Hydroxylamine Based Chemistries for Copper CMP

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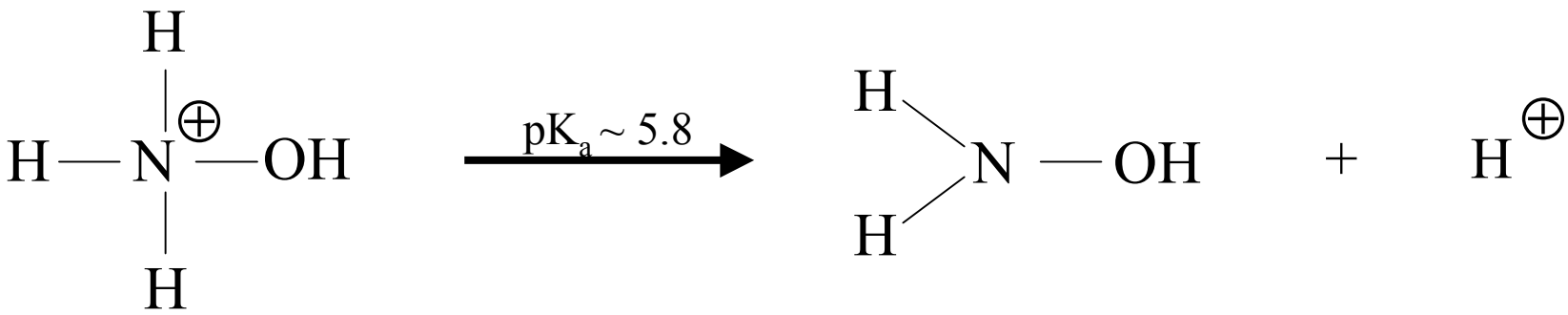
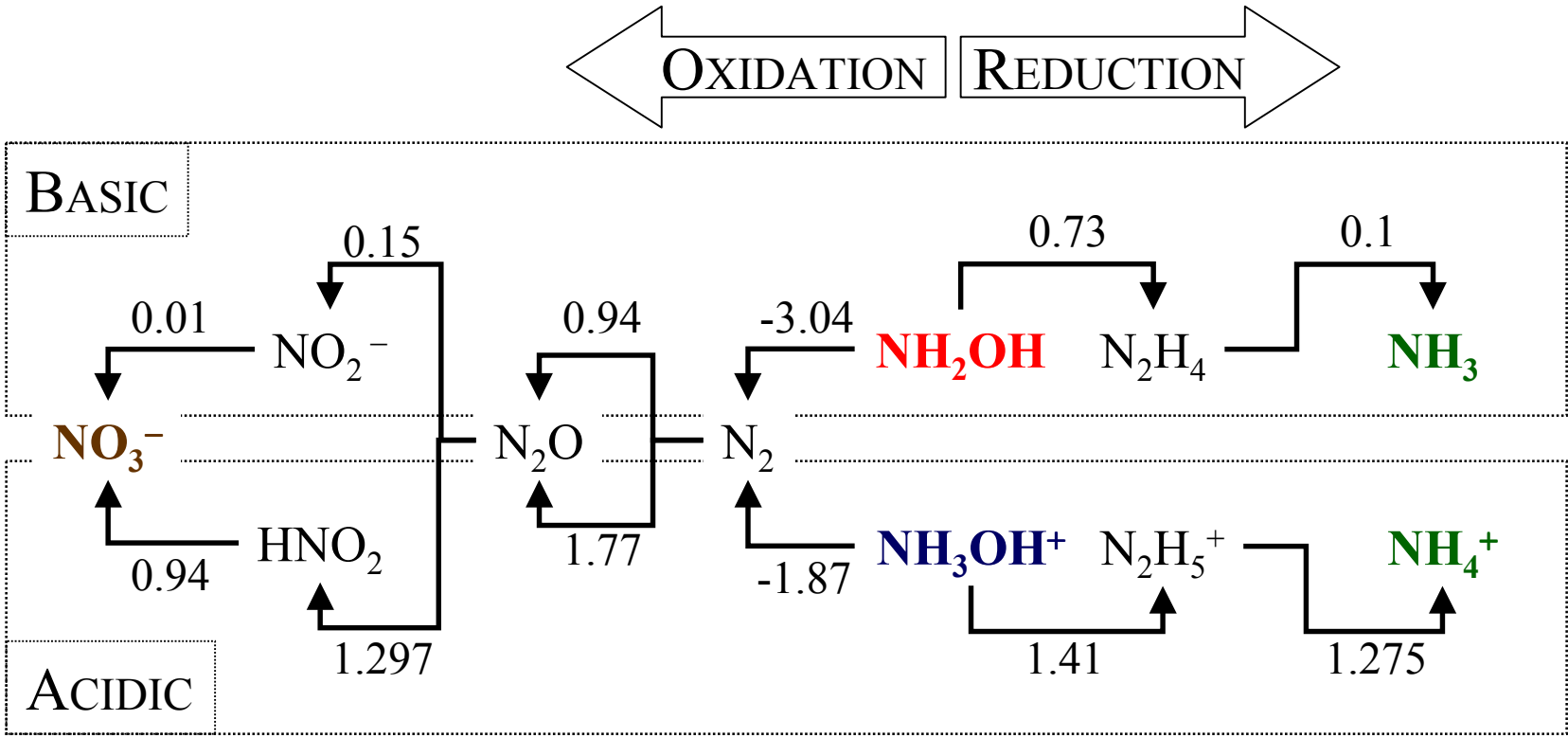
Hydroxylamine



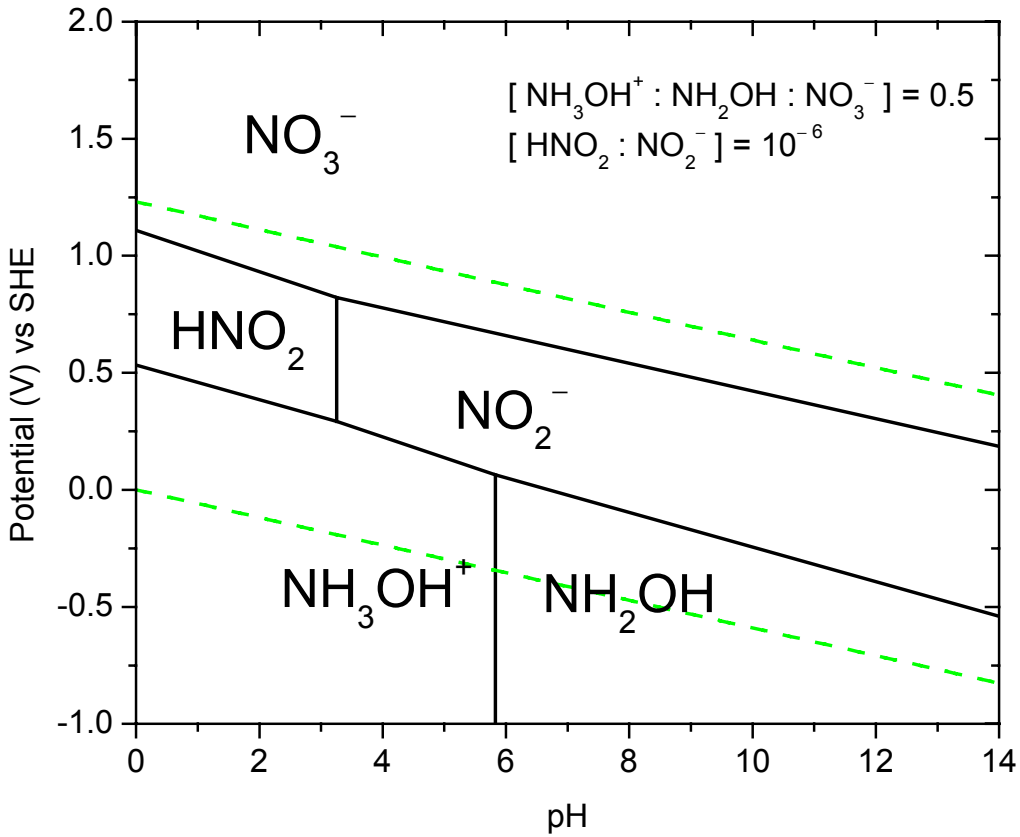
- Density of liquid (295K) : 1.11 ~ 1.13 g/cm^3
- Appearance: Colorless liquid
- Odor: Slightly ammoniacal
- Melting point: –10^{o}C (approximately)
- Solubility in water: All proportions
- Decomposes in the presence of heavy metals.

Electrochemistry of Hydroxylamine



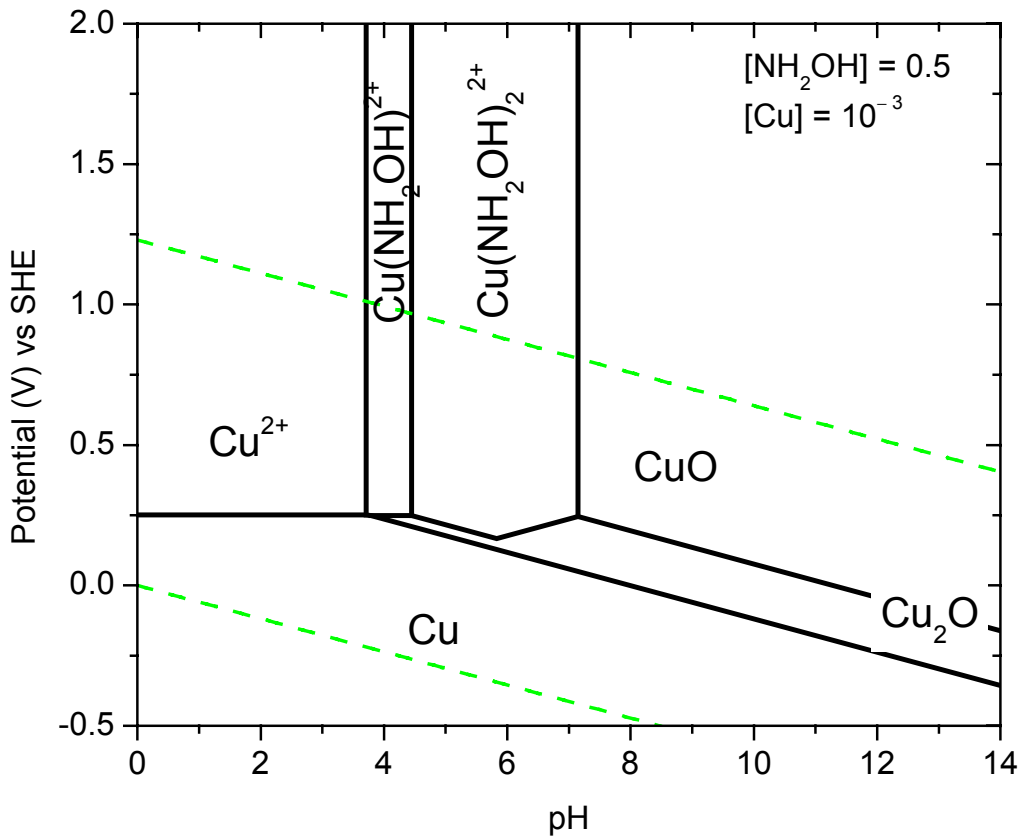
- Numbers are reduction potentials in volt(s).

Potential-pH Diagram of N-H_2O System

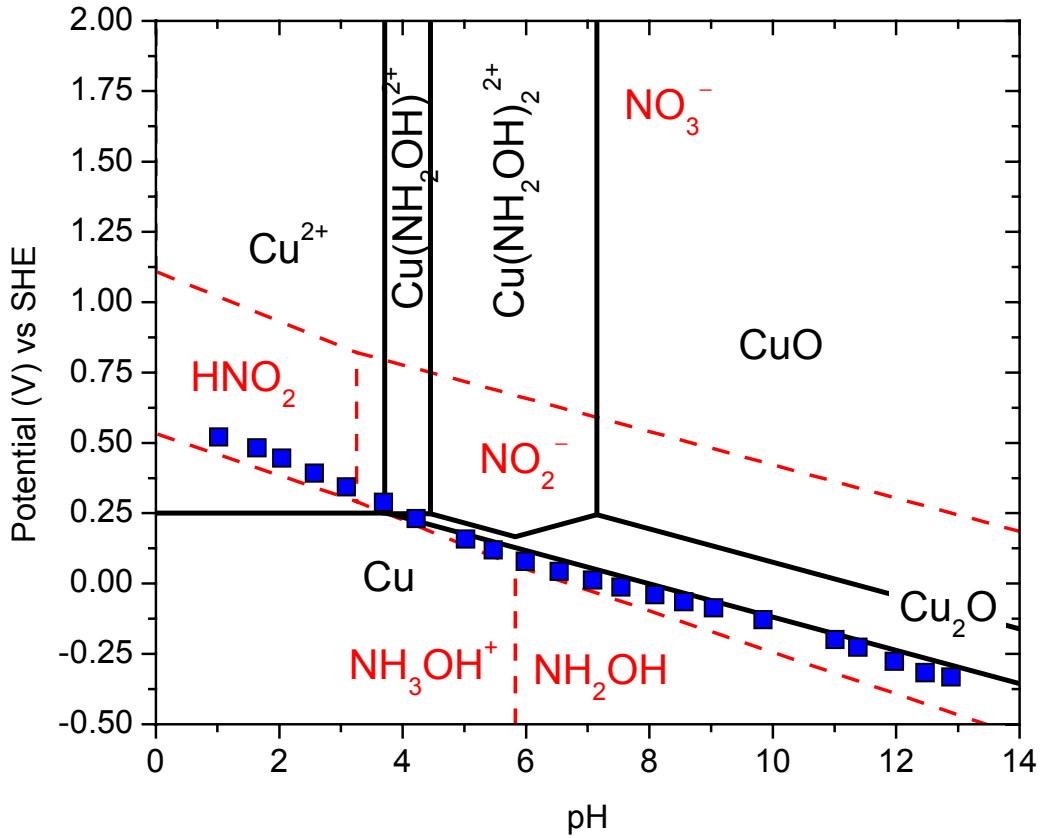


- Species excluded from the calculation: N_2, N_2O, NH_3, NH_4^+, N_2H_4, and $N_2H_5^+$

Potential-pH Diagram of Cu-NH_2OH-H_2O System



Potential-pH Diagrams



- Cu-NH_2OH-H_2O ([Cu] = 10^{-3}, [NH_2OH] = 0.5) superimpose with N-H_2O ([NH_2OH] = 0.5) diagram
- Redox measurements (■) of 0.5*M* NH_2OH + 10^{-3}*M* $CuSO_4$ solution

Research Objectives

- Characterize the removal of copper thin film in hydroxylamine based slurries using electrochemical techniques.

- Establish the mechanistic aspects of the removal process.

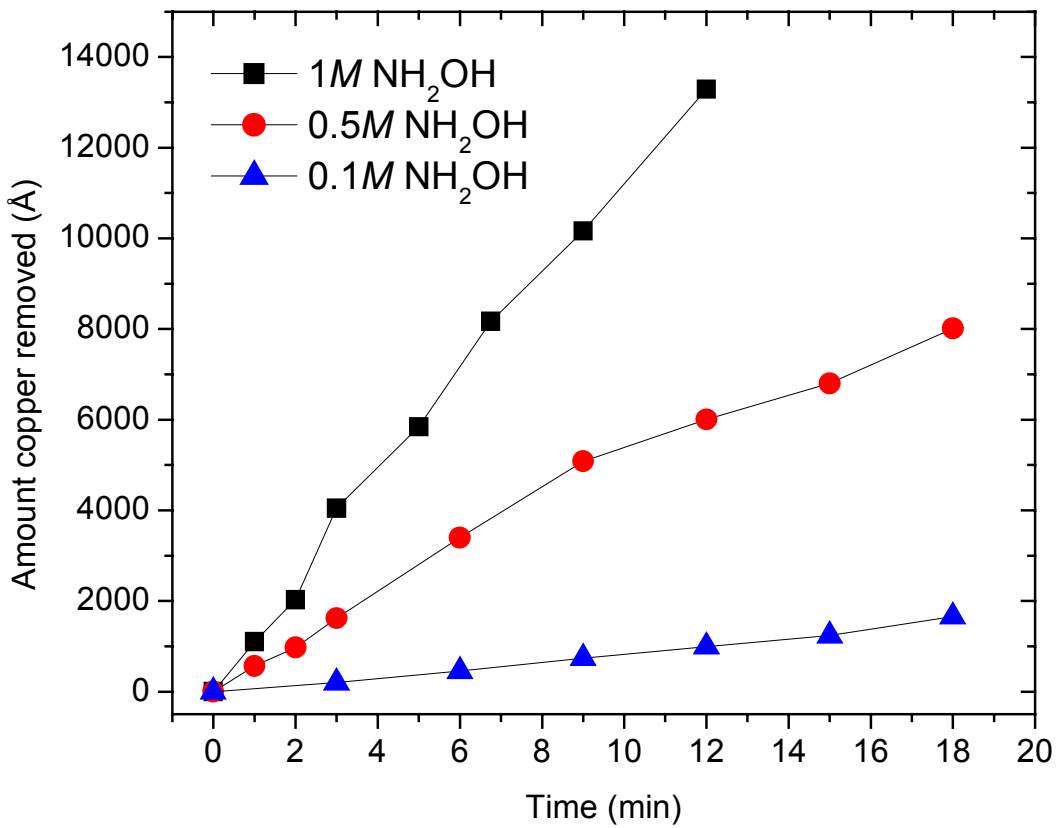
Materials

- Chemicals
  - Hydroxylamine (17 *M*)
  - Nitric acid (16 *M*)
  - Sulfuric acid (18 *M*)
  - DuPont Syton® colloidal SiO_2 particles (~ 70 nm)
- Metal coated blanket wafers
  - Electroplated copper (16 kÅ)

(Provided by EKC Technology, Inc.)

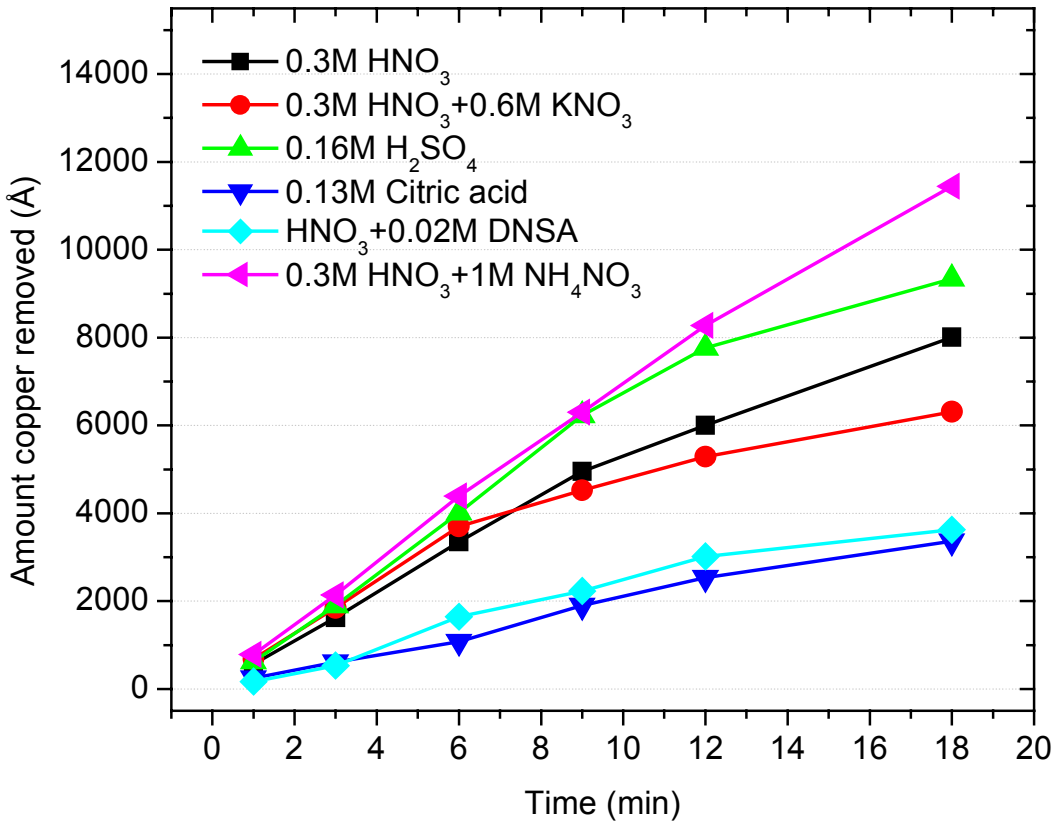
Etching of Copper in Hydroxylamine Based Solution & Slurry

Effect of Hydroxylamine Concentration on Static Etching



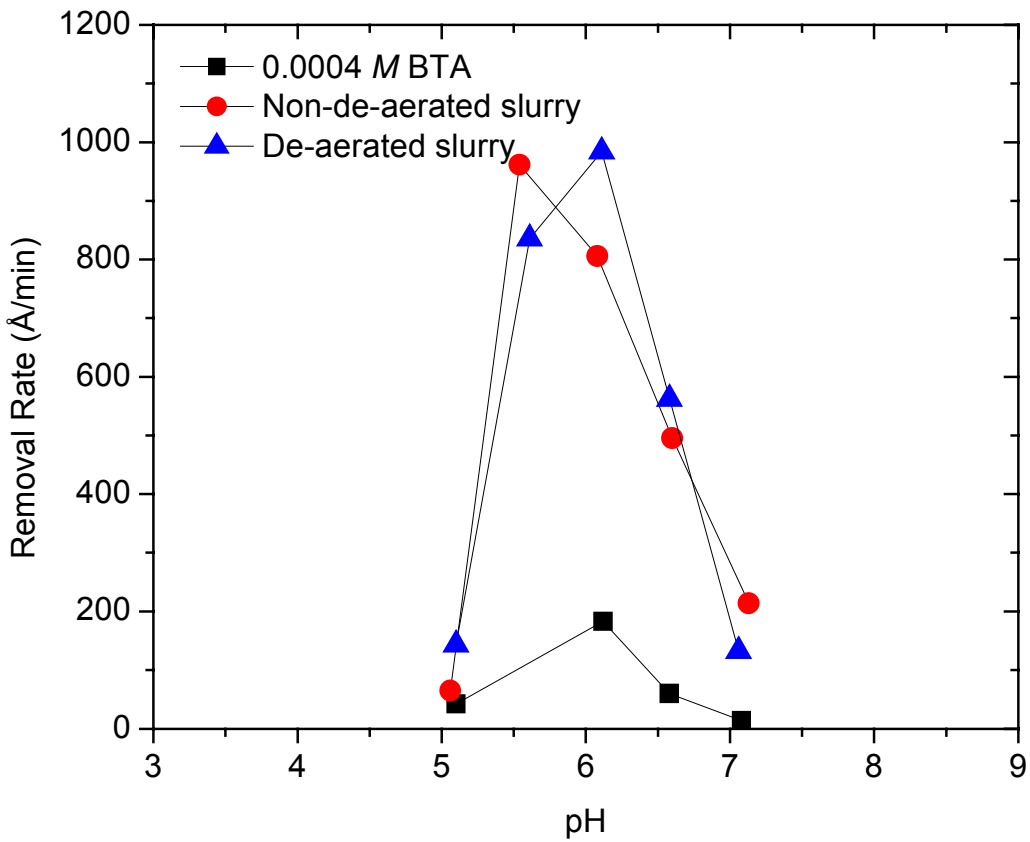
- Thickness of Cu etched as a function of time at different hydroxylamine concentrations at pH 6

Static Etching of Cu in Hydroxylamine with Different Additives



- 0.5*M* hydroxylamine with different additives at pH 6

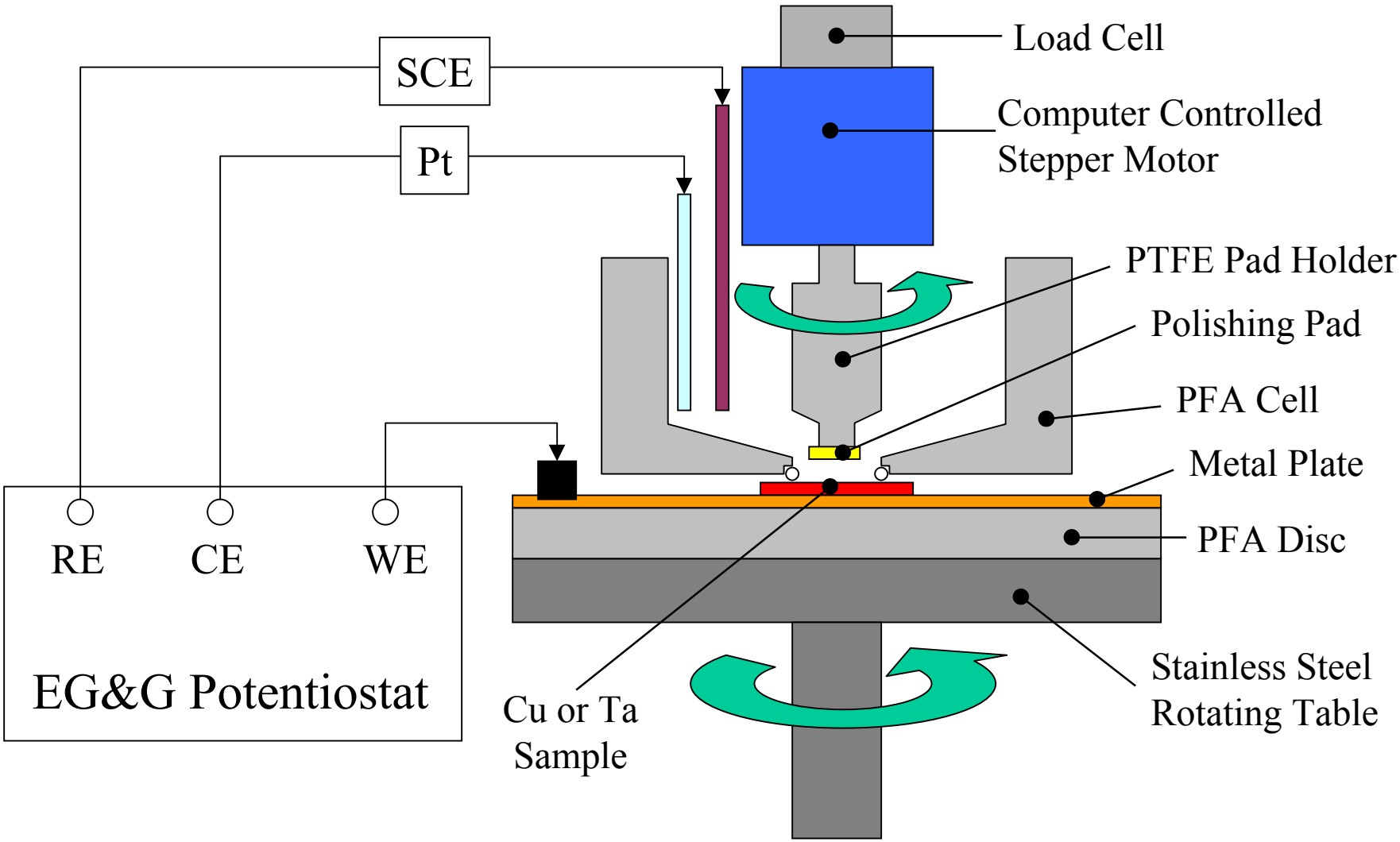
Static Etching of Cu in Hydroxylamine Chemistry



- Etching solution contains: 0.5 *M* hydroxylamine + 4% SiO_2
- In de-aerated slurry, 96% of O_2 was removed

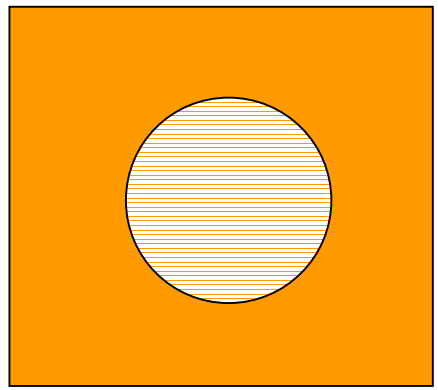
Copper Abrasion in Hydroxylamine Based Chemistries

Electrochemical Polishing Setup

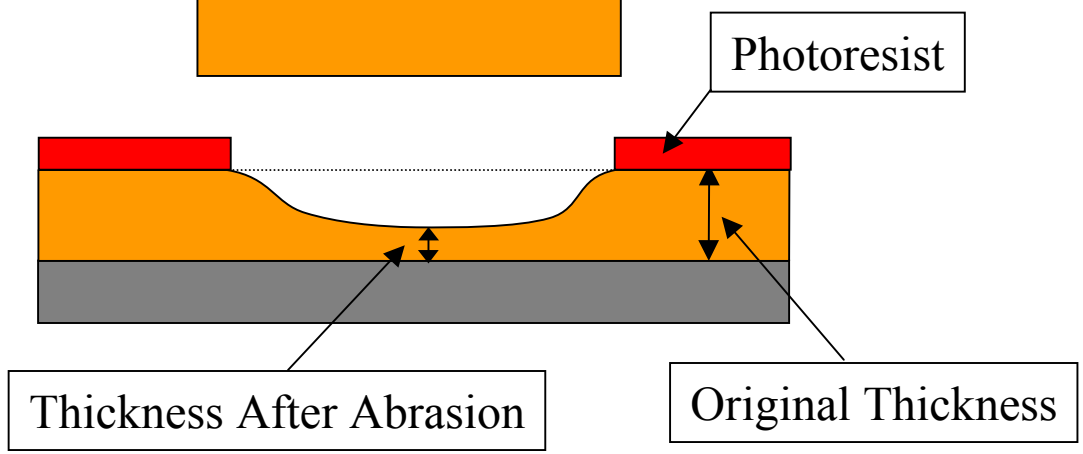


Physical Measurements

Top View

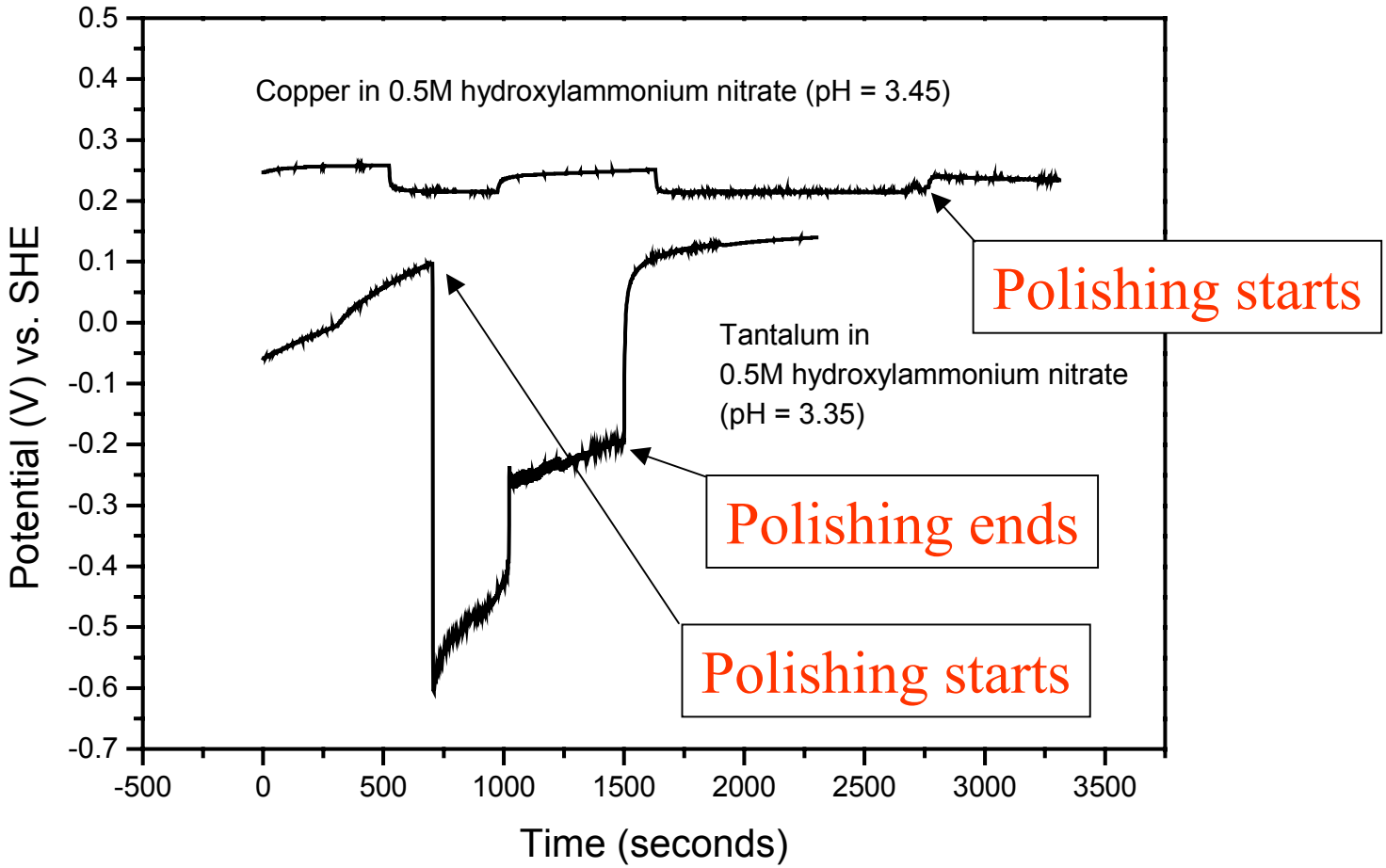


Cross-section View

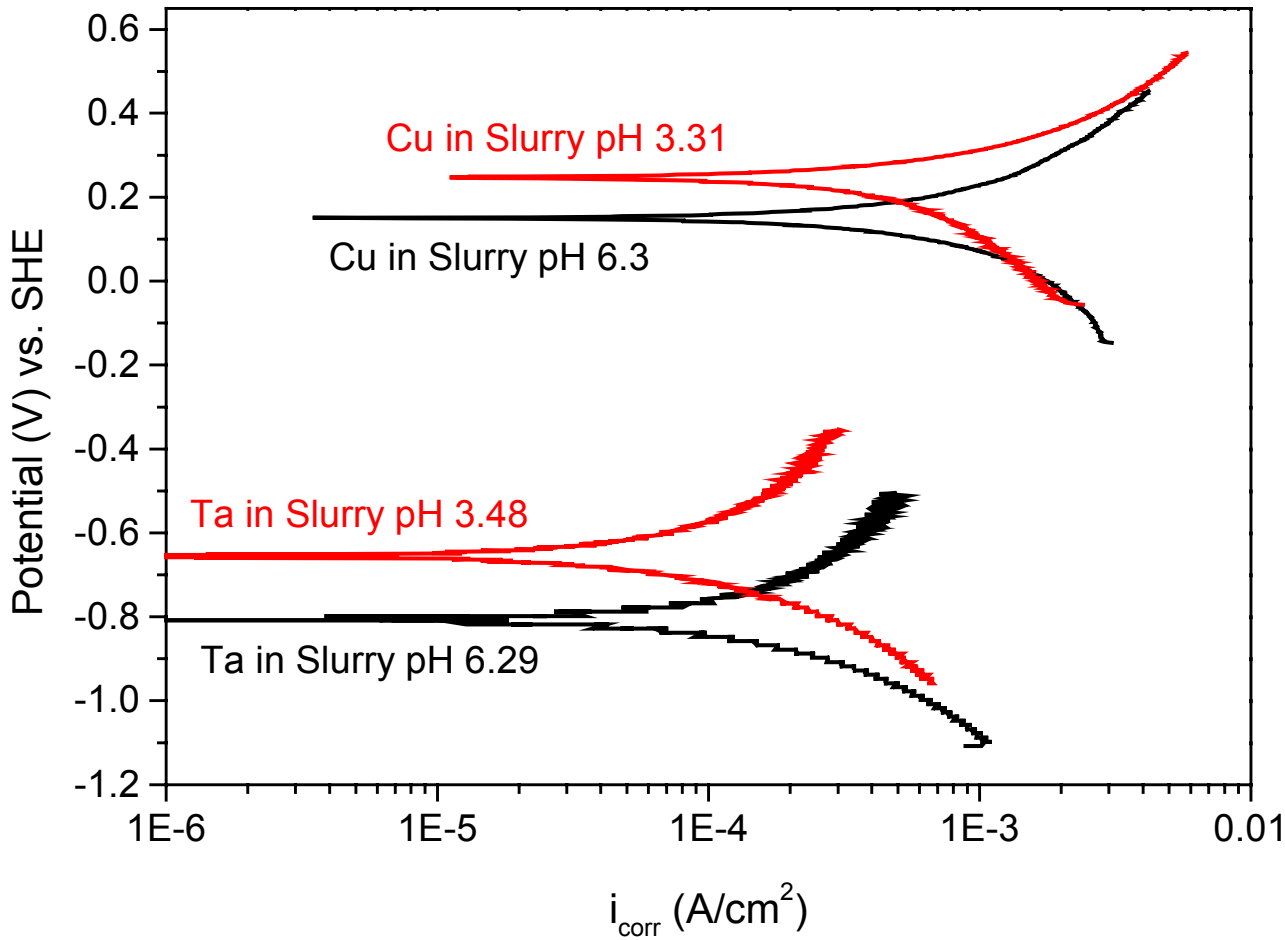


- Tencor α-2000 profilometer
- 4-point probe

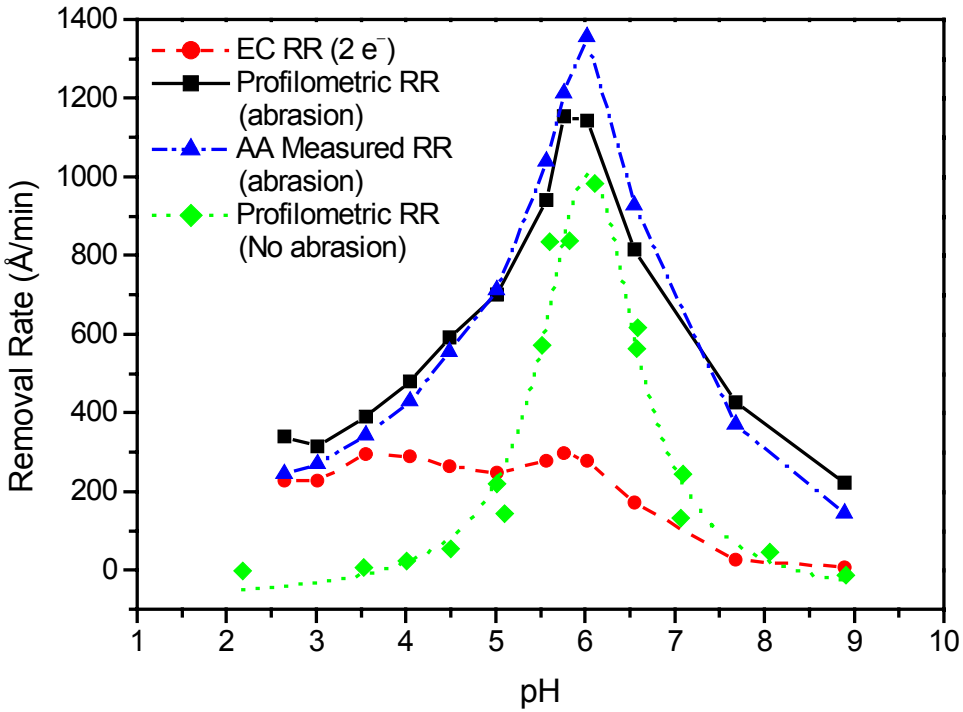
Open Circuit Potential as a Function of Time



Tafel Polarization Plots for Copper and Tantalum in Hydroxylamine Based Slurries

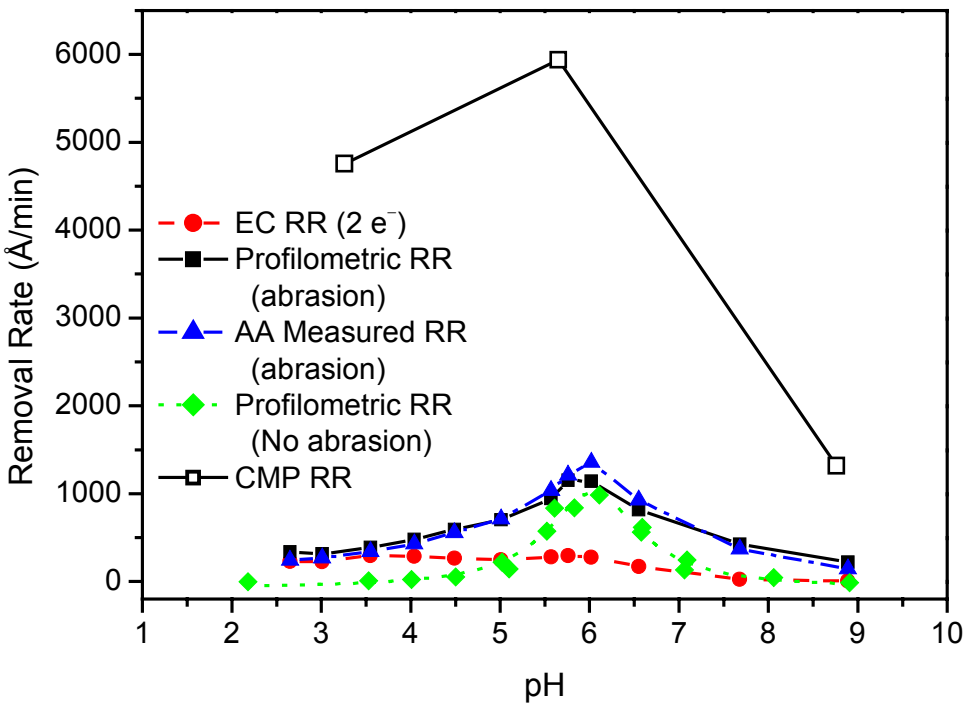


Copper Removal in 0.5*M* Hydroxylamine Based Slurries



- Slurry Chemistry
  - 0.5 *M* hydroxylamine
  - Nitric Acid (pH adjustments)
  - 4% Colloidal SiO_2 (~ 70 nm)
- Abrasion Parameters
  - IC1000 pad at 240 rpm
  - Copper wafer at 220 rpm
  - Pressure at ~28 psi
  - Photoresist covered surface to prevent static etching in the unabraded area

Small Scale Polisher vs. Actual CMP Tool



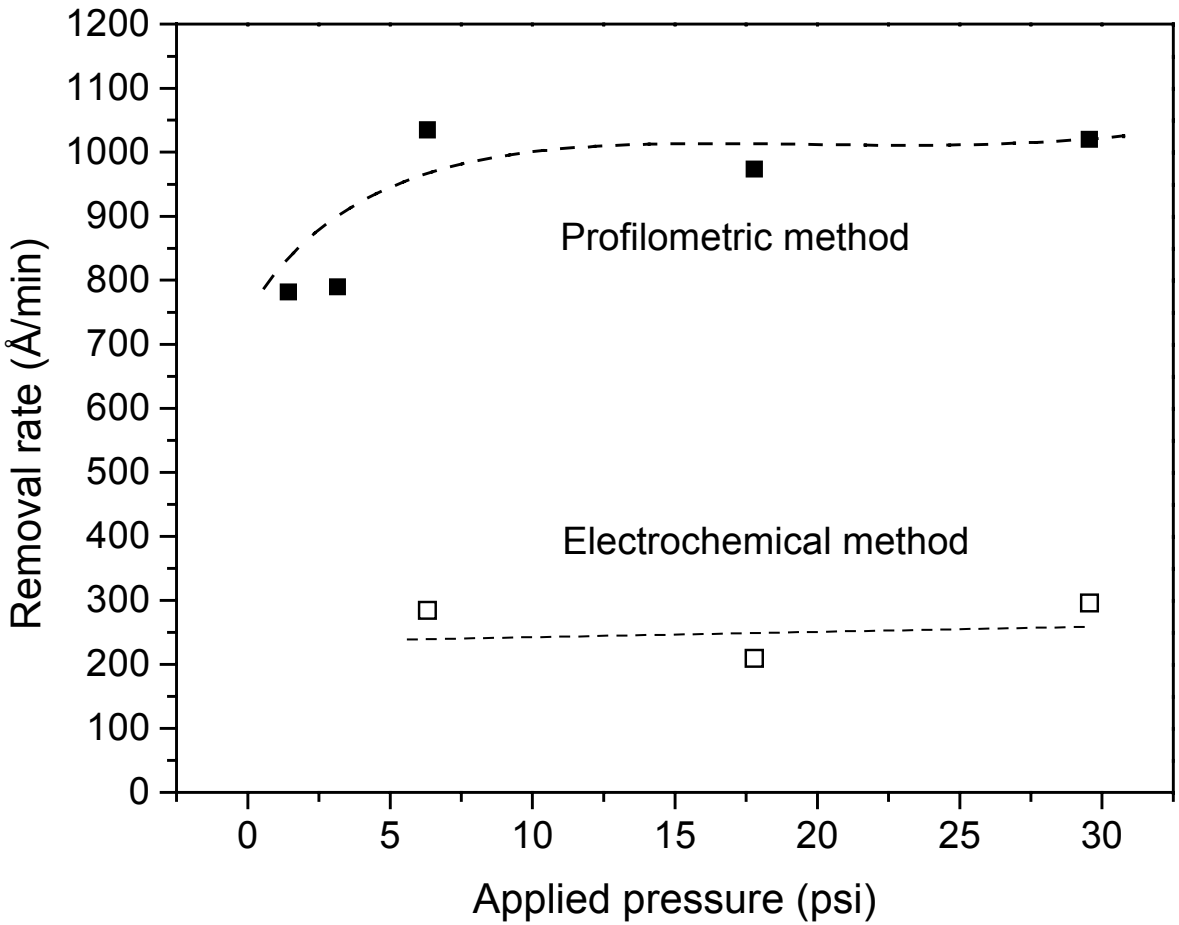
- Slurry Chemistry
  - 0.5 *M* hydroxylamine
  - Nitric Acid (pH adjustments)
  - 4% Colloidal SiO_2 (~ 70 nm)
- Abrasion Parameters
  - IC1000 pad at 240 rpm
  - Copper wafer at 220 rpm
  - Pressure at ~28 psi
  - Photoresist covered surface to prevent static etching in the unabraded area
- CMP Parameters
  - IPEC 472 Polisher
  - IC1400 pad at 75 rpm
  - 8" Copper wafer at 75 rpm
  - Pressure ~ 6 psi

Effect of BTA in Hydroxylamine Based Slurries on Copper Corrosion

- Electrochemical data obtained with copper electroplated films
- Slurry contained 0.0004 *M* BTA and 4% SiO_2 at pH 6.24

Conditions	Chemical Composition	βa (V)	βc (V)	i_{corr} (μA/cm^2)
No Abrasion	0.5*M* $NH_3OH^+NO_3^-$	0.314	-0.332	753
	0.5*M* $NH_3OH^+NO_3^-$ + BTA	0.278	-0.267	160
Abrasion	0.5*M* $NH_3OH^+NO_3^-$	0.333	-0.335	894
	0.5*M* $NH_3OH^+NO_3^-$ + BTA	0.306	-0.404	980

Copper Removal as a Function of Applied Pressure

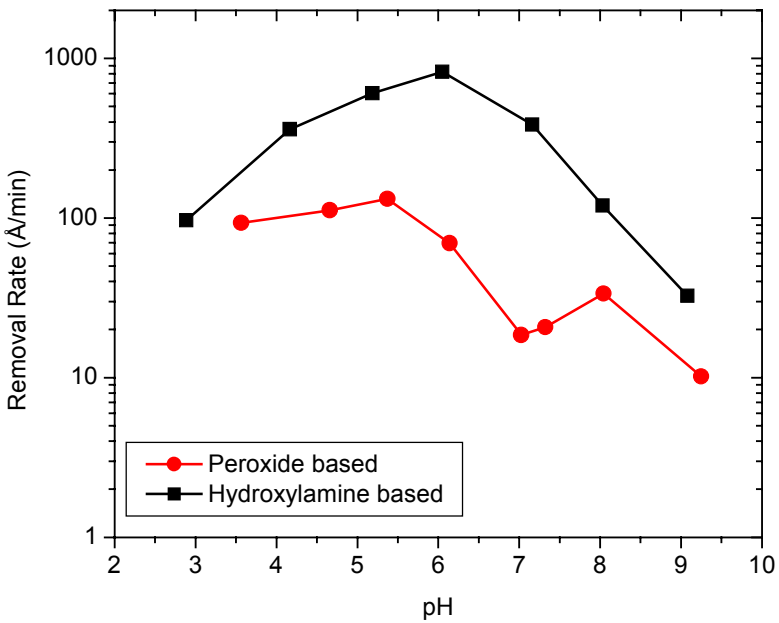


(0.5 *M* hydroxylamine based slurry at pH 6)

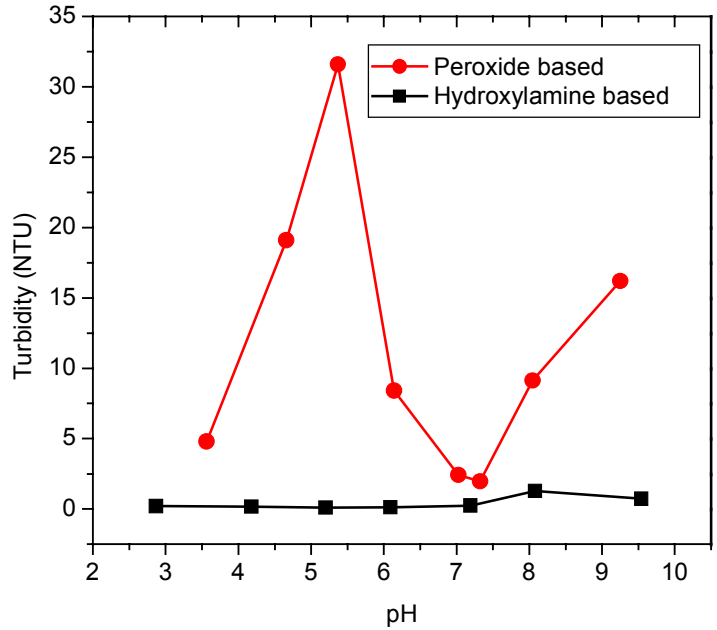
Copper Abrasion Using Fixed Abrasive Pad

Copper Abrasion in Peroxide and Hydroxylamine Based Chemistries

Removal Rates



Contamination Levels

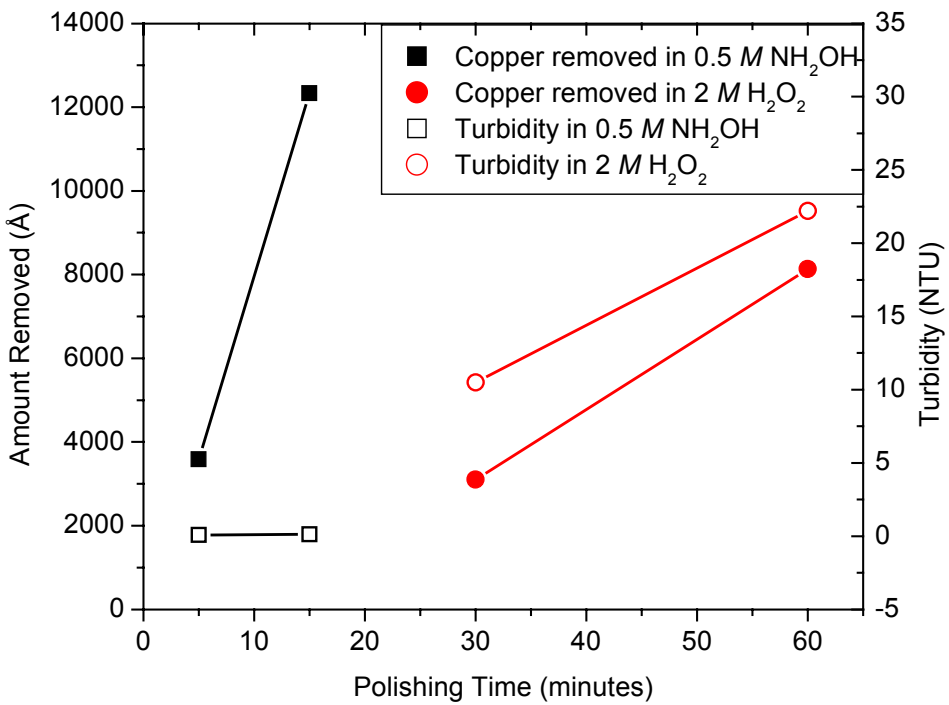


- Abrasion Time:
  - Peroxide: 60 minutes
  - Hydroxylamine: 15 to 60 minutes (depending on pH)

- Removal Rates:
  - Hydroxylamine based chemistry > peroxide based chemistry
- Contamination Levels:
  - Peroxide based chemistry > hydroxylamine based chemistry

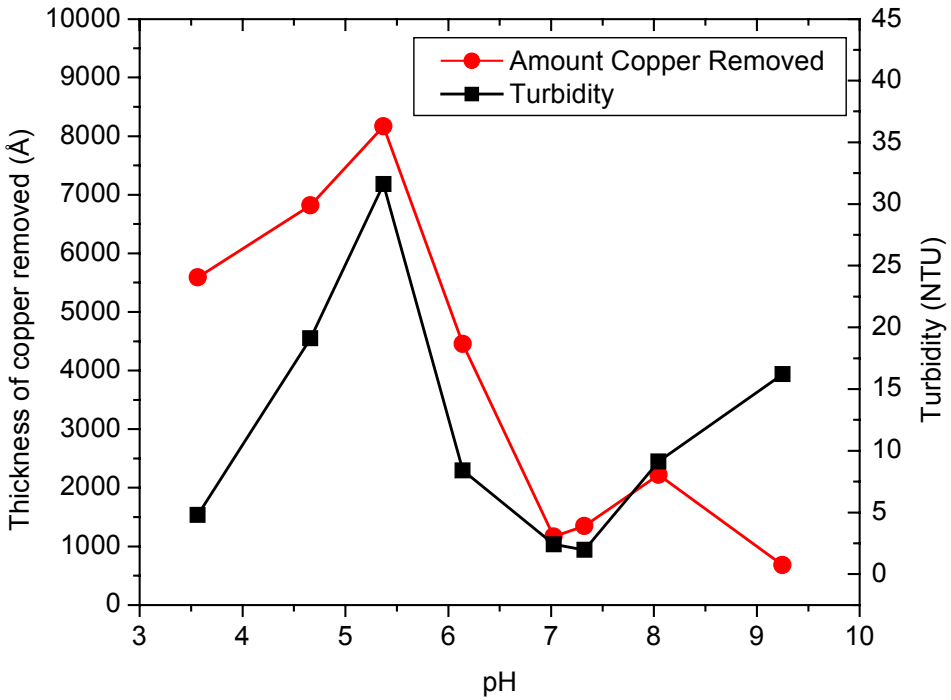
Copper Abrasion in Peroxide and Hydroxylamine Based Chemistries (continued)

pH ~ 6



- Hydroxylamine chemistry
  - Higher copper removal but low particulate generation
  - Copper actively dissolved
- Peroxide chemistry
  - Lower copper removal but higher particulate generation
  - Addition of 0.01*M* citric acid increase Cu removal rates from 120 to 760 Å/min and decrease turbidity from 10 to 3 NTU

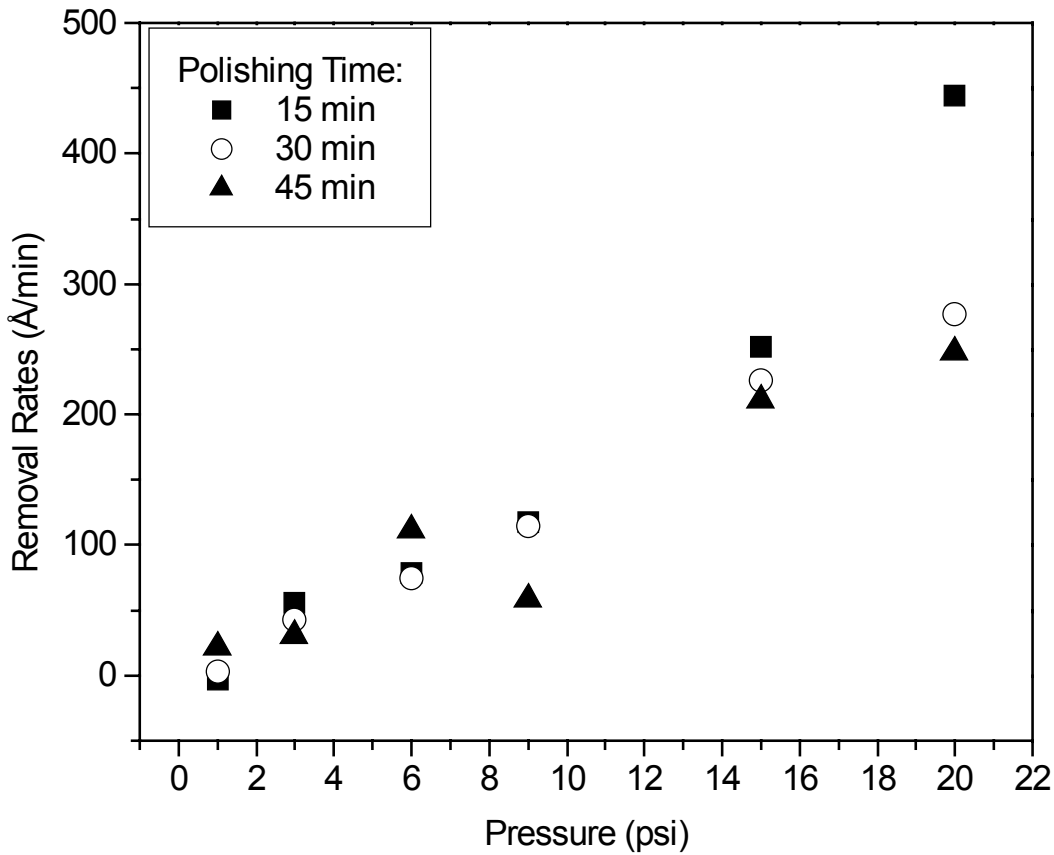
Abrasion in Peroxide Based Chemistry



- Extent of copper removal and amount of particulate materials generated follow a similar trend
- 0.03% SiO_2 (70 nm) particles in solution is equivalent to a turbidity of ~35 NTU.

- Acidification of waste generated at pH 5 to pH 1 decreases the turbidity to less than 1 NTU. This indicates that sparingly soluble copper species (ex. CuO or Cu_2O) are generated during CMP

Copper Removal Rates as a Function of Polishing Pressure



(2 *M* hydrogen peroxide :pH ~5)

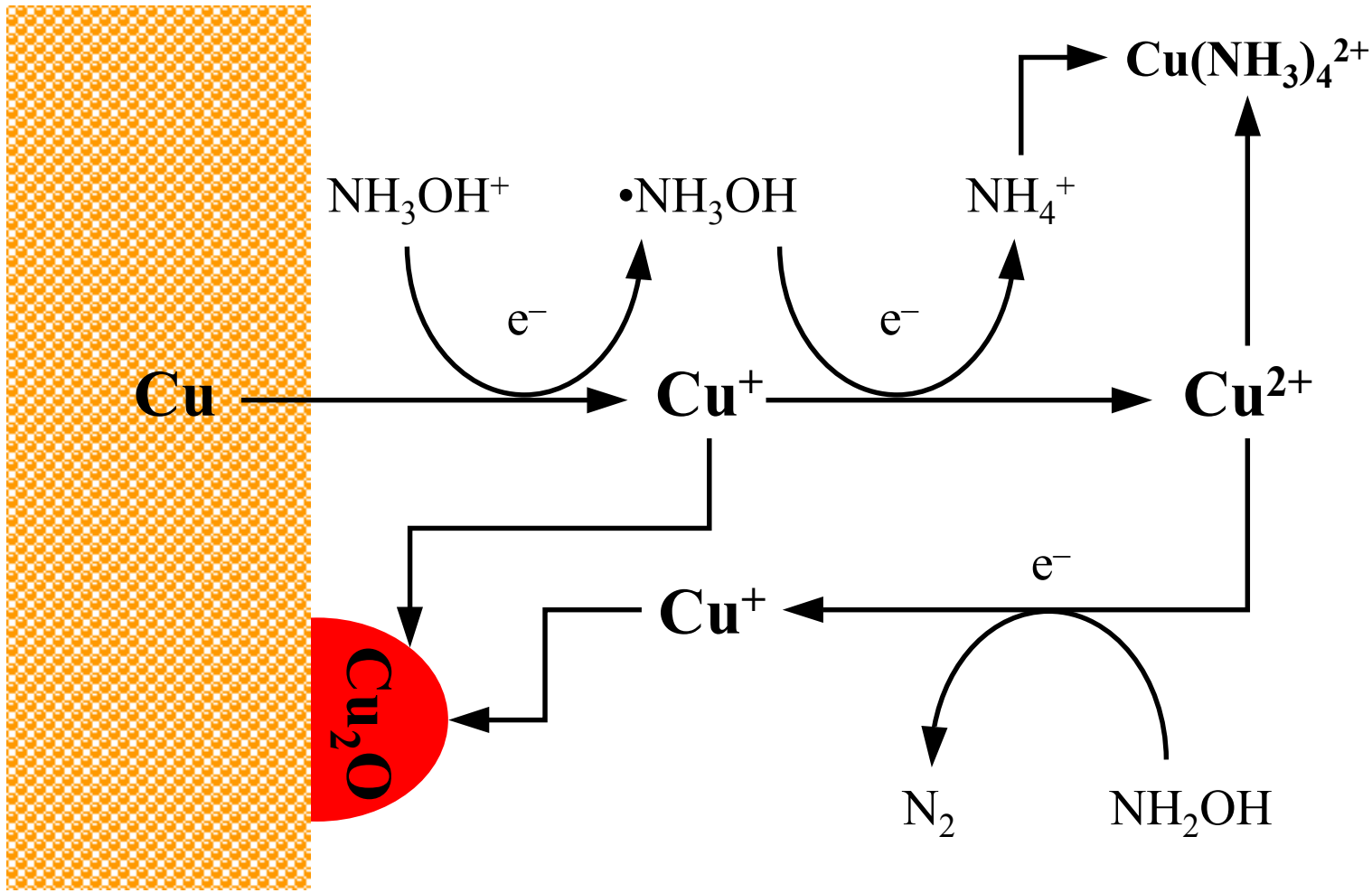
Proposed Mechanism That May Explain the Effect of pH

$NH_2OH + H^+ \leftrightarrow NH_3OH^+$ — Electroactive form

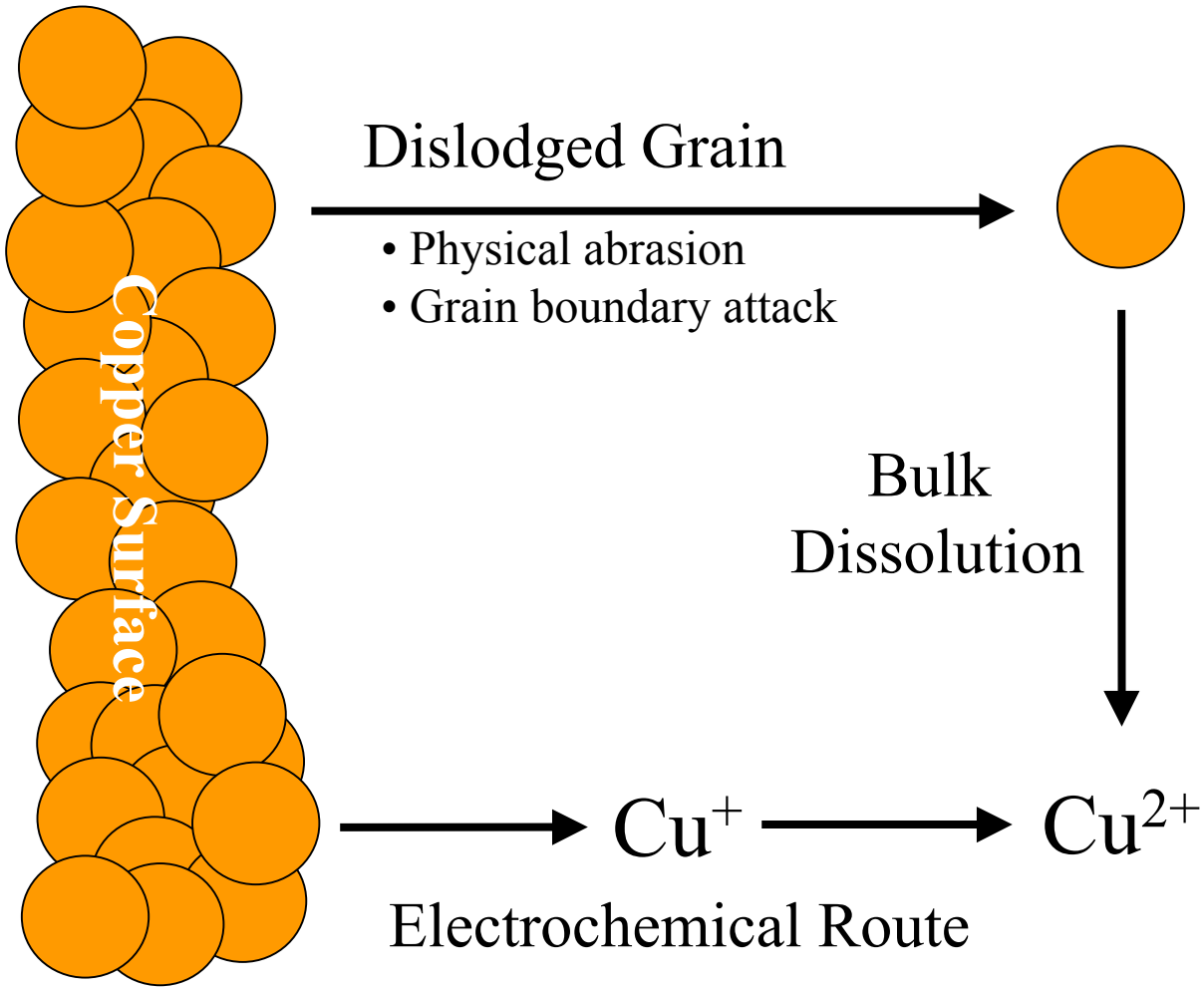
$NH_3OH^+ + e^- \leftrightarrow \bullet NH_3OH$ — Intermediate radical specie

Near Neutral pH	Low pH
$\bullet NH_3OH + e^- \leftrightarrow NH_3 + OH^-$	
$NH_3 + OH^- + 2H^+ \leftrightarrow NH_4^+ + H_2O$	$\bullet NH_3OH + H^+ + e^- \leftrightarrow NH_2OH + H_2$
Net Reaction	
$NH_3OH^+ + 2H^+ + 2e^- \leftrightarrow NH_4^+ + H_2O$	$2H^+ + 2e^- \leftrightarrow + H_2$
* Hydroxylammonium ion is reduced to ammonium.	* Hydroxylamine catalyzes the evolution of hydrogen.

Proposed Mechanism for Dissolution of Copper



Differences Between EC Removal Rate Versus Physical Removal Rate



Summary

- Removal rate of copper films in the absence as well as in the presence of abrasion is sensitive to pH

- The removal rate calculated by electrochemistry is less than physical (profilometry) measurements at pH 5 to 6