Anodic Dissolution Of Copper In Dilute Hydroxylamine Solutions - Applications To ECMP Of Copper

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Outline

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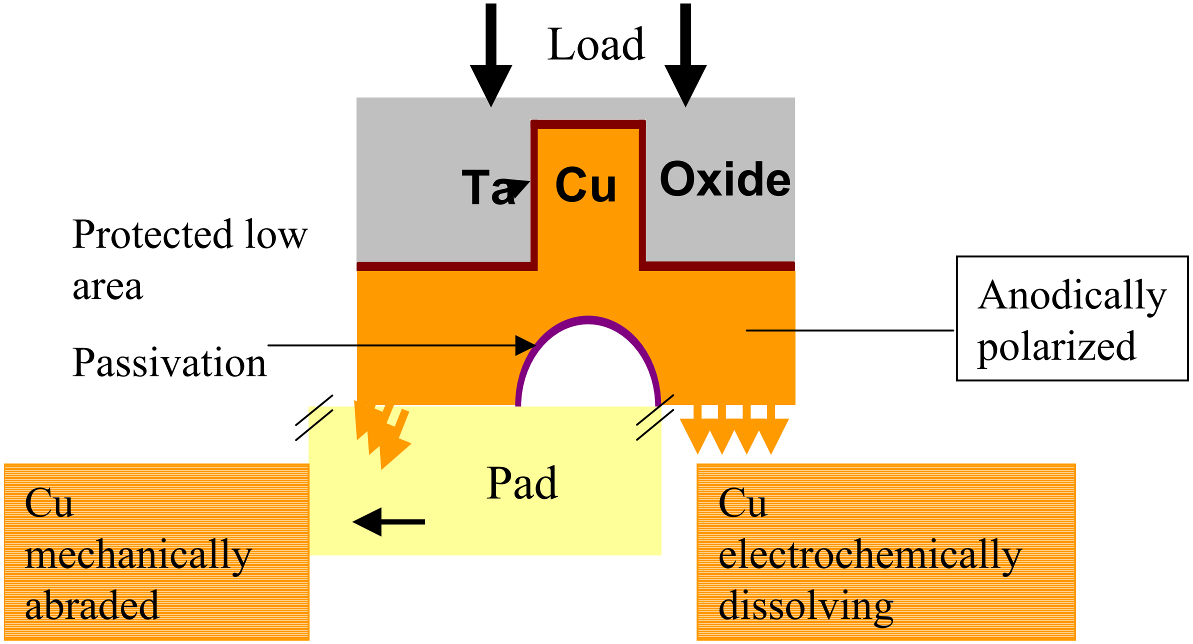
- Objective
- Materials and Methods
- Results and Discussion
- Summary
- Ongoing Work
- Acknowledgements

ECMP for Bulk Copper Removal



Protected low area

Passivation

Anodically polarized

Cu mechanically abraded

Cu electrochemically dissolving

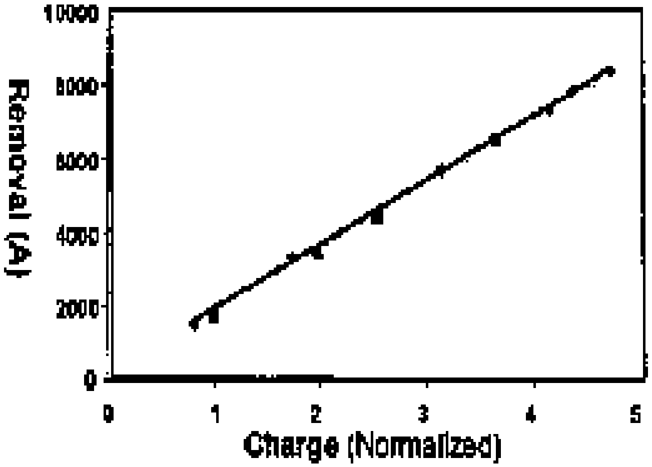


Fig. 1: Cu removal vs. Charge

- ➢ Wafer is anodically biased during polishing.
- ➢ Passivating agent/corrosion inhibitor is added to slurry which protects low lying areas while higher areas are polished.
- ➢ Inhibitors must be stable at anodic overpotentials
- ➢ Conventional inhibitor is benzotriazole (BTA).

Source : L. Economikos et al., *IEEE International Interconnect Technology Conference*, pp. 233-235, June 2004.

- ➢ Applied charge controls the amount of copper dissolution

Objectives

- Investigate the use of hydroxylamine chemistry in ECMP of copper
- To conduct removal rate experiments under applied pressure and potential and relate to QCM results
- Characterize the effect of applied anodic overpotential on the dissolution of electrodeposited copper films in hydroxylamine chemistry using quartz crystal microbalance
- Investigate the effectiveness of benzotriazole in inhibiting copper dissolution

Quartz Crystal Microbalance (QCM)

- Extremely sensitive sensor capable of measuring mass changes in the nanogram/cm^2 range
- Sauerbrey equation:

Relates the change in oscillation frequency of the crystal (QCM electrode surface) to mass change per unit area at the electrode surface.

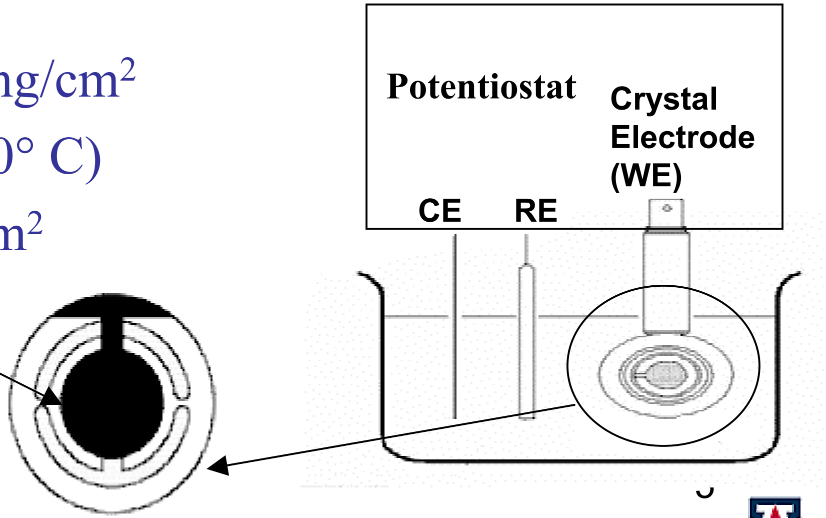
$$\Delta f = - C_f \times \Delta m$$

Δf = Observed frequency change in Hz,

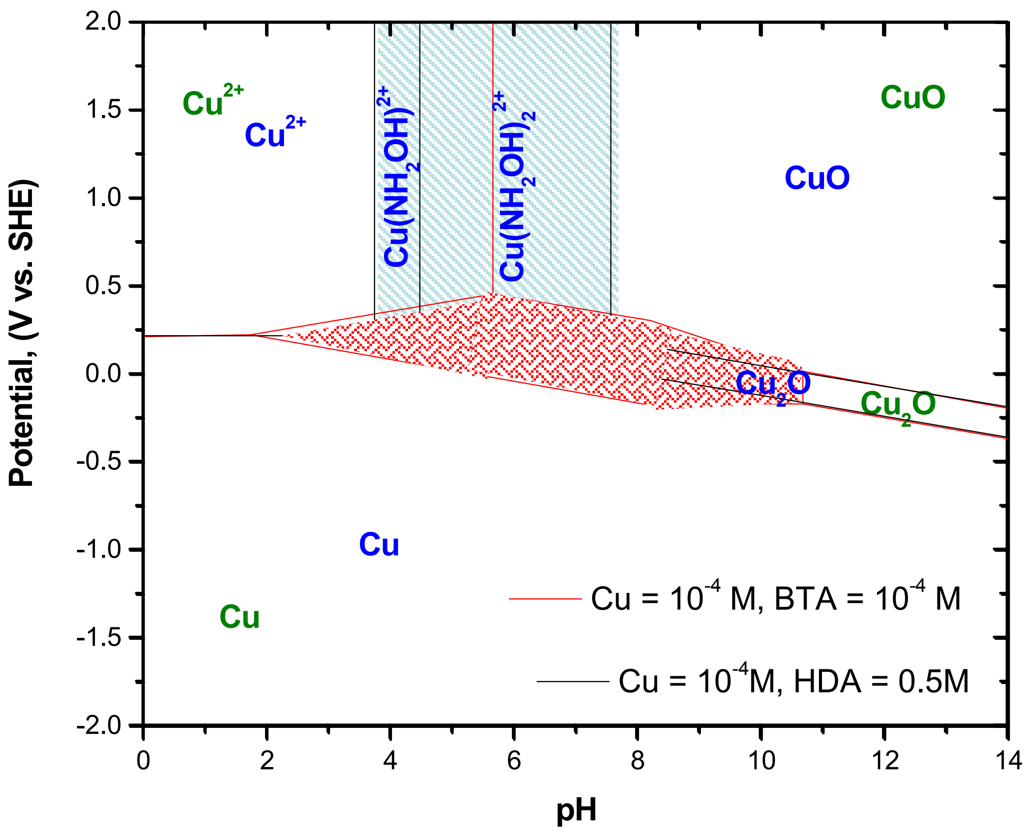
C_f = Sensitivity factor of the crystal in Hz/ng/cm^2

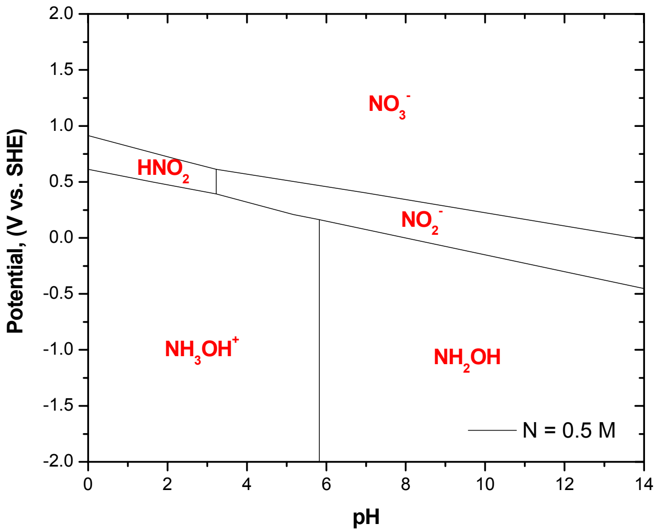
(0.056 Hz/ng/cm^2 for a 5 MHz crystal @ 20° C)

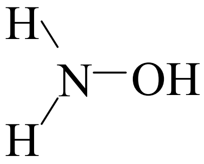
Δm = Change in mass per unit area, in ng/cm^2



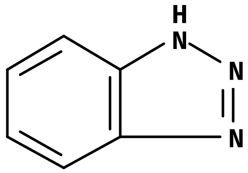
Pourbaix Diagram







HDA



BTA

- $NH_3OH^+ \Leftrightarrow NH_2OH + H^+$, pKa = 5.8
- Oxidizing agent at acidic pH
- Reducing agent at alkaline pH
- Complexes copper in pH range 4-7

- BTA^- forms a solid cuprous complex, CuBTA(s) for a wide pH range (3 -11)
- Copper oxide dominates the rest of alkaline region

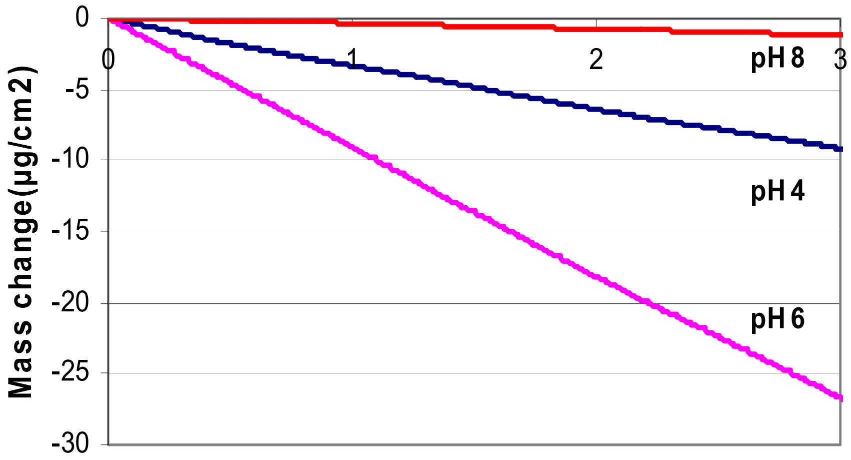
Materials and Methods

- MAXTEK - RQCM
  - 5 MHz crystal with Gold electrode (Active area ~ 0.8 cm^2)
- Copper was electroplated on gold
  - Commercial copper plating bath: $CuSO_4$ solution + accelerator + suppressor
  - Current density = 2 mA/cm^2 and plating duration = 45 mins
  - Thickness of Copper film - 2 µm
  - Non-porous and uniform copper film
- Electroplated copper film(~0.8µm) on Tantalum (polishing expts)
- Electrochemical experiments
  - EG&G PARC 273A potentiostat (Interfaced with RQCM)
  - Specially designed laboratory scale Electrochemical abrasion cell (EC-AC) tool
  - Perkin Elmer 2380 Atomic absorption spectrophotometer
  - Ref. electrode - SCE, Counter electrode - Platinum

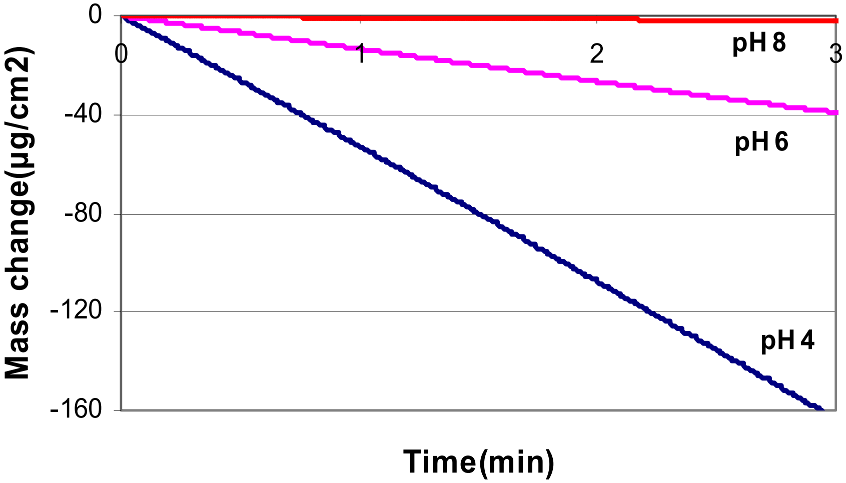
Results and Discussion

Effect of Overpotential and pH on Cu Removal in 0.1M Hydroxylamine System

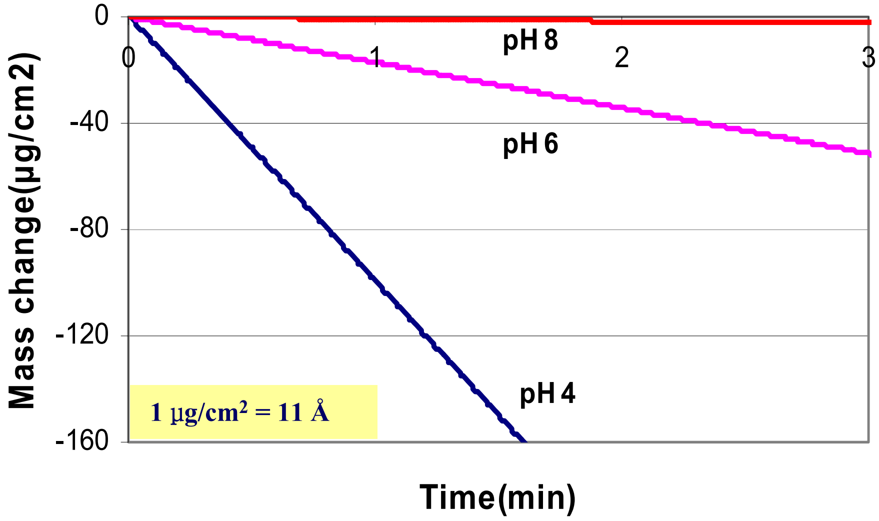
OCP (-160mV vs SCE)



250mV

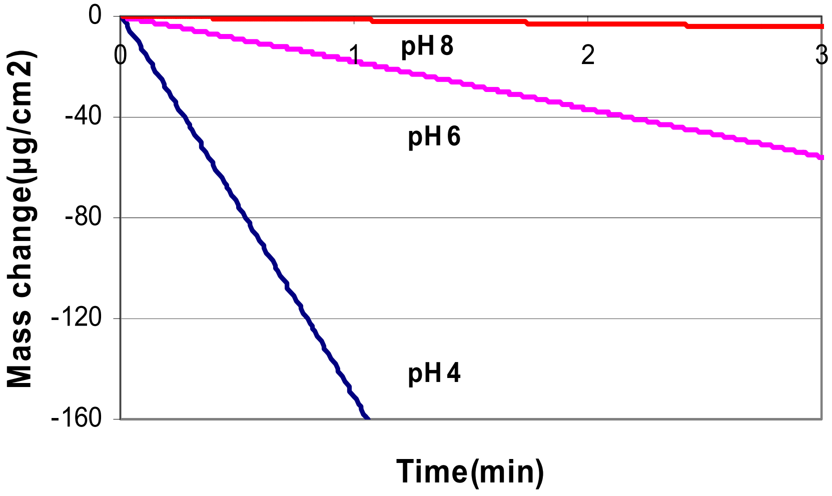


500mV



1 µg/cm² = 11 Å

750mV



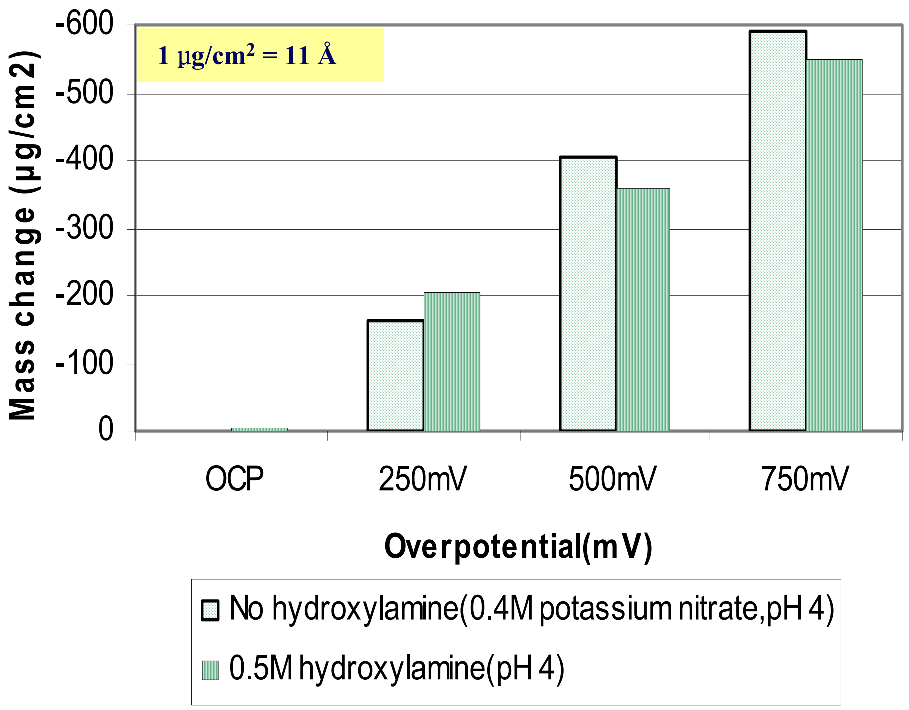
Dissolution Rate of Copper in Hydroxylamine Solutions

NH_2OH	Overpotential (η) (vs SCE)	Dissolution rate of copper (Å/min)		
		pH 4	pH 6	pH 8
0.1 M	OCP(-160mV)	30	100	5
	250mV	600	145	7
	500mV	1115	190	10
	750mV	1730	205	15
0.5M	OCP (10mV)	55	500	40
	250mV	2270	2200	625
	500mV	3940	1200	760
	750mV	**6030**	1200	920

Note:

- Dissolution rate of copper in hydroxylamine solution was found to be strongly dependent on pH and overpotential
- Exhibits a maximum dissolution in the vicinity of pH 6, and the rate drops off significantly on either side

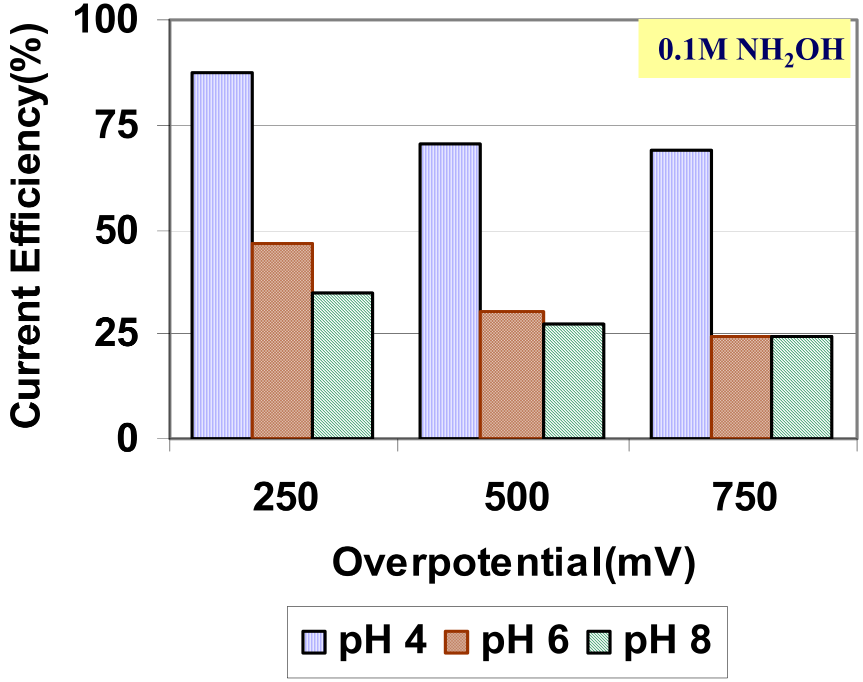
Comparison of Mass Change of Copper - With and Without Hydroxylamine Solution (pH 4)

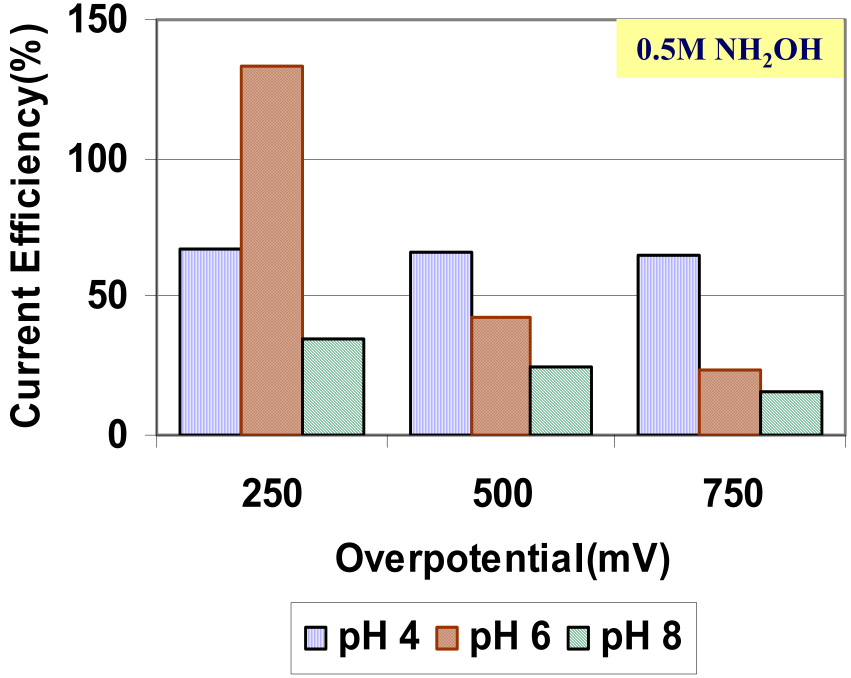


- Conductivity of 0.5M NH_2OH = 43mS/cm
- Conductivity adjusted (using KNO_3) to 43mS/cm for solution containing no hydroxylamine.
- No significant difference in mass change may indicates that the acidic nature of hydroxylamine solution is responsible for higher dissolution rate of copper

Note: copper gets peeled off from the surface and uniform dissolution was not achieved in the solution without hydroxylamine.

Current Efficiency vs. Overpotential





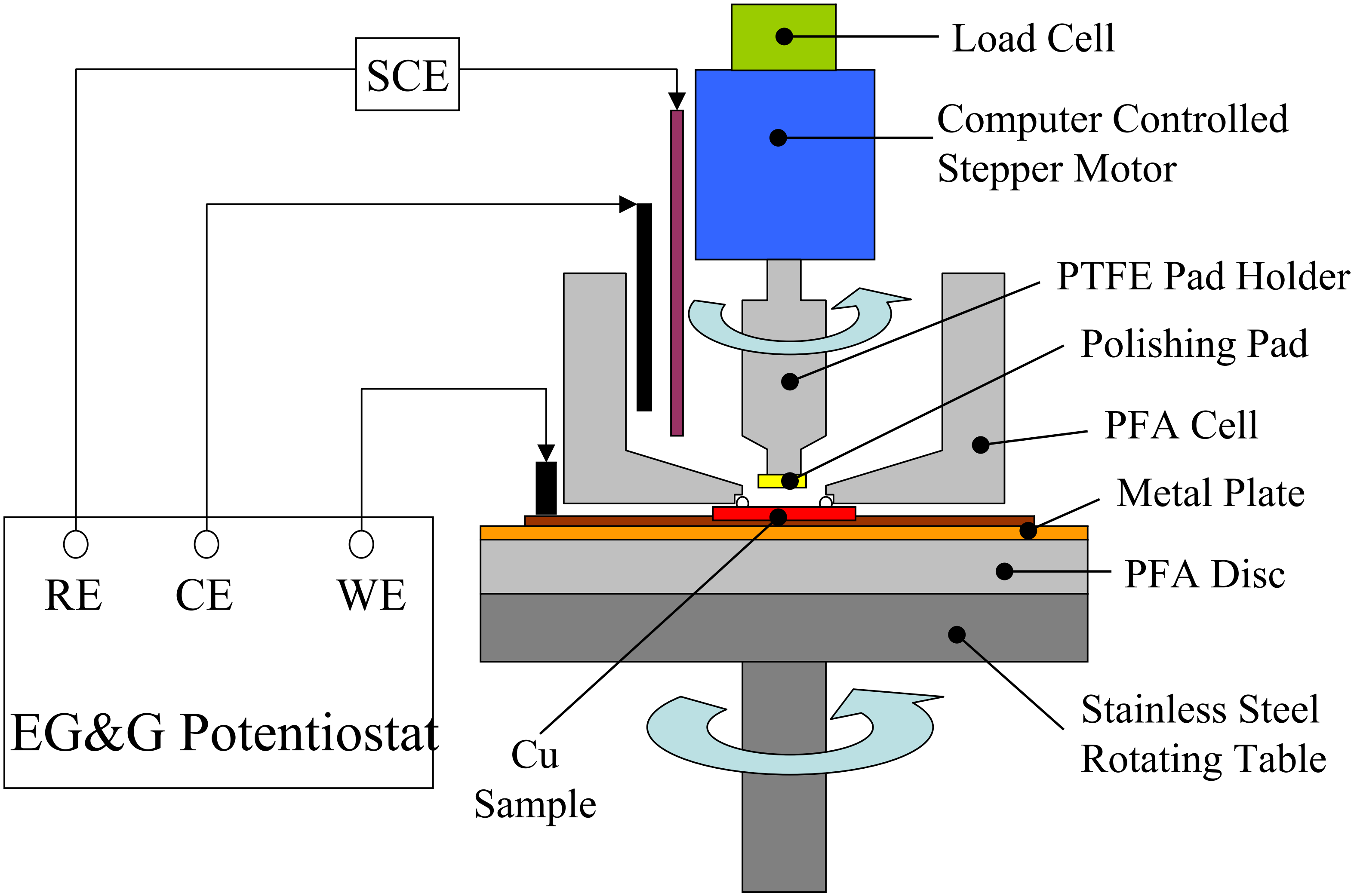
- At pH 4, the current efficiency is above 70% under all applied anodic overpotentials.
- Relatively low current efficiency is observed at pH 6 and 8

$$\text{Current Efficiency}\,(\%) = \frac{[\text{Actual RR} - \text{Estimated RR}]}{\text{Actual RR}} \times 100$$

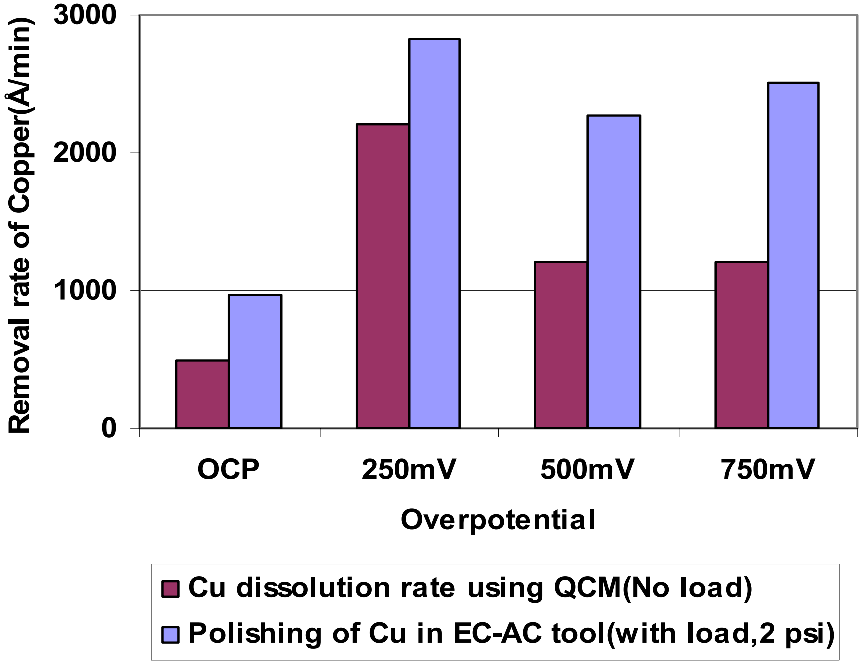
- At pH 4, the current efficiency is above 65% under all applied anodic overpotentials.
- At pH 6 for η = 250mV, the current efficiency is above 130% (???)
- Current efficiency drops as the overpotential is increased

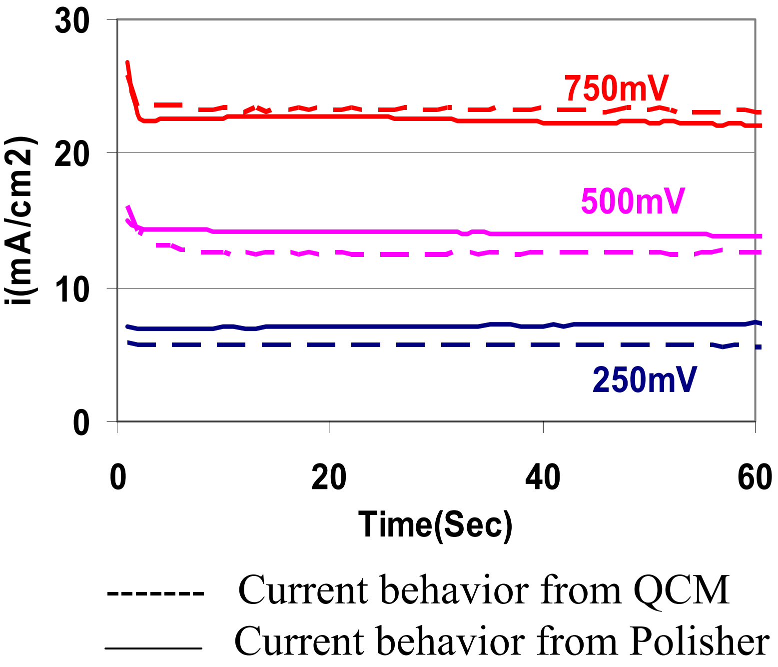
Polishing Experiments

ElectroChemical Abrasion Cell (EC-AC) Tool



Comparison of Polishing and QCM Rates – 0.5M Hydroxylamine Solution (pH 6)



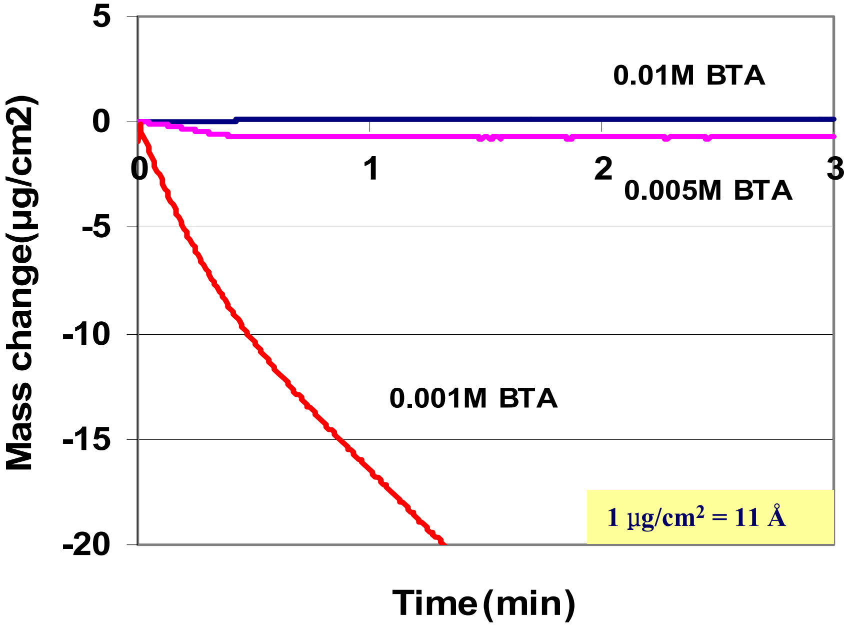


- Copper polished in 0.5M hydroxylamine solution (pH 6) in EC-AC tool with a load of 2 psi.
- Polishing of copper increases the total removal rate under all applied overpotential.
- Current density profile is almost the same in both QCM and the polisher which may indicate that the increase in removal rate is only due to the applied load.

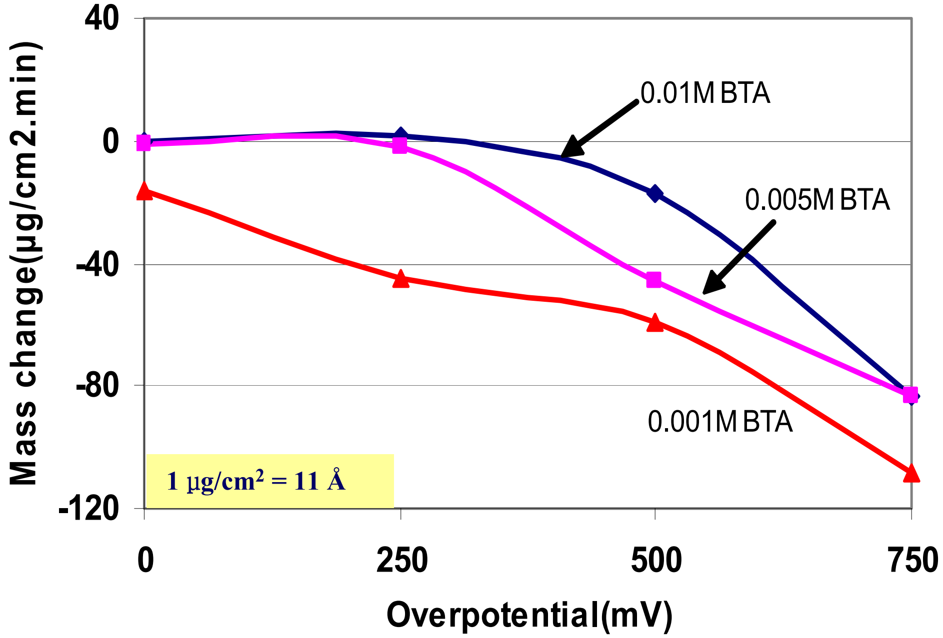
Effectiveness of BTA

Effect of BTA Concentration on Cu Removal in 0.5M Hydroxylamine System (pH 6)

OCP



1 µg/cm² = 11 Å



1 µg/cm² = 11 Å

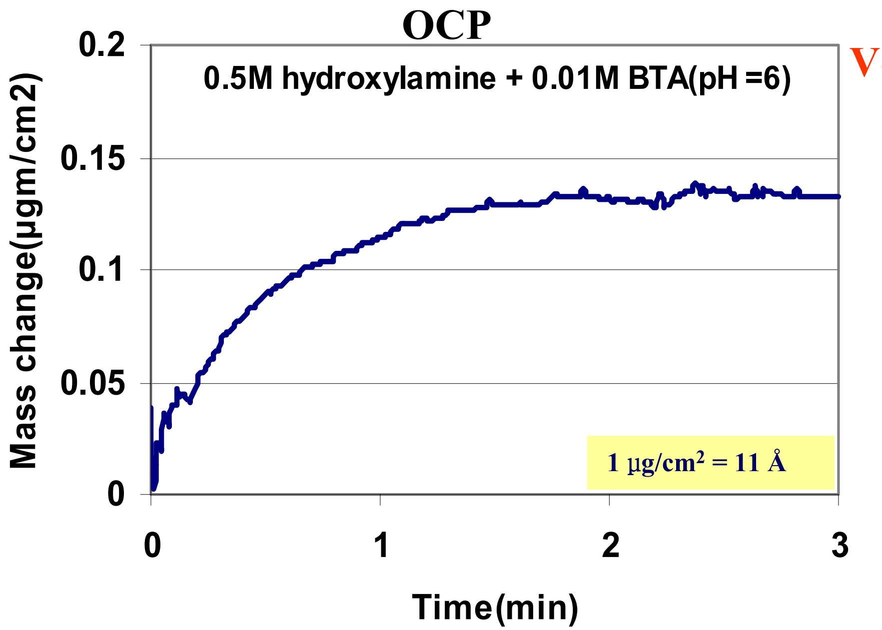
- OCP of Cu is 10mV (vs SCE)
- Rate of Copper removal in hydroxylamine is significantly reduced in the presence of BTA at η < 500mV
- At higher overpotentials (>500mV), BTA becomes ineffective.

Dissolution Rate of Copper in Hydroxylamine Solution Under Different Anodic Overpotentials at Different BTA Concentrations

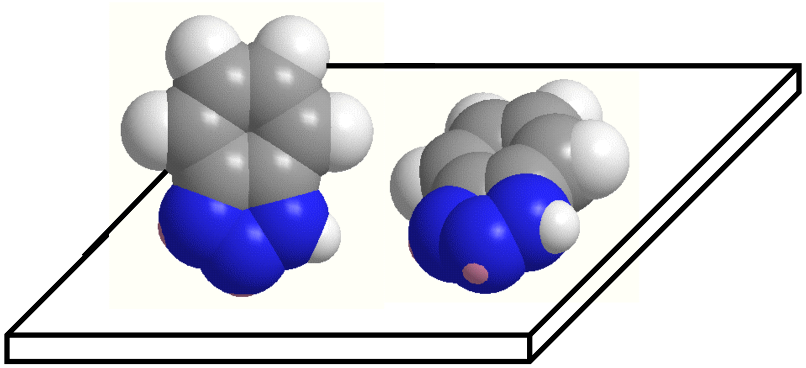
Overpotential(η)	Dissolution rate (Å/min) of copper in 0.5M hydroxylamine (pH = 6)			
	0.001M BTA	**0.005M BTA**	**0.01M BTA**	**No inhibitor**
OCP	180	8	*	500
250 mV	490	14	*	2200
500 mV	670	460	395	1200
750 mV	1200	1100	1000	1200

Note: * denotes that the mass is increasing (BTA adsorption on Copper)

Kinetics and Mechanism of Copper Passivation by BTA

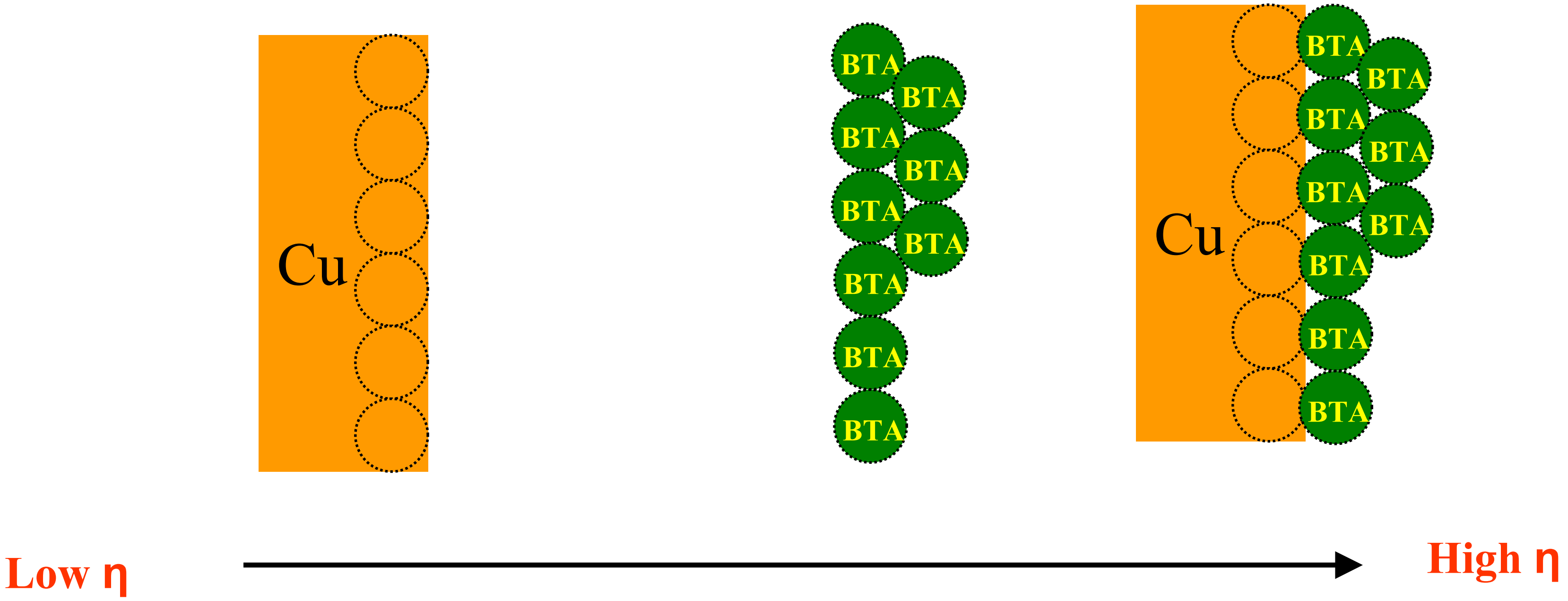


Vertical and horizontal orientation of BTA molecules

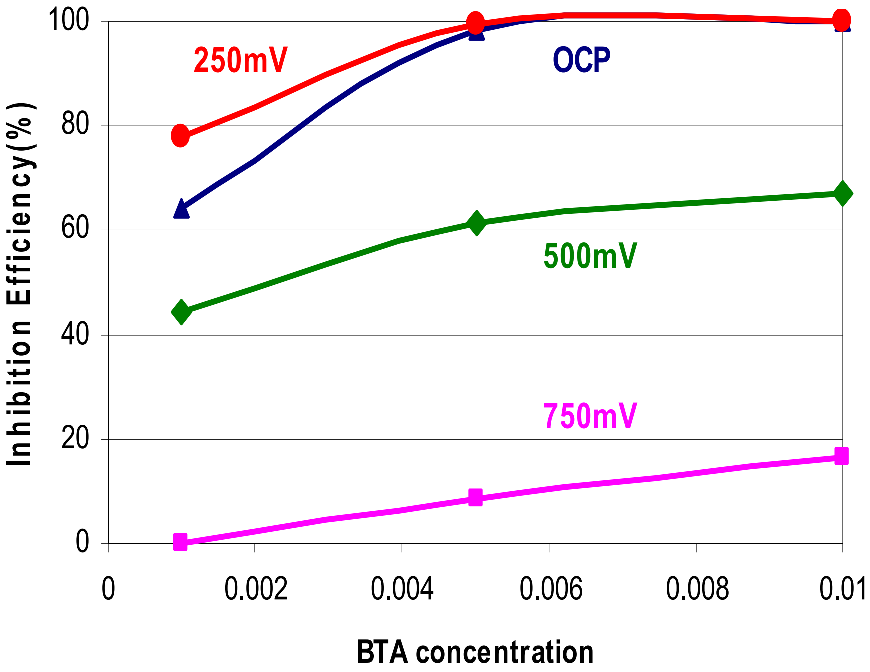


- BTA rapidly forms a passive layer on copper surface
- Multilayer adsorption of BTA (2 or 4 layers depending on orientation) on to the copper surface.
- Adsorbed BTA in the first layer forms a cuprous-BTA polymeric complex, while the subsequent BTA layers attach by physisorption

Passivation Mechanism – Copper/BTA



Inhibition Efficiency as a Function of BTA Concentration in 0.5M Hydroxylamine Solution (pH 6)



- 0.005M and 0.01M BTA offer excellent protection up to η ~ 250 mV
- At higher overpotential, η > 250 mV, BTA becomes ineffective
- Increase in BTA concentration, increases the inhibition efficiency

Summary

- Copper dissolution in hydroxylamine increases with respect to overpotential.
- At pH 4, dissolution rate of copper in 0.5M hydroxylamine solution is 6030 Å/min at 750mV overpotential.
- Maximum current efficiency is observed at pH 4.
- In 0.5 M hydroxylamine solution at pH 6, the removal rate of copper during polishing is higher than that observed in QCM experiments
- BTA rapidly forms a passive layer and offers very good protection at lower overpotential (≤ 250mV). At higher overpotential, BTA films dissolve actively and the dissolution rate increases with overpotential.
- Under OCP condition, BTA forms a multilayer film on copper surface.

Ongoing Work

- Developing new chemistries for ECMP of Copper.
- Investigating the feasibility of removal of barrier layers (Ta/TaN) using ECMP technique.

Acknowledgements

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