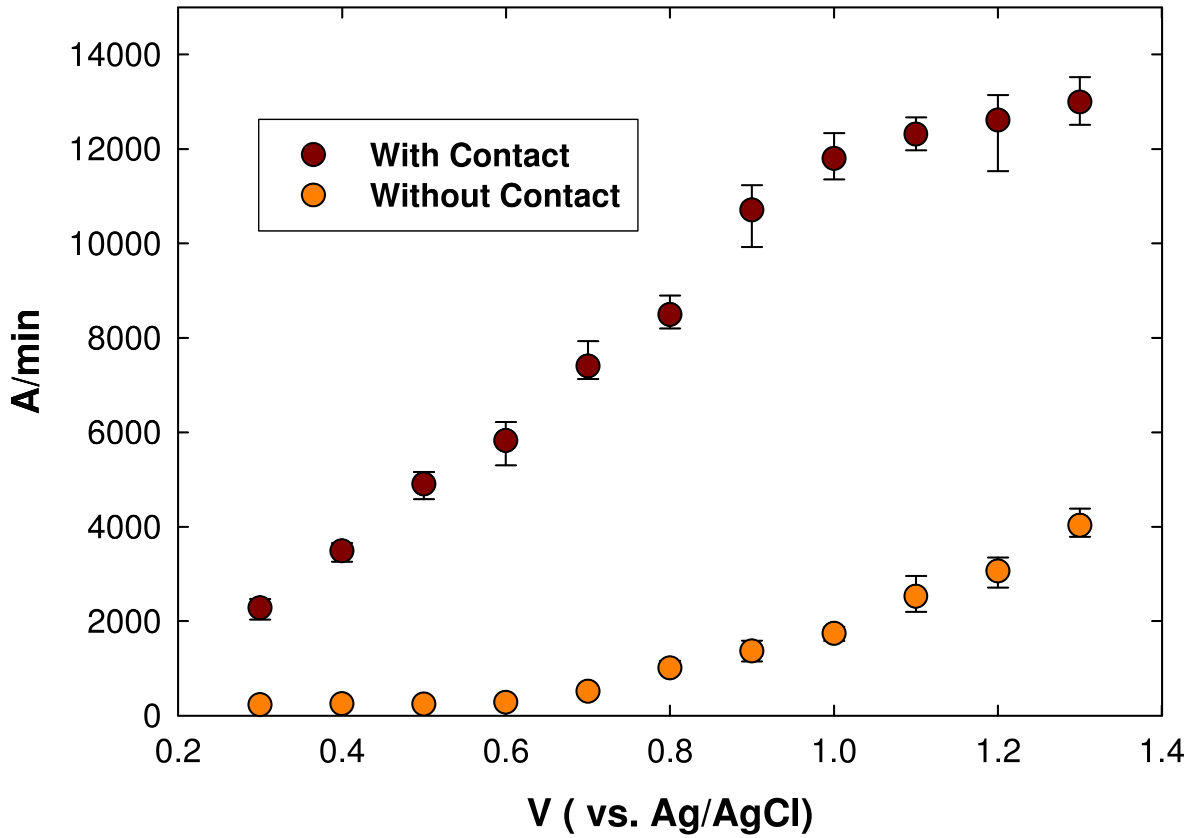
Removal Rates

- 1M pH 2, data from various experiments including:
  - **w/ out BTA, w & w/out contact**
  - **w/ 0.001 M BTA with contact**
- Removal rate calculated by weight loss
  - **Downforce ~1 psi**



Removal Rates

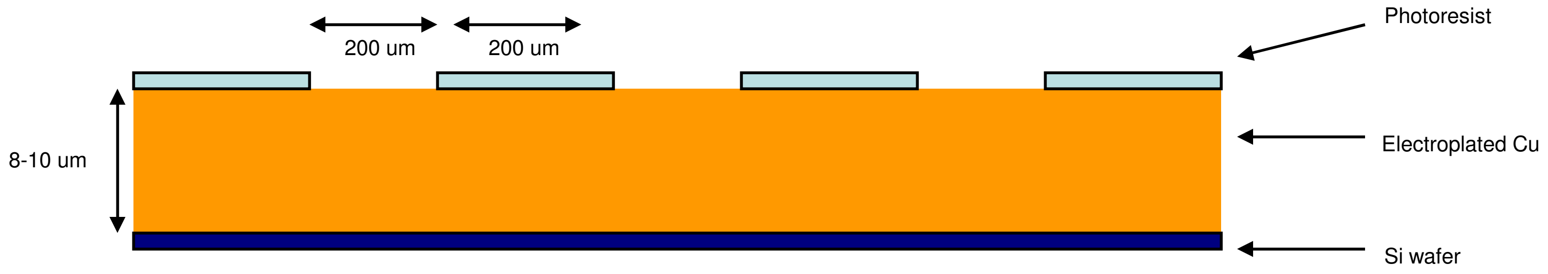
- 1M pH 2, 0.01 M BTA *
  - **With and without contact**
  - **Downforce: 0.5 psi**



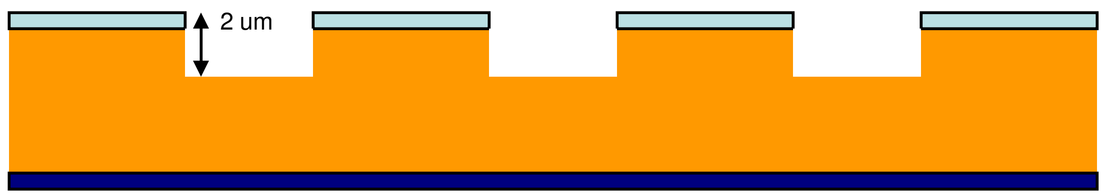
•Data aquired from research group in Tawain - TSMC

ECMP Test Structure

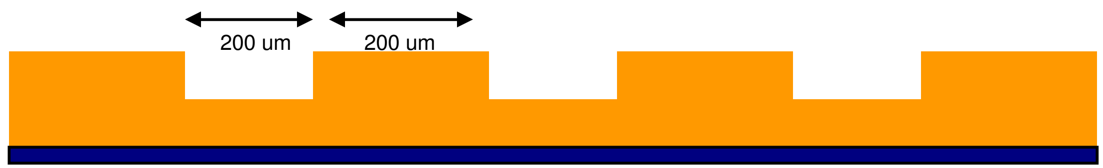
Step 1: Starting with a thick Cu layer (~8-10 um), a photoresist (SU-8) was spin coated (5-10 nm) and then lithography is used to pattern a structure with line spacing ~200 um



Step 2: After the pattern is made with SU-8, it is then electropolished in phosphoric acid operating in the limiting current range (~1.5 V vs. ref) for 200s for 2 um trenches (500s for 2.5-3 um trenches)



Step 3: To remove the photoresist, SU-8 developer was used. Exposure time was ~10s. Because the developer increased surface roughness, another electropolishing treatment is used post developer, to yield the final test structure. Trench heights can vary by using different electropolishing regimes.

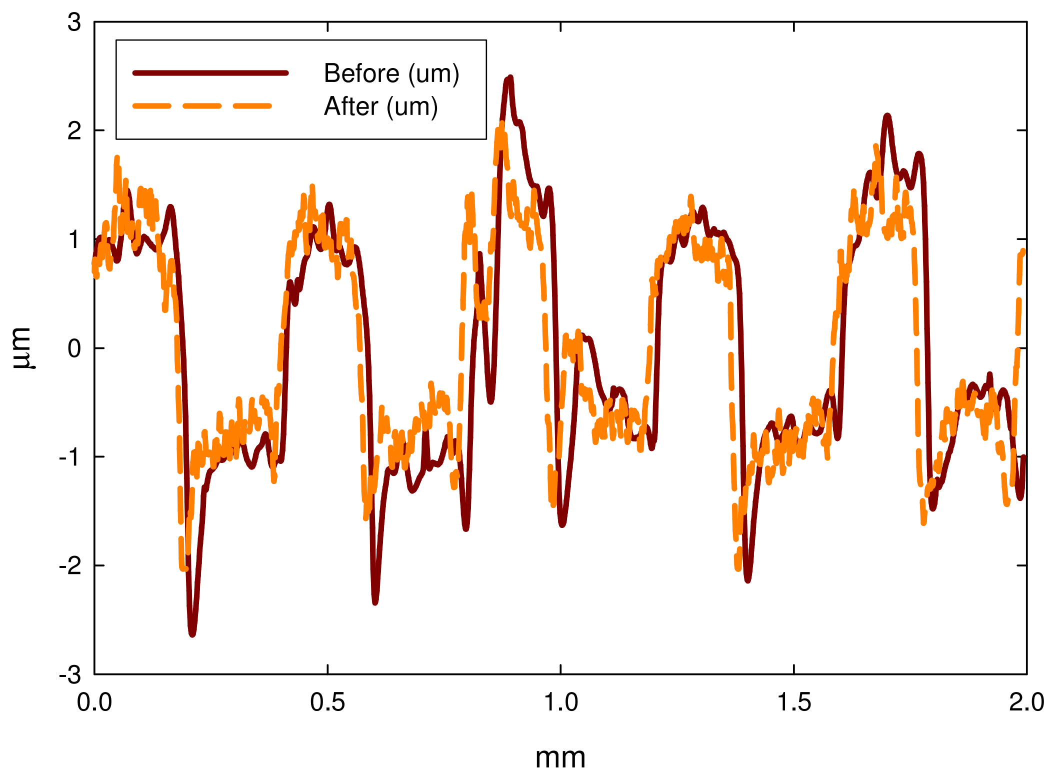


schematics not to scale

ECMP Planarization

- Control experiment showing NO planarization
- 1 M pH 2, No BTA, No Contact
- Treatment:
  - 0.5 V vs. Ag/AgCl
  - 300 s
  - No BTA

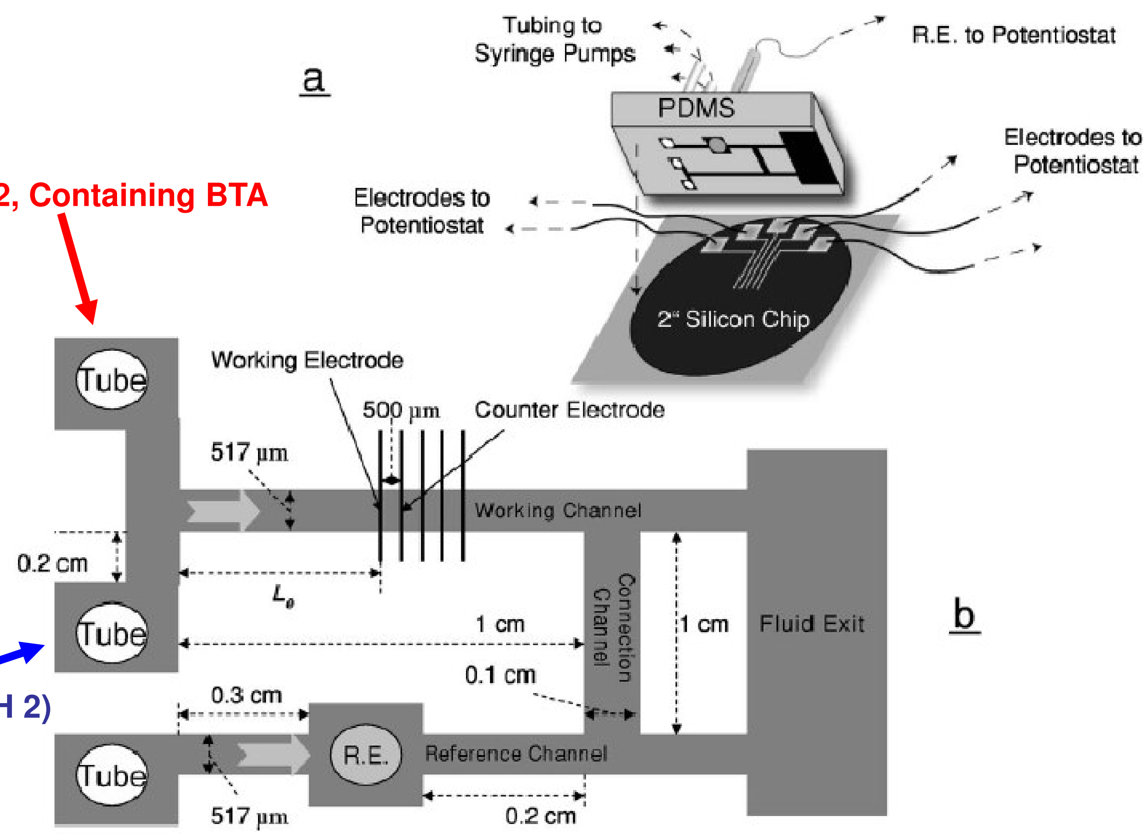
Currently working towards planarization capabilities with pad contact when BTA is present



Microfluidics

Microfluidic Device Setup[1]

- Allows quick change of electrolytes to study BTA adsorption/ desorption

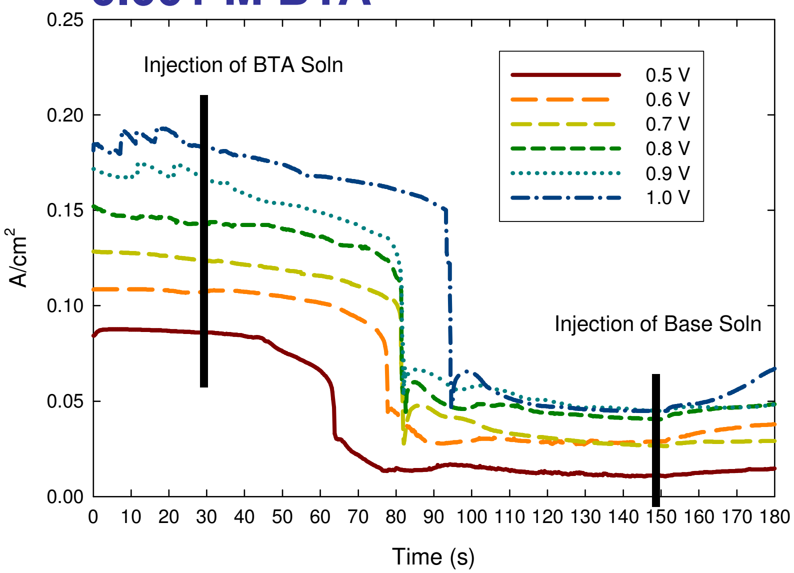


[1] Willey, M. J., A.C. West, A Microfluidic Device to Measure Electrode Response to Changes in Electrolyte Composition. *Electrochemical and Solid-State Letters,* **9** 7 E17-E21 2006

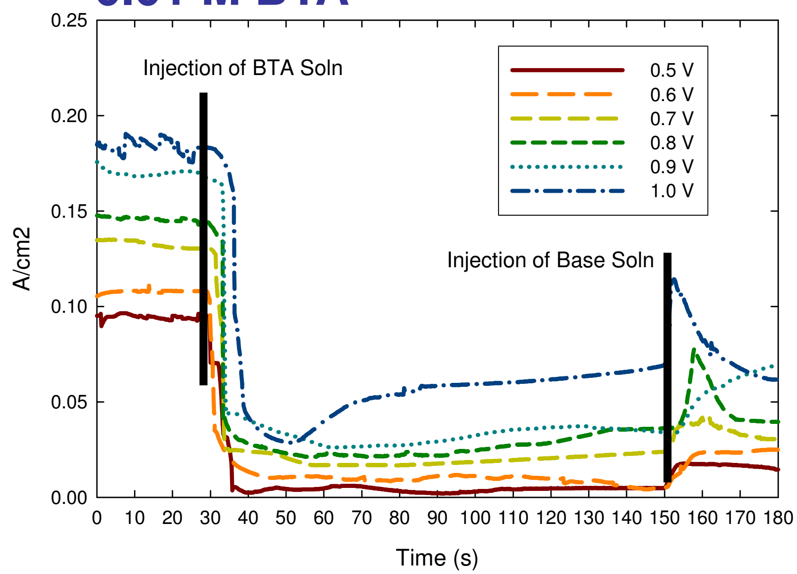
Microfluidics

- BTA adsorption in phosphate based electrolyte
- **0 - 30 sec**, Base Solution (1M pH 2),
- **30 – 150 sec**, BTA electrolyte (1M pH 2, 0.001 & 0.01 M BTA)
- **150 – 180 sec**, Base Solution (1M pH 2)

0.001 M BTA



0.01 M BTA



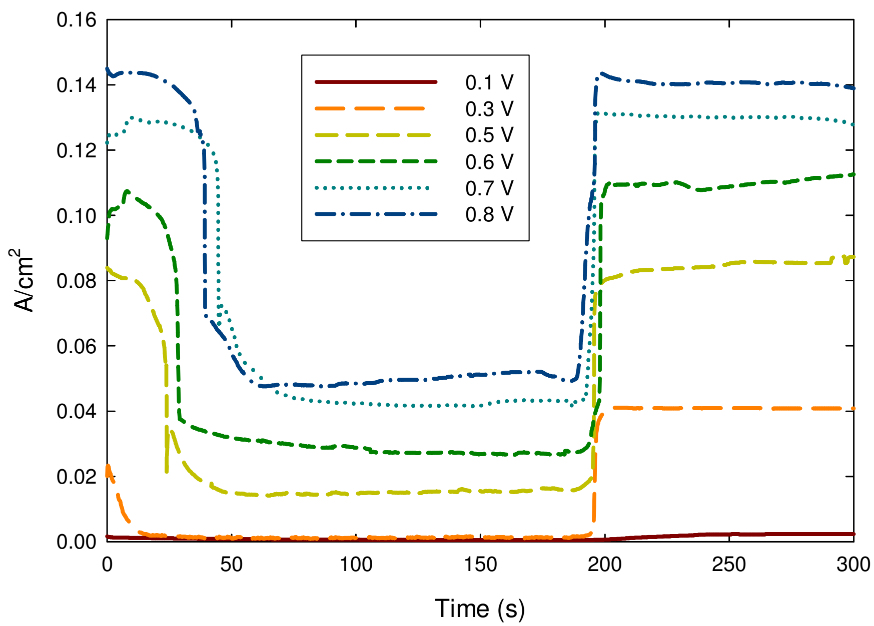
Microfluidics

•BTA desorption in phosphate based electrolyte

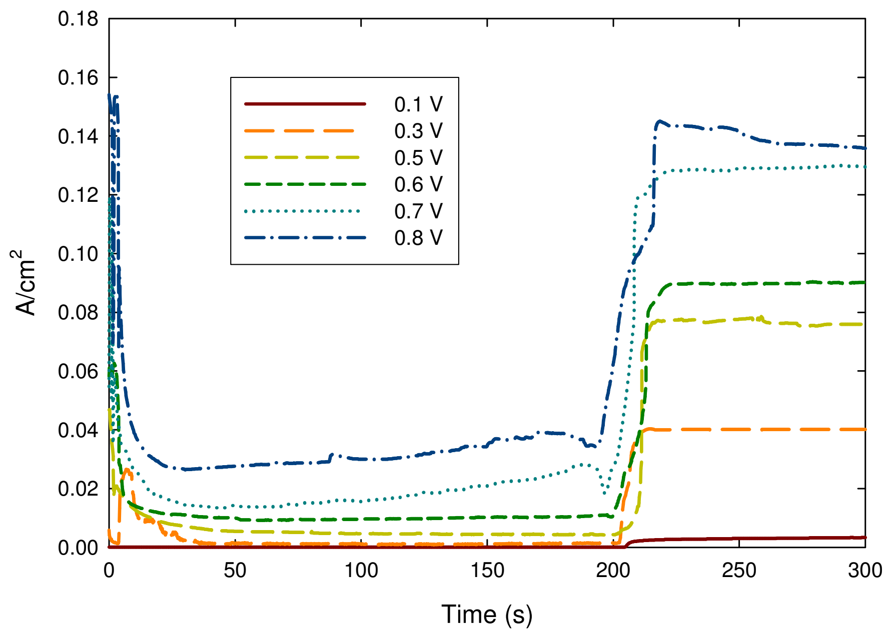
•**0 – 180 sec**, BTA electrolyte (1M pH 2, 0.001 & 0.01 M BTA)

•**180 – 300 sec**, Base Solution (1M pH 2)

0.001 M BTA



0.01 M BTA



Summary

- **Microfluidic Experiments**
  - Device working
  - Showing unique results concerning BTA adsorption/desorption
    - Important for inhibitor optimization to reduce appearance of microscratches on Cu surface
    - Important for cleaning

- **ECMP Experiments**
  - Device accuracy confirmed with RDE experiments
  - Removal rates established for operation window of applied potential (0.5 V to 1.0 V)
    - Above 1.0 V BTA loses passivation ability
  - Test structure build for characterizing planarization
    - Initial patterned structure testing has commenced

Future Work

- Finish up investigation of phosphate based electrolyte using ECMP tool
  - Acquire solid planarization data
- Begin investigation on polishing liner materials
  - Ru

- **Acknowledgments**
  - Alan West
  - Jeng-Yu Lin

  - Columbia University
  - SRC/Sematech
  - Cabot
  - Rohm & Haas
  - TSMC