Characterizing Copper-Hydrogen Peroxide Film Growth and Dissolution Kinetics for Application in Multi-Step Chemical Mechanical Planarization Models

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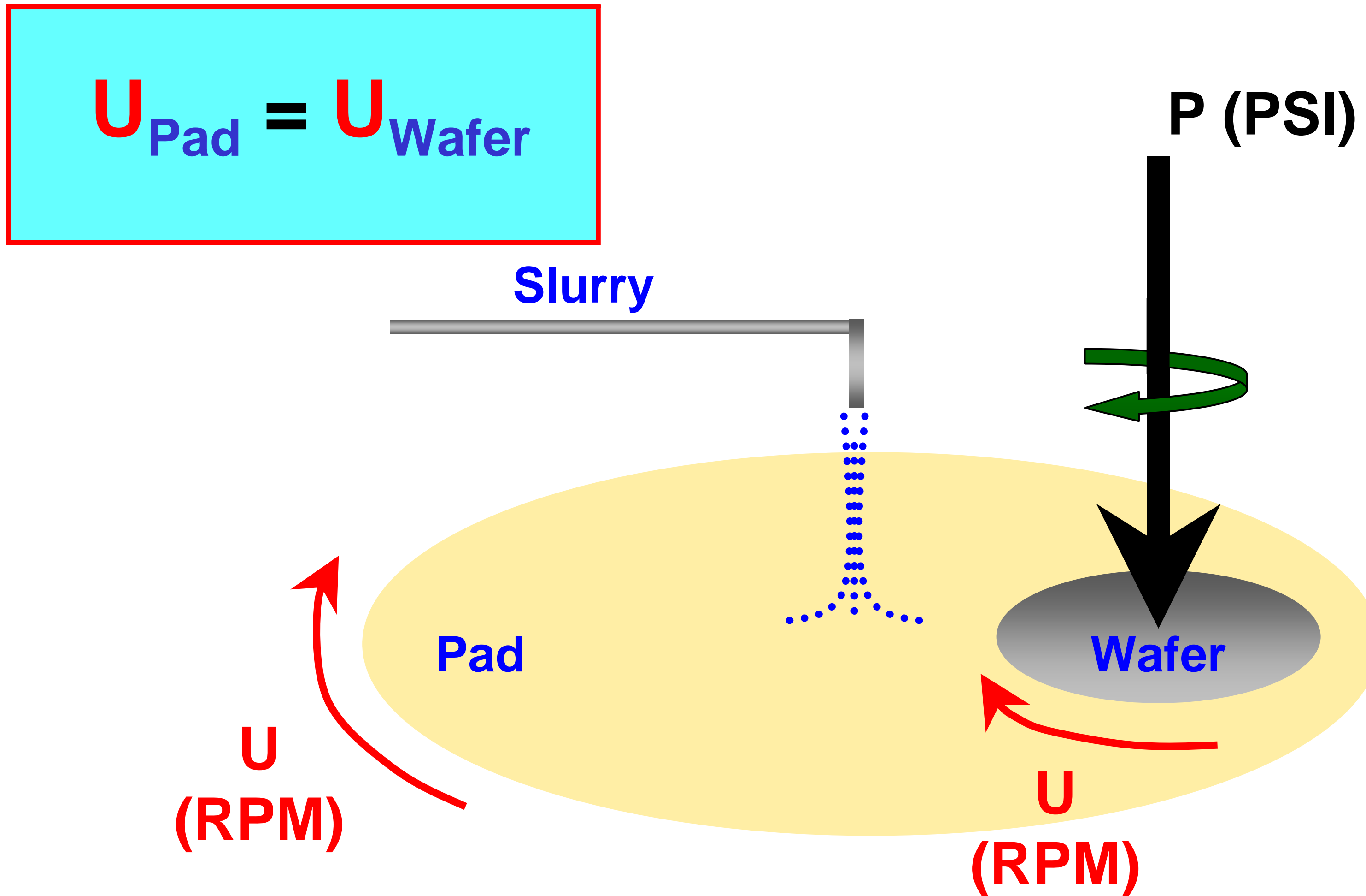
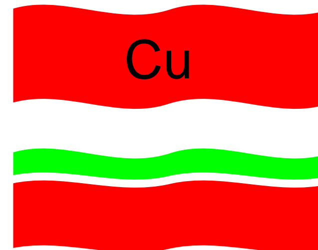
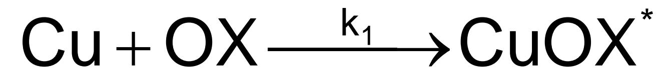
CMP Process Background



Two-Step Removal Mechanism

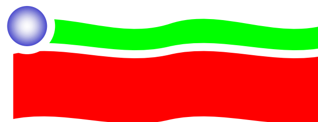
Passivation layer formation

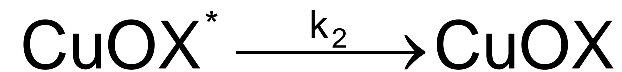




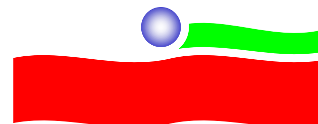
$$k_1 = A \cdot \exp\left(\frac{-E}{kT}\right)$$

Mechanical abrasion with slurry



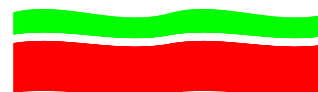


Fresh surface regeneration



$$k_2 = c_p \mu_k P U$$

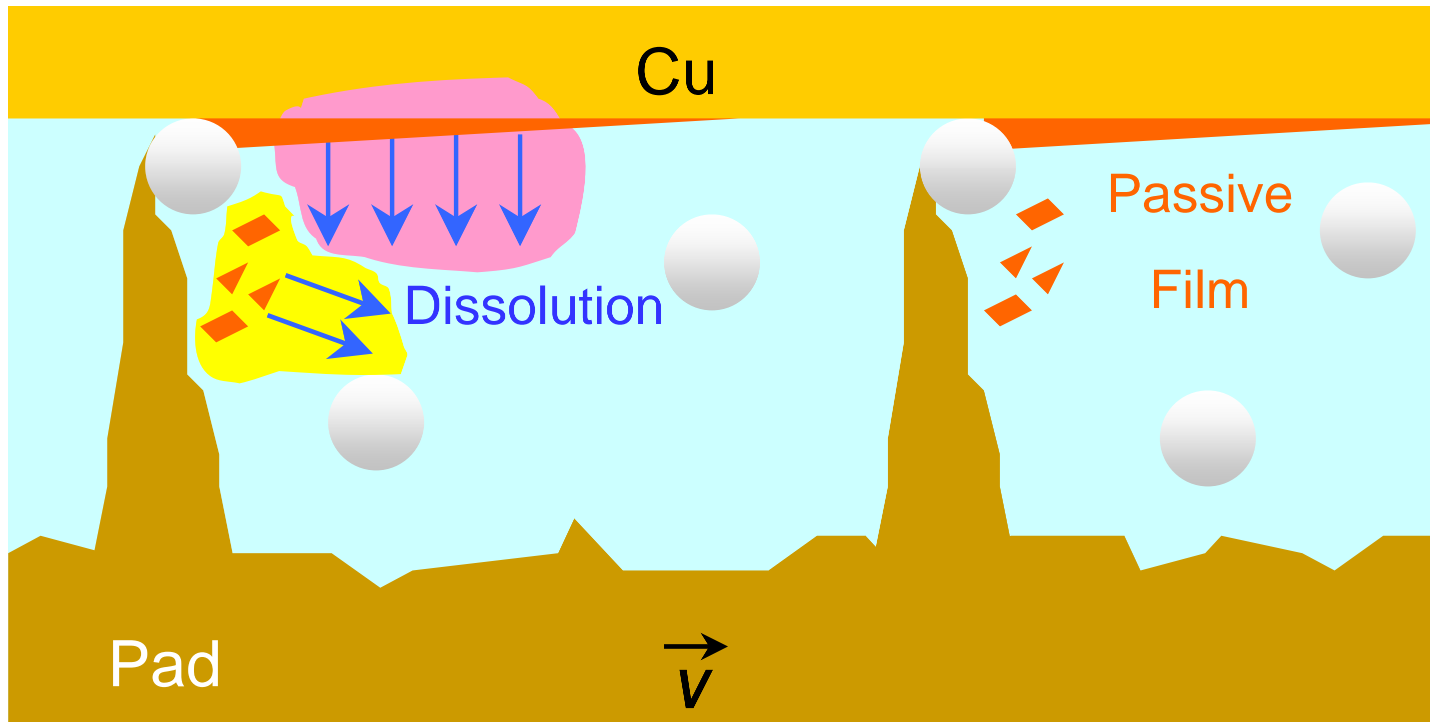
Repeat ...



$$RR = \frac{M_w}{\rho} \frac{k_2 k_1}{k_2 + k_1}$$

** Indicates surface species*

Driving Force



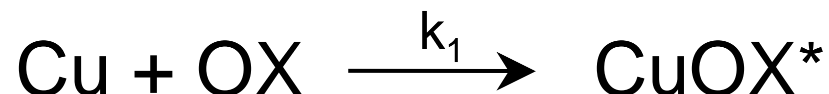
Important at low oxidizer concentrations - CAP

Important at 1wt% H_2O_2

Static etch rate is 150 A/min at 25°C

Driving Force

Passive Film Formation

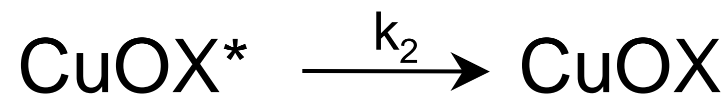


- [OX]
- [Inhibitor]
- pH
- Potential
- Buffers

Chemical Processes: f(T)

Mechanical Attributes

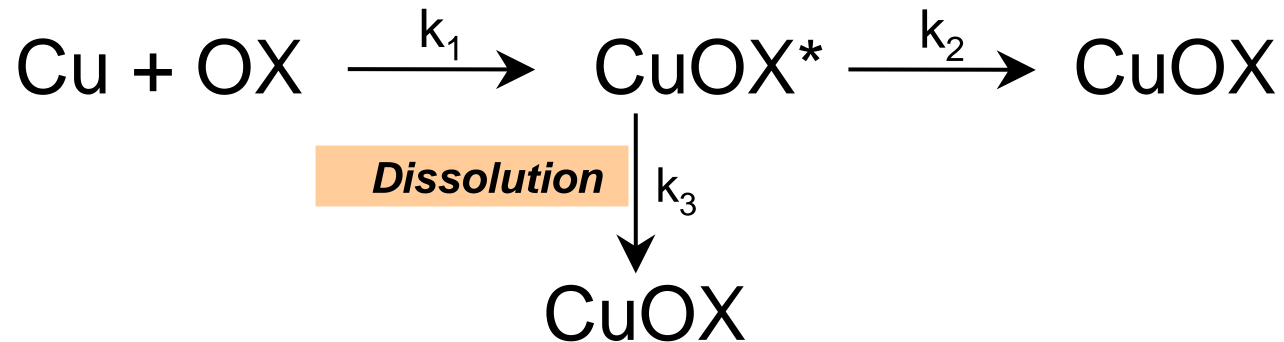
Film Removal



- Pressure
- Velocity
- Abrasives
- Pad grooving
- Conditioning
- COF
- Slurry flow
- Pad properties
- Dissolution

<u>Limitation:</u> Film removal rate constant depends on both chemical AND mechanical processes

Separation of ‘C’ and ‘M’ in CMP



- If k_1 and k_3 can be experimentally determined *a priori*, k_2 comprises mechanical processes only and can be extracted from CMP experiments

- The chemical and mechanical contributions can be quantified separately

In this study, characteristics of Steps 1 and 3 are investigated

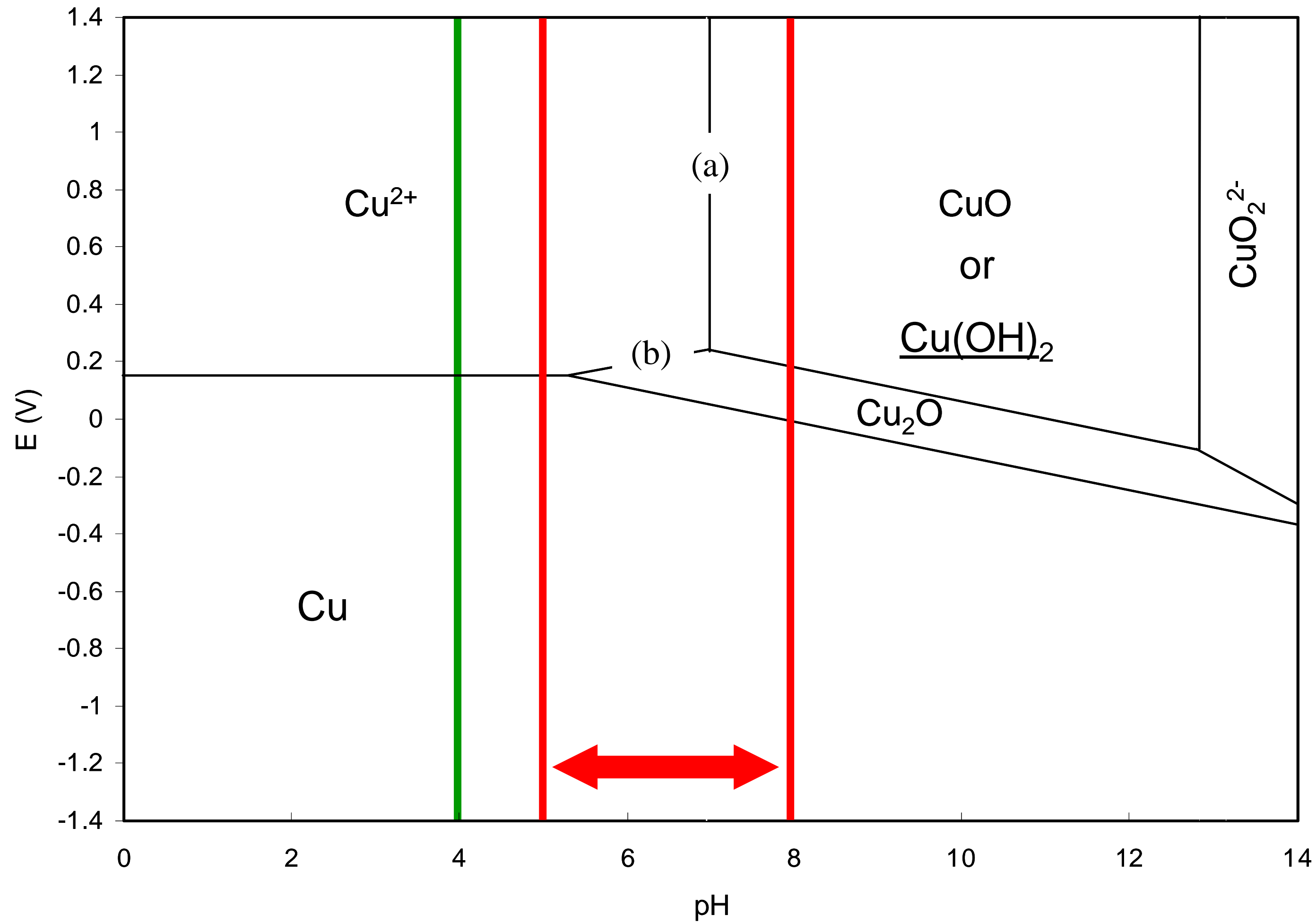
Topics

- Characterize Cu – H_2O_2 system in general

- Passive film formation as f(T)

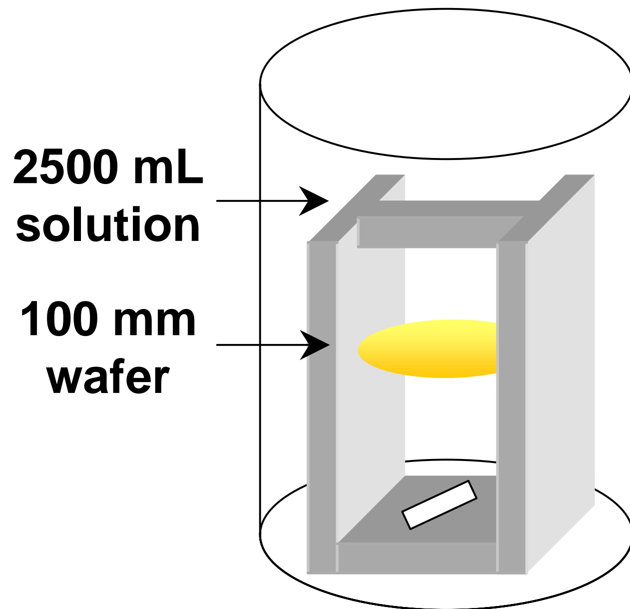
- Passive film dissolution as f(T)

pH Ranges of Interest



Etch rates reported in Cu – H_2O_2 systems

Experimental



Characterize Cu – H_2O_2 Interactions using:

- Ellipsometry
- XPS
- AA
- SEM

- CMP before each test to remove native oxides
- Wafers dried with UHP N_2 and weighed
- pH = 5 – 6
- Solutions were stirred
- $Cu/TaN/SiO_2/Si$ stacked wafers
- $H_2O_2 – H_2O$ solutions only

Preliminary Results

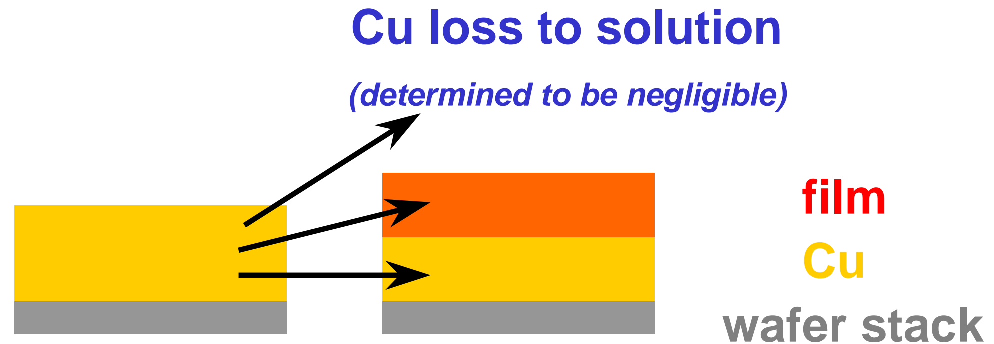
At 1 wt% H_2O_2, increases in mass were observed indicating film growth

$$m_i = m_{Cui} + m_{ws}$$

$$m_f = m_{Cuf} + m_{film} + m_{ws}$$

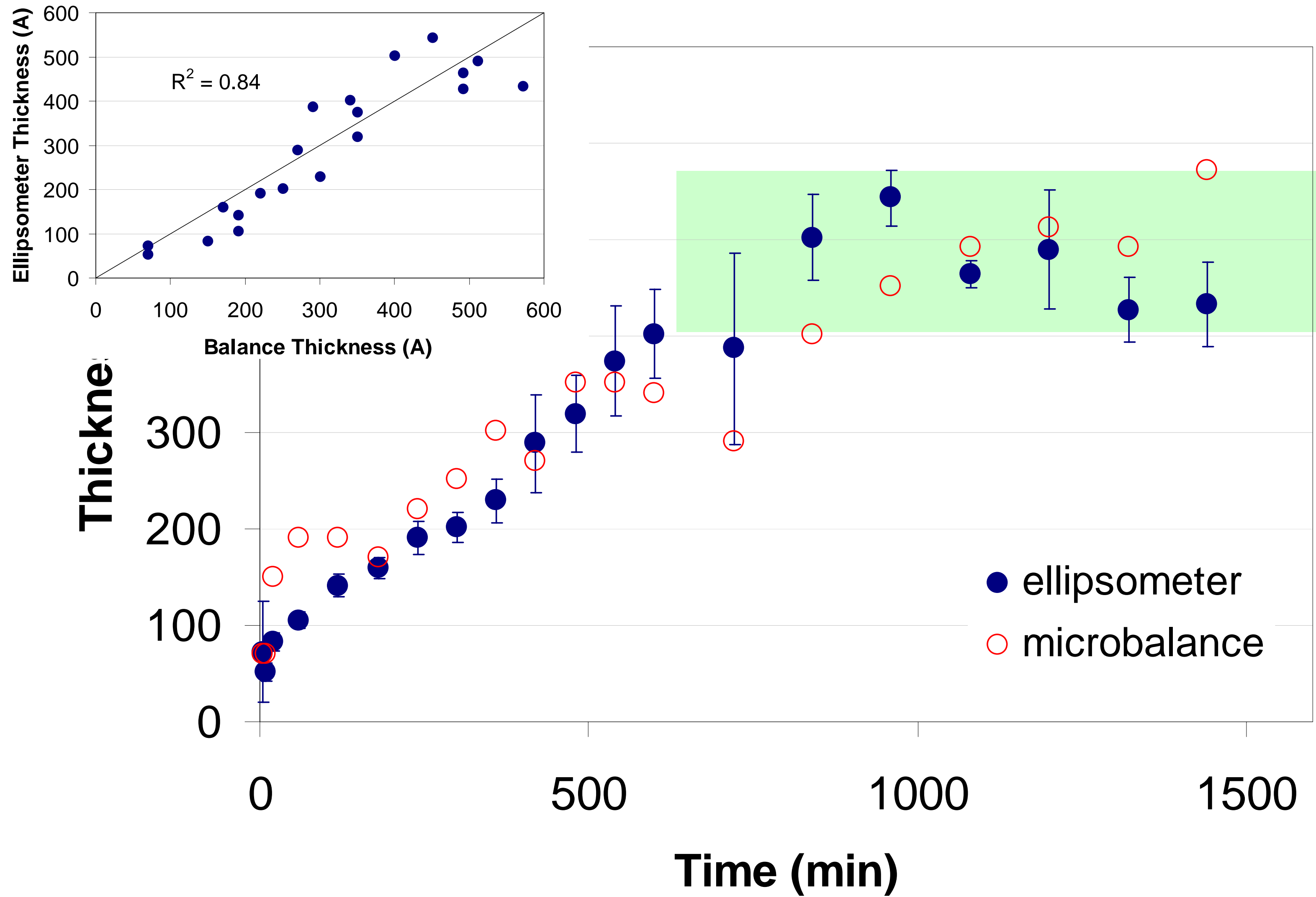
$$m_{Cui} = m_{Cuf} + m_{film(asCu)}$$

$$t_{film} = \frac{4}{\pi d^2 \rho_{film}} \frac{(m_f - m_i)}{\left(1 - \frac{MW_{Cu}}{MW_{film}}\right)}$$

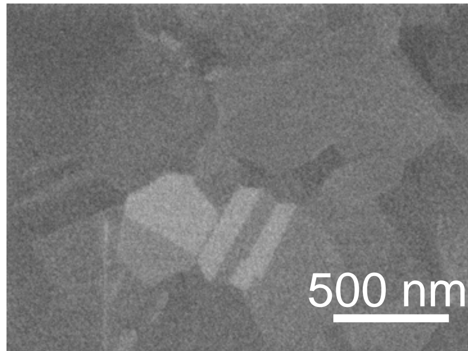


Assumes uniform film growth, so Δm results were compared to ellipsometric results

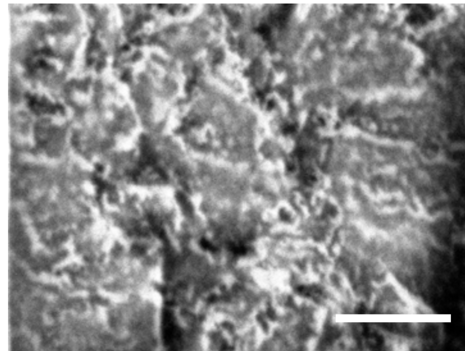
1 wt% H_2O_2 Growth Profile



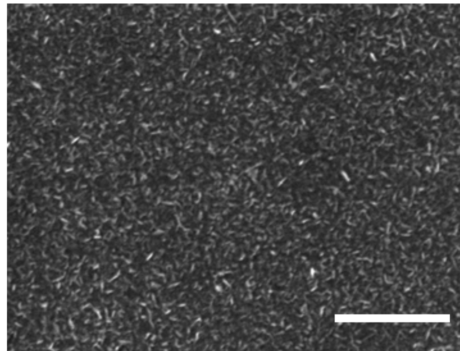
Surface Characterization



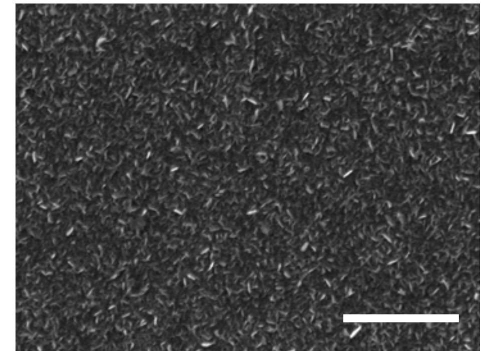
After CMP



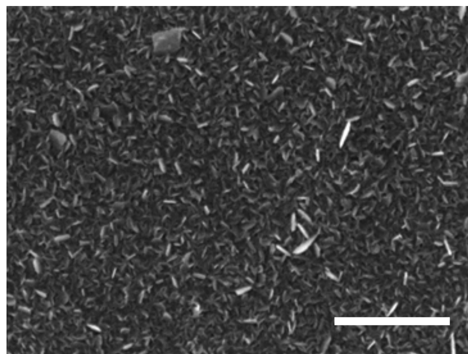
5 min



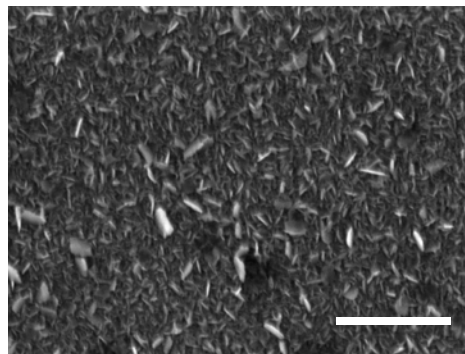
10 min



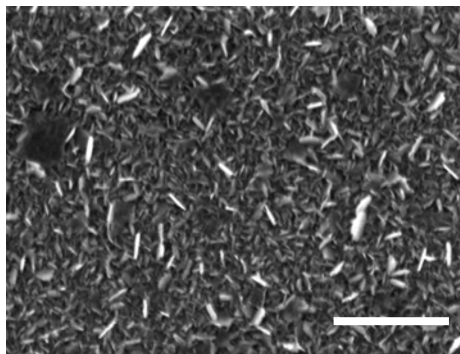
20 min



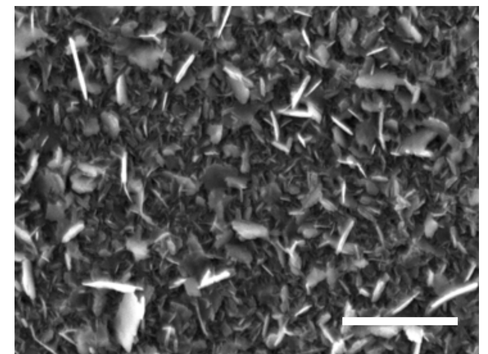
1 hr



5 hr



7 hr

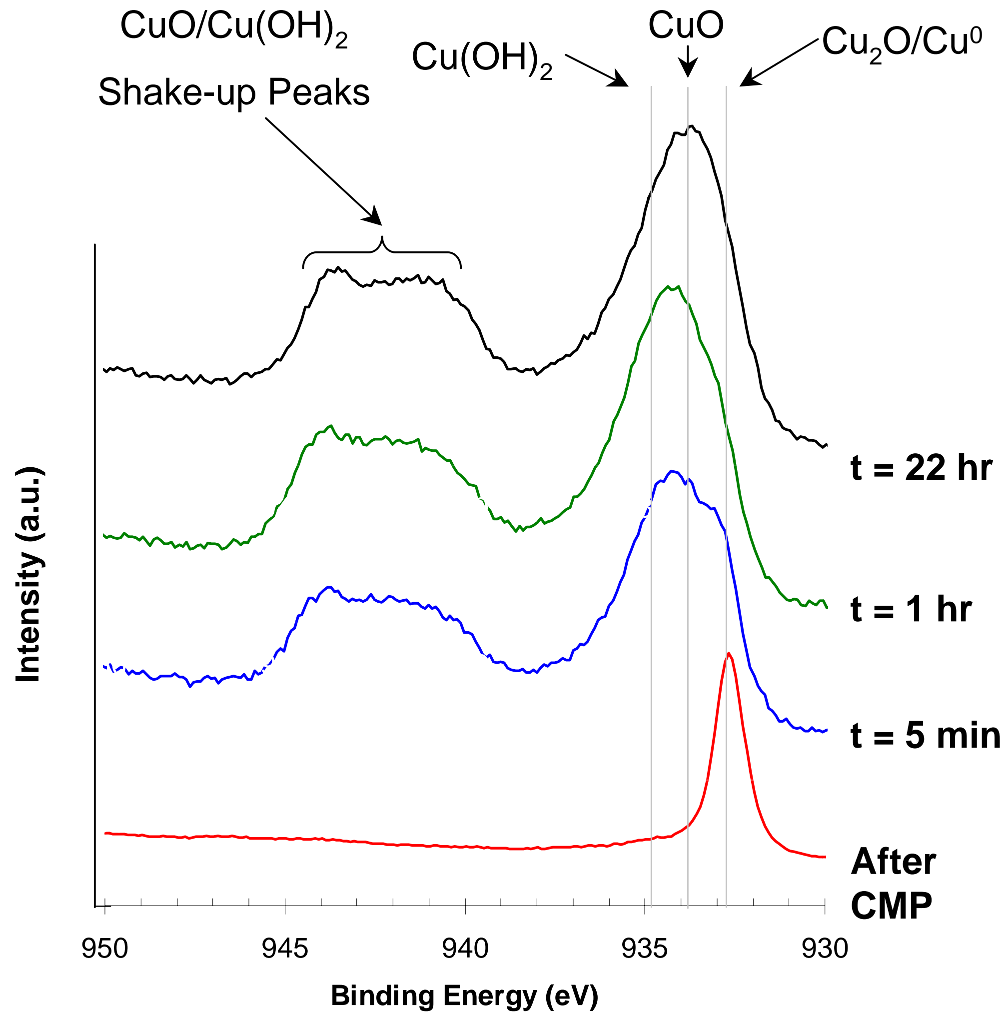


22 hr

Growth Profile and SEM Summary

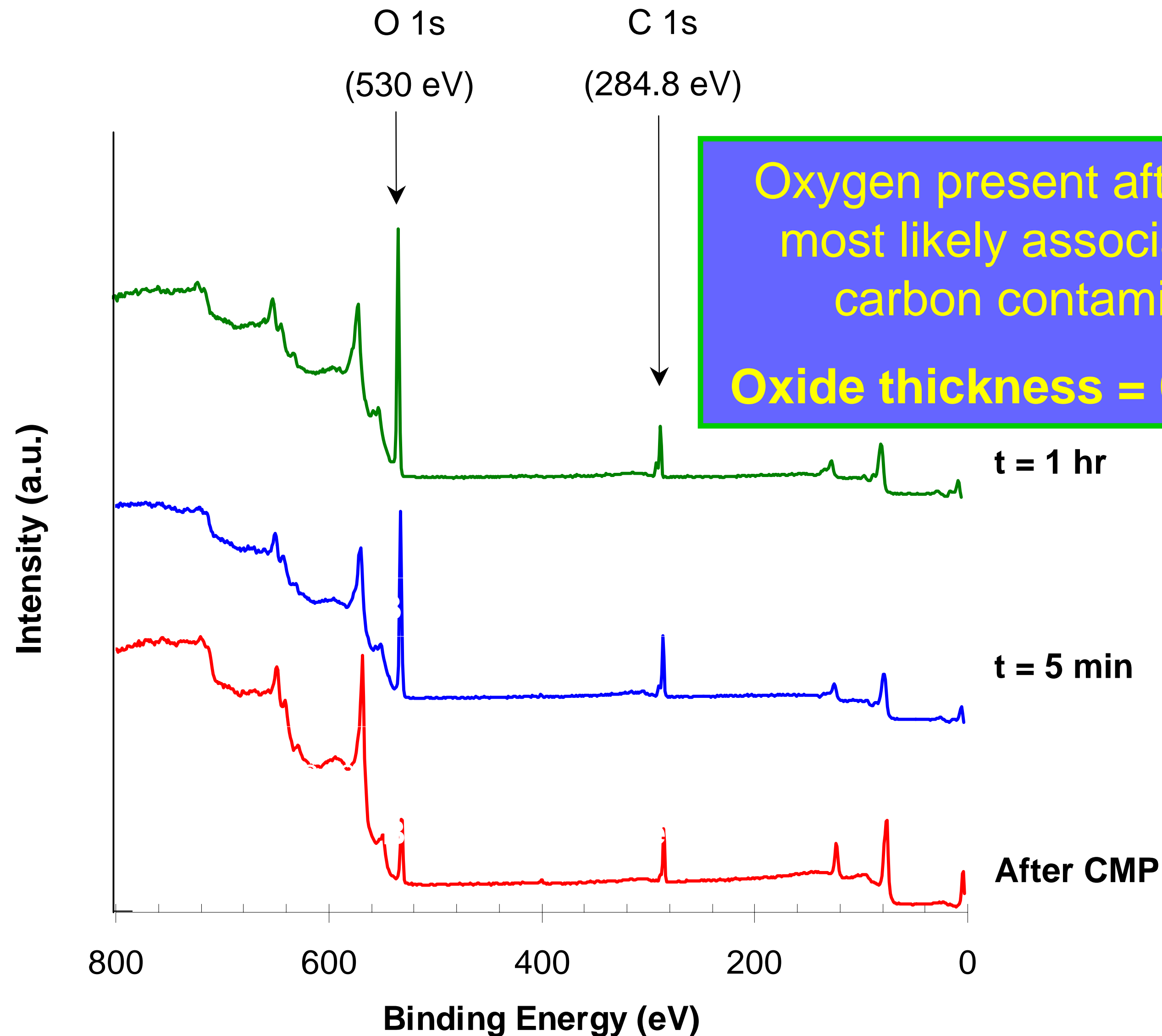
- **Growth saturation occurs at 500 A after 12 hours in 1 wt% H_2O**
  - How do saturation thickness and time change with [H_2O_2]?
- **After CMP, images may indicate:**
  - Bare copper metal and/or thin layer of copper oxide
  - XPS analysis to clarify
- **After 5min, a non-uniform film is observed – no distinct crystals**
- **Distinct crystals are observed on the surface for $t \geq 10$min**
  - It is difficult to determine if crystals increase in size for $t < 1$ hour
  - The crystals at the solid-liquid interface clearly increase in size for $t > 1$ hour
  - A Deal-Grove type model is *not directly* applicable to this system
- **Does the film composition change with time?**

Cu $2p_{3/2}$ XPS Spectra



- **After CMP, a mixed Cu_2O/Cu^0 system is indicated**
  - **Is oxide present?**
- **Peak broadening and apparent shoulder indicate Cu^+ as well as Cu^{2+} after 5 min**
- **Presence of Cu^+ diminishes as time increases**
- **Suggests Cu_2O forms first**
  - Corroborates earlier work
- **Use full spectra to determine if oxide is present after CMP**

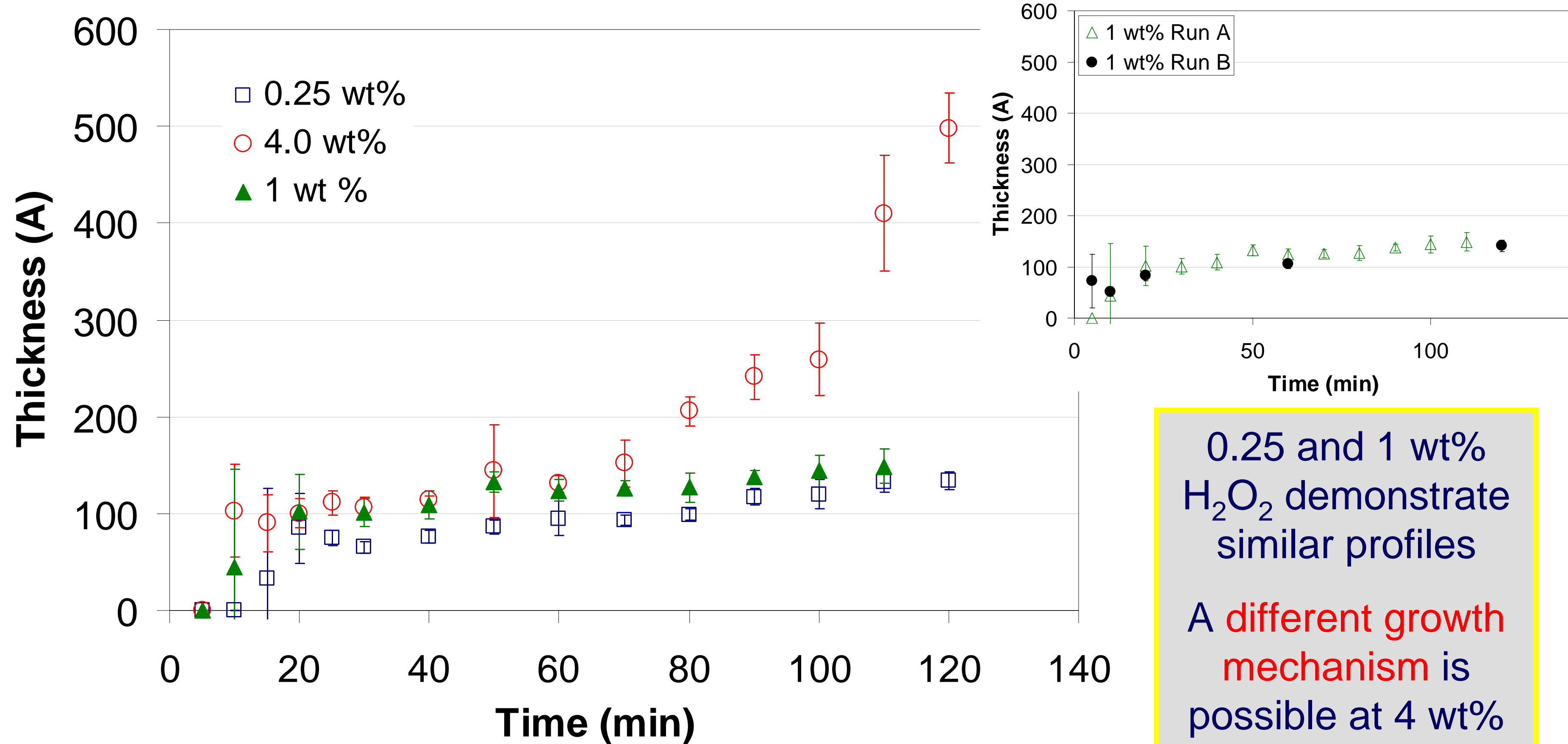
Full XPS Spectrum *(excluding Cu 2p)*



Oxygen present after CMP is most likely associated with carbon contamination

Oxide thickness = 0 A at t = 0

Effects of H_2O_2 Concentration



0.25 and 1 wt% H_2O_2 demonstrate similar profiles

A different growth mechanism is possible at 4 wt% H_2O_2

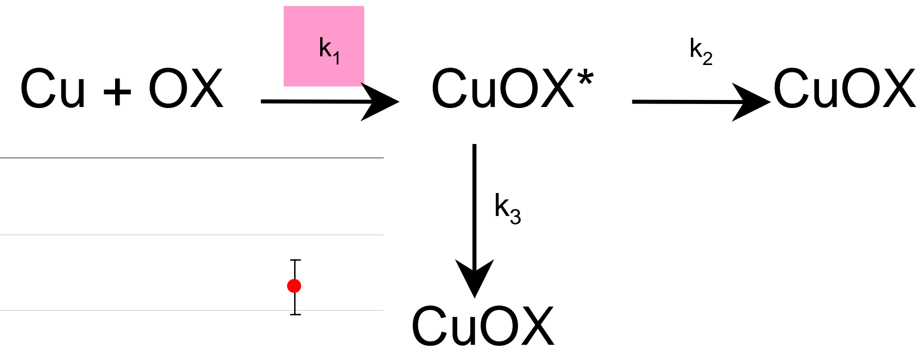
Conclusions

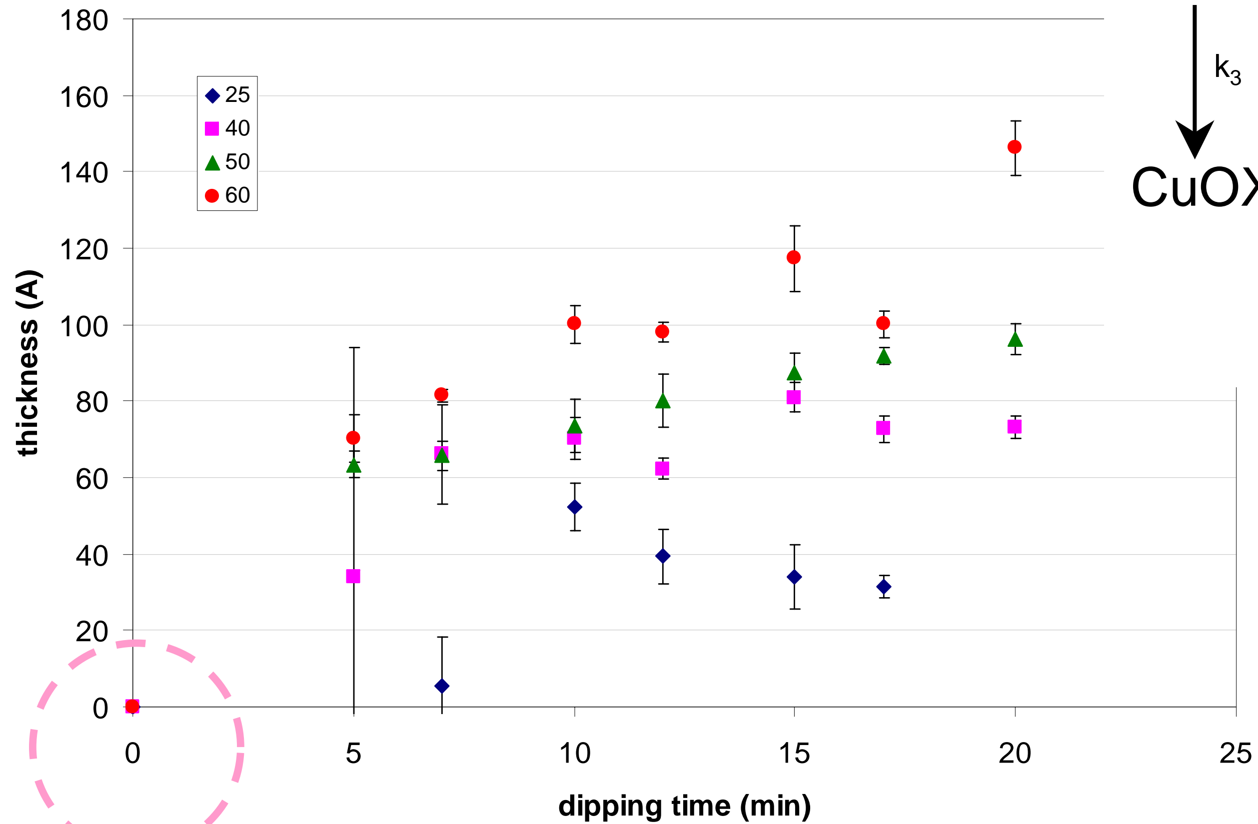
- **Copper film growth occurs at pH = 5 to 6 in H_2O_2 systems**
  - Two or three step models are applicable and should continue to apply at higher pH
  - Dissolution dominates pH 4 H_2O_2 systems so alternative models must be applied
- **The copper surface after CMP consists of little or no oxide**
- **Cu_2O forms at short times**
  - Corroborates previous aqueous- phase work using other oxidants
- **Solid-liquid surface morphology changes with time**
- **At pH values studied, increasing [H_2O_2] increases growth rate**

Topics

- Characterize Cu – H_2O_2 system in general
- Passive film formation as f(T)
- Passive film dissolution as f(T)

Effect of Temperature on Oxidation

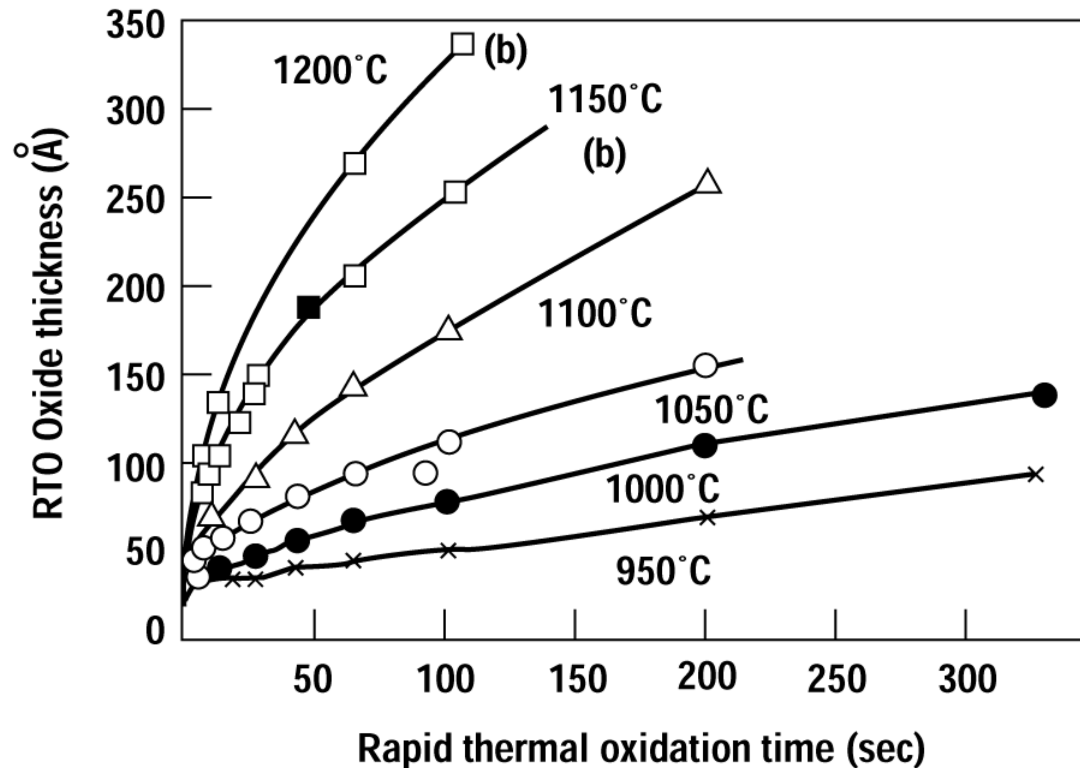




Fast initial growth rates that decrease as film thickens

Is Cu Oxidation Similar to Si?

Typical silicon oxidation trends

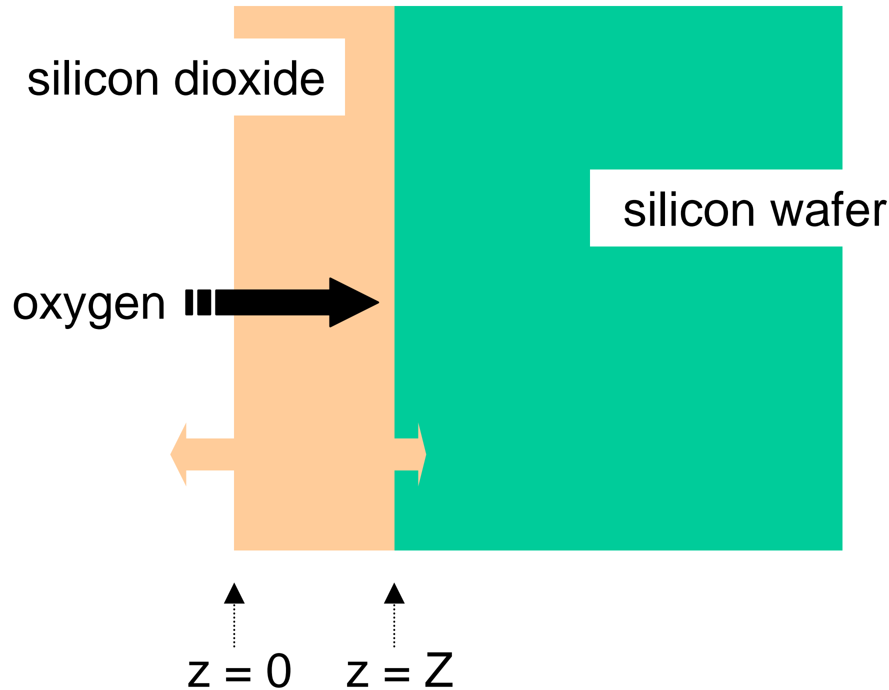


after Mosleh et al. *App. Phys. Lett.* **47**(12) (1985) 1353.

Fast initial growth rates that decrease as film thickens

System has been adequately characterized…examine model development

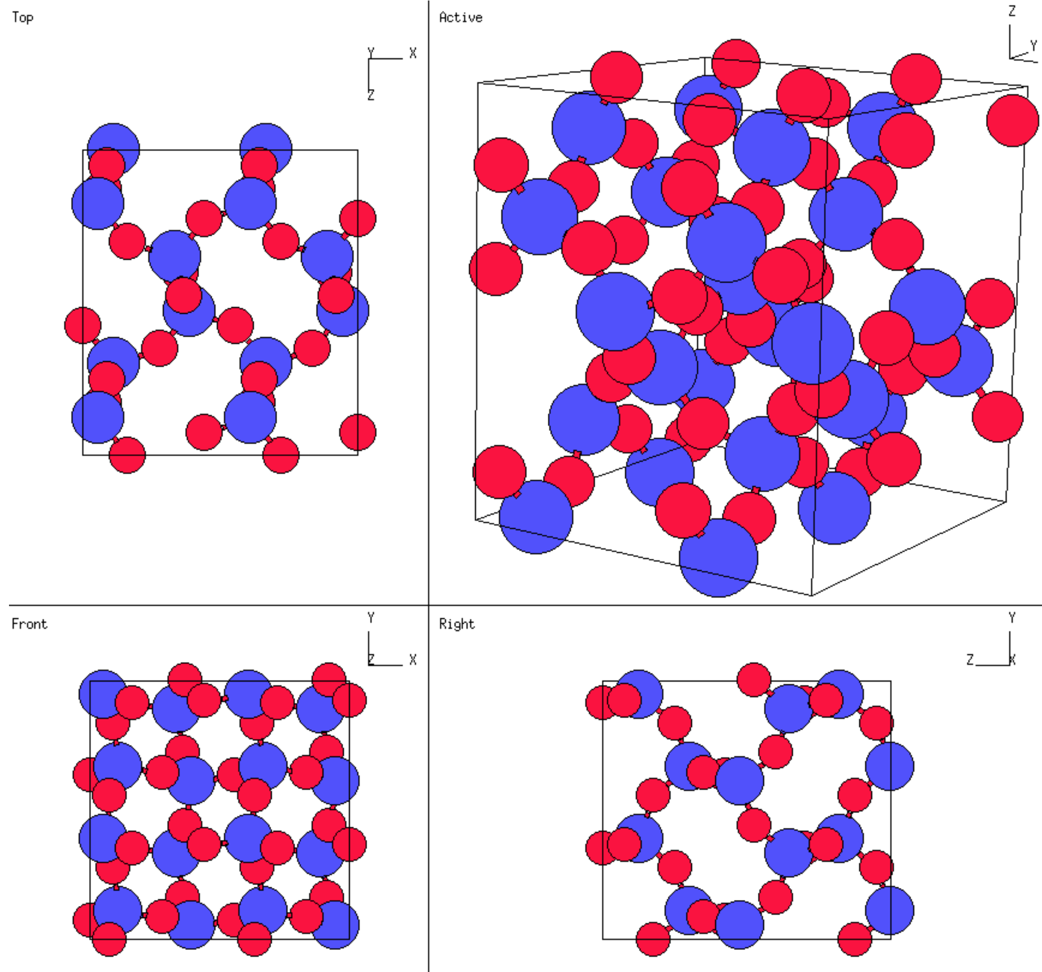
Thermal Oxidation of Silicon



- In order for SiO_2 to form, Si must be consumed
- Two step process:
  - O_2 must reach Si - SiO_2 interface
  - O_2 must react at the Si - SiO_2 interface
- Constantly moving boundaries:
  - Si - SiO_2
  - O_2 - SiO_2 (since ρ [SiO_2] < ρ [Si], for every X thickness of SiO_2 formed, 0.44X thickness of Si is consumed)

$$t - t_o = \left(\frac{1}{kC_s \nu} \right) (Z - Z_o) + \left(\frac{1}{2DC_s \nu} \right) \left(Z^2 - Z_o^2 \right)$$

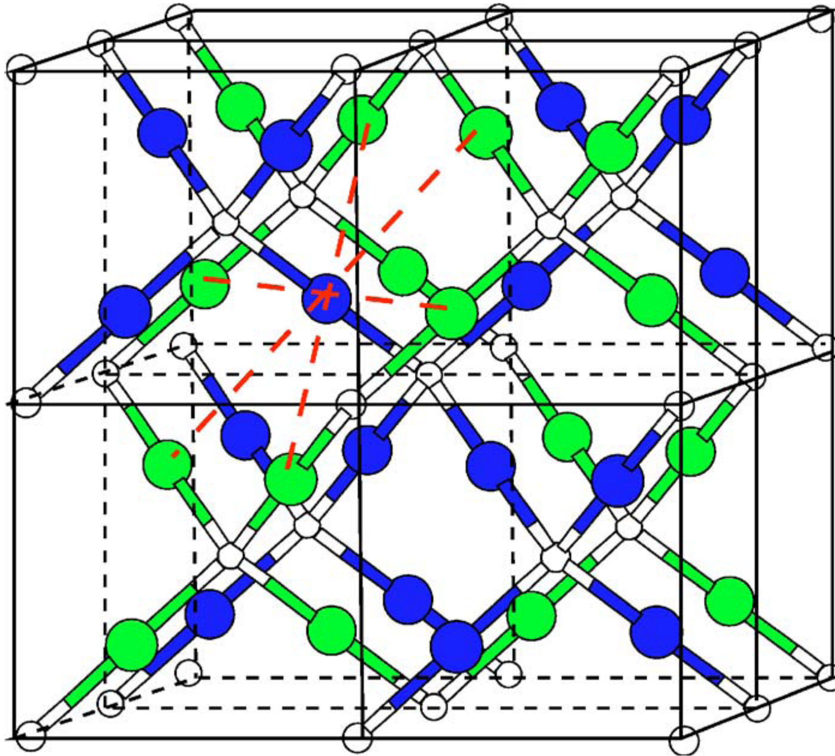
Silicon Dioxide Structure



- network former
- high covalent bond strength
- forms channels (5 – 6 member rings) that **facilitate anion transport**

Cation transport unlikely because cations are tightly held

Cuprous Oxide Structure



after Filippetti et al. *Phys. Rev. B* **72** (2005) 035128.

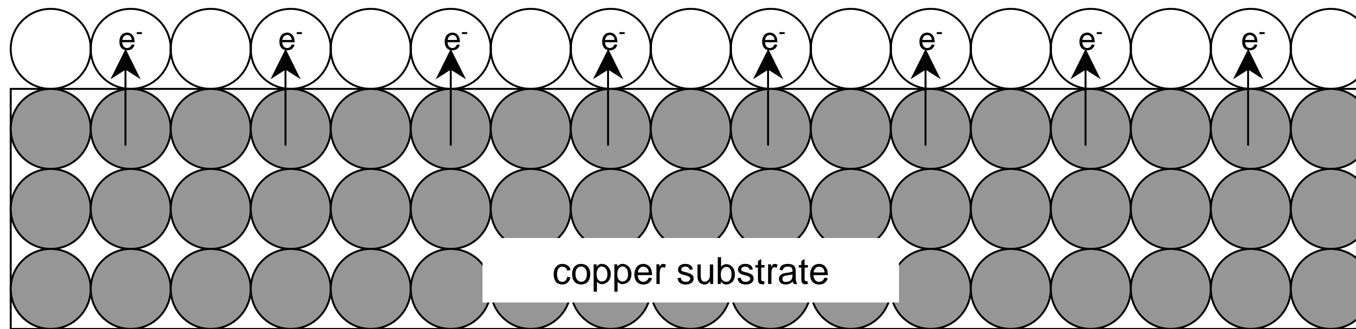
- network modifier
- ionic bonding
- **cations held loosely**
- inter – twined sheets

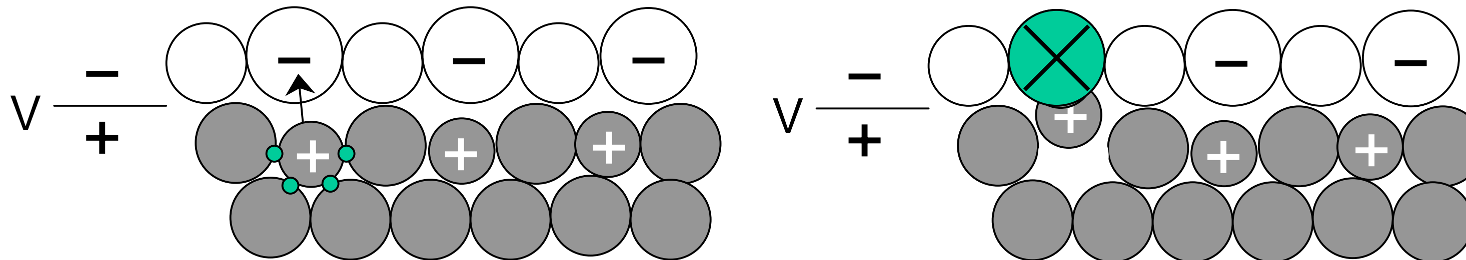
No large channels are likely to exist to facilitate anion transport

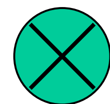
Cations are most likely to move

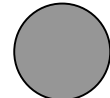
Explains surface morphology and composition changes with time

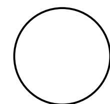
Copper Oxidation Mechanism



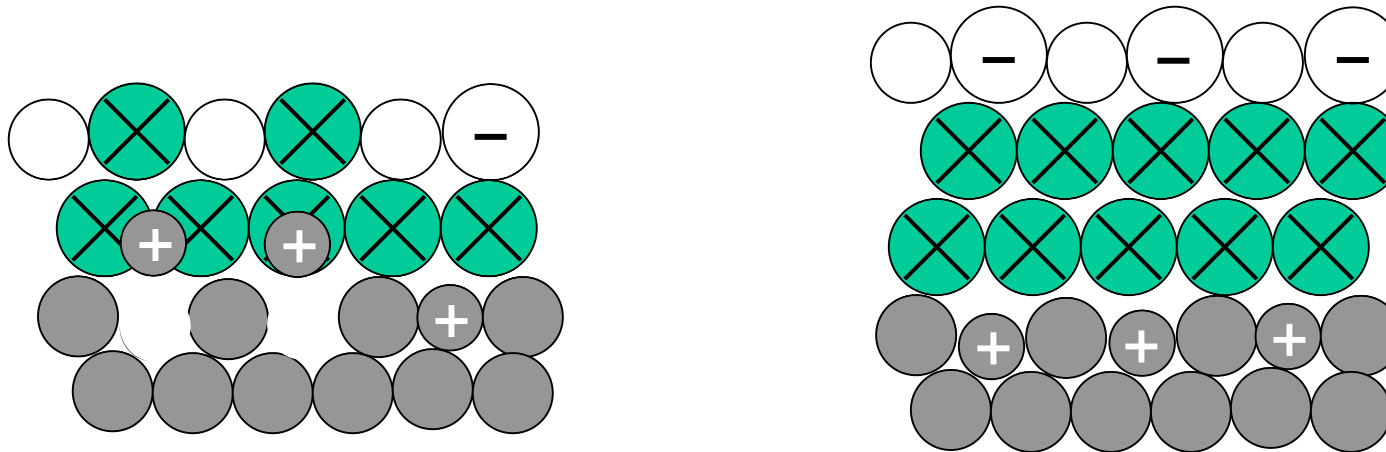


 = Cu_2O

 = Cu

 = oxidant (H_2O_2, O_2, O, etc.)

Copper Oxidation Mechanism



$$\frac{dx}{dt} = N\Omega f \exp\left(\frac{-W}{kT}\right)\exp\left(\frac{qa}{2kTx}V\right)$$

V = potential developed across oxide film

W = sum of the energy of solution of a metal ion in the oxide (U) and the activation energy for the ion to transit from one interstitial position to the the next (U′)

* based on original derivation by N. Cabrera and N.F. Mott: *Rep. Prog. Phys.* **12** (1949) 163.

Model Basis: Drift Velocity

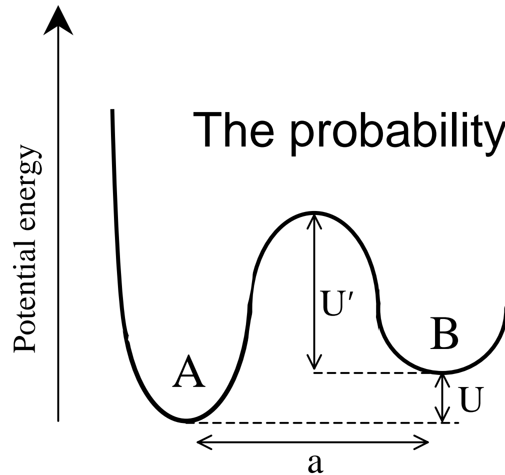
$$\nu = \mu_B E$$

υ = drift velocity

μ_B = ionic mobility

E = electric field

However, for very thin films (10^{-6} cm) the field is so strong that ν is no longer proportional to it.



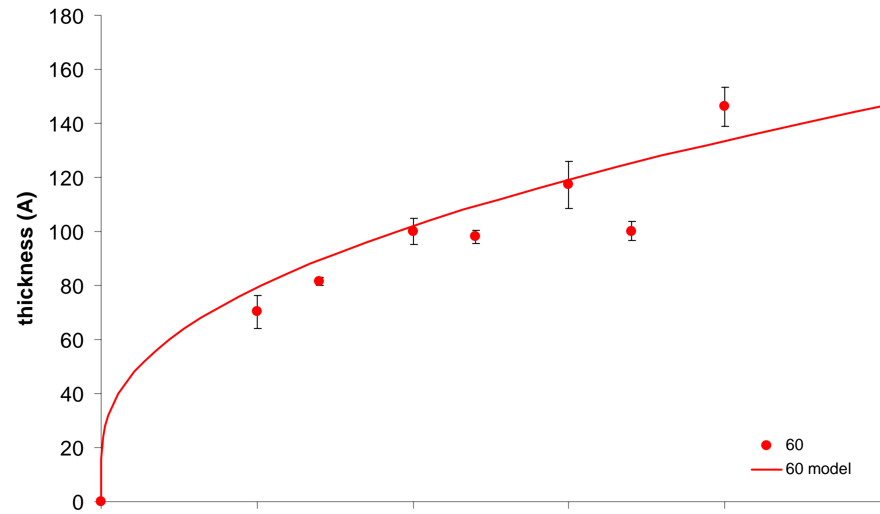
The probability per unit time that an ion will move from one site (A) to another (B) is:

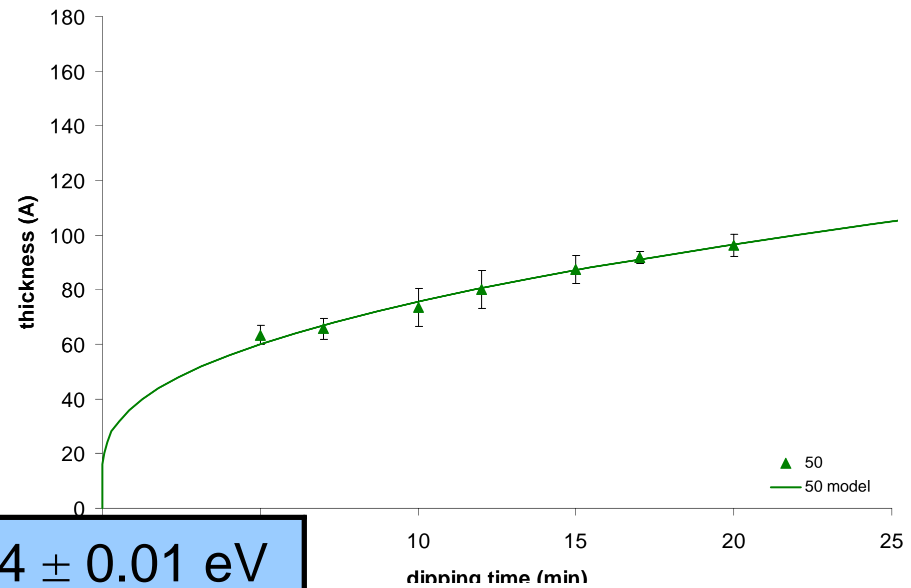
$$p = f \exp\left\{ -\left(\frac{W}{kT} - \frac{qaE}{2kT} \right) \right\}$$

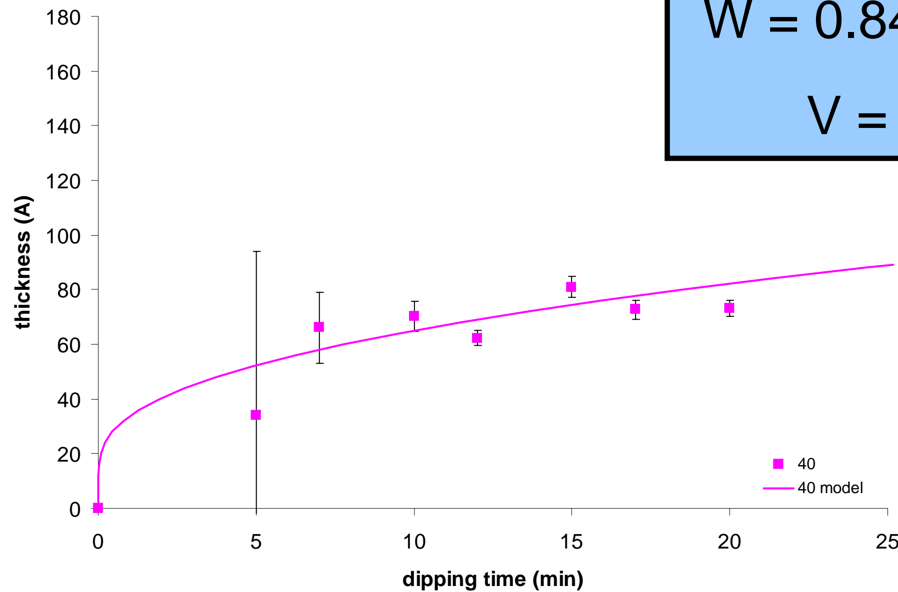
$$\nu = ap$$

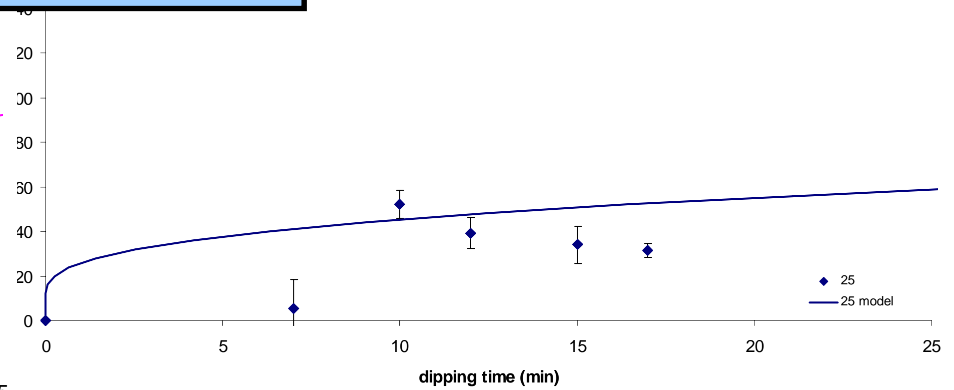
Rate of oxide growth = (volume of oxide per cation) (# cations per area) (p)

Model Evaluation









$W = 0.84 \pm 0.01$ eV

$V = 0.95$ V

Model Evaluation

	oxidant		T(^{o}C) = 8	25	30	40	50	60
Cabrera and Mott*	$O_{2(g)}$	W (eV)		1.0				
1949		V (V)		1.0				
Krishnamoorthy, *et al.*	$O_{2(g)}$	W (eV)	0.9		0.965		1.05	
1970		V (V)	0.5		0.5		0.5	
Current Study	$H_2O_{2(aq)}$	W (eV)		0.831		0.837	0.849	0.85
		V (V)		0.95		0.95	0.95	0.95

** = based on theortical calculations*

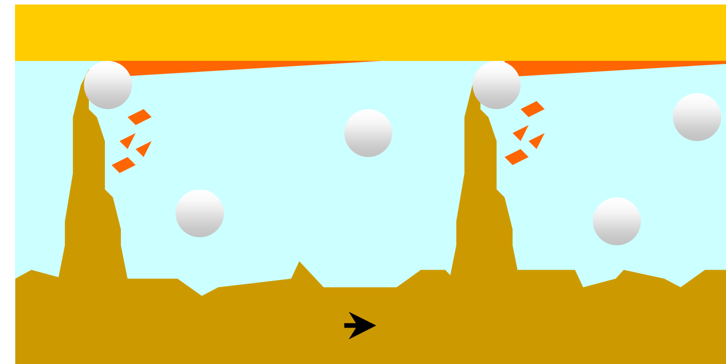
- Values from current study agree well with theoretical values and measured values for historical studies using oxygen
- Suggests that oxidation process at low temperatures and very thin films is not a strong function of oxidizer type
- Slight increase in W (2 kcal) with temperature has been previously observed and attributed to an increase in the energy of the solution in the metal with increasing temperature

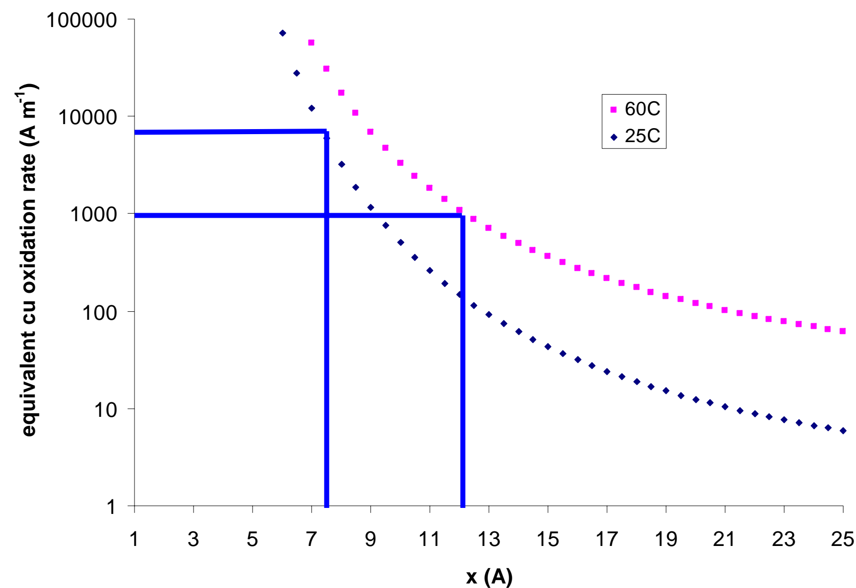
Incorporation into Proposed RR Model

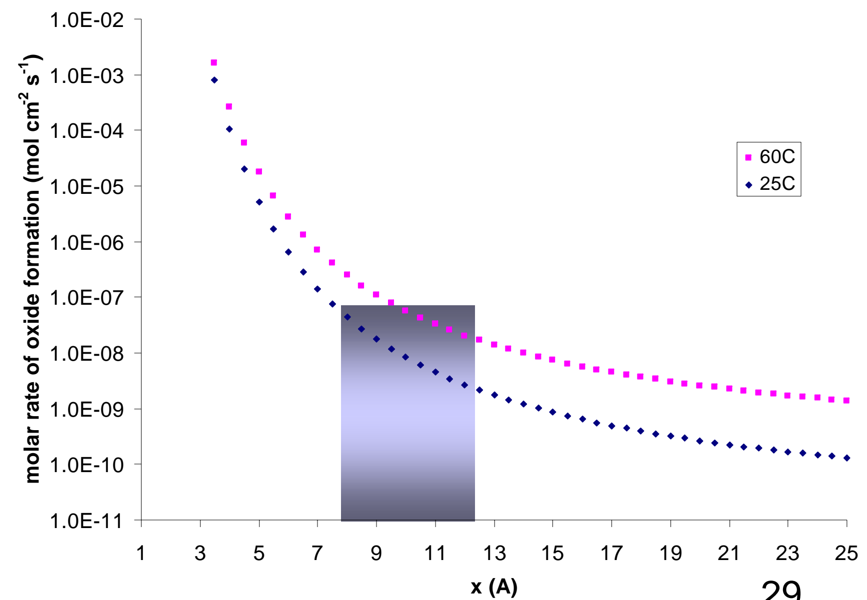
$$\frac{dx}{dt} = N\Omega f \exp\left(\frac{-W}{kT}\right)\exp\left(\frac{qa}{2kTx}V\right)$$

Typical Cu RR:

1000 – 7000 A/min







Topics

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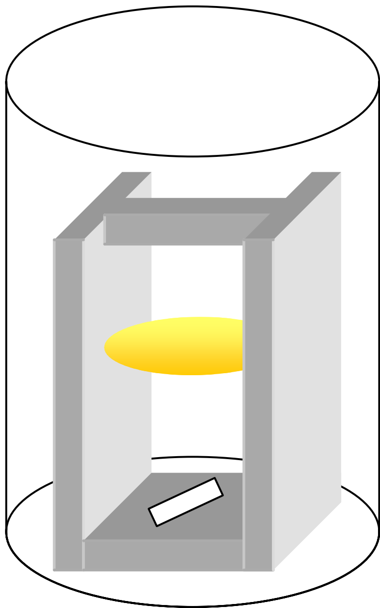
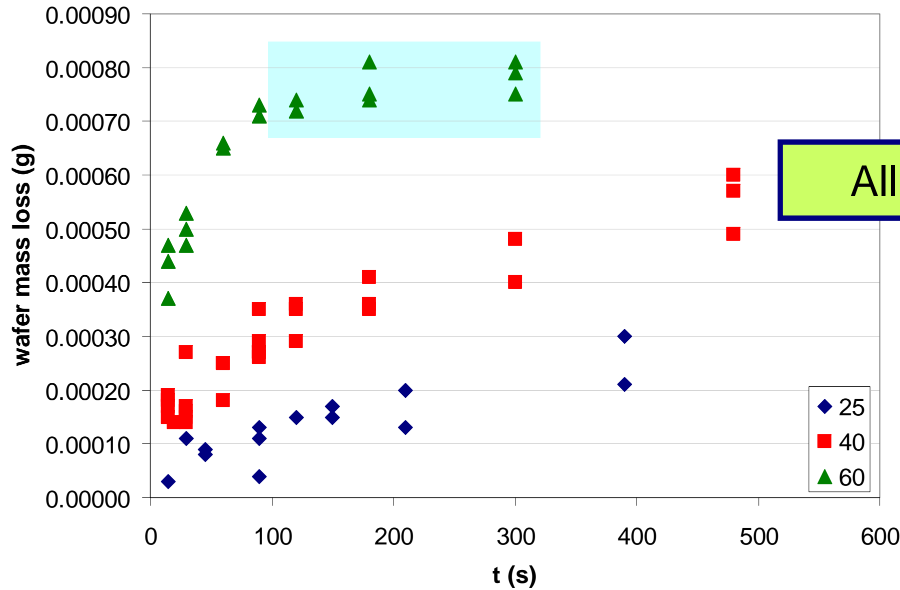
- Passive film dissolution as f(T)

Experimental

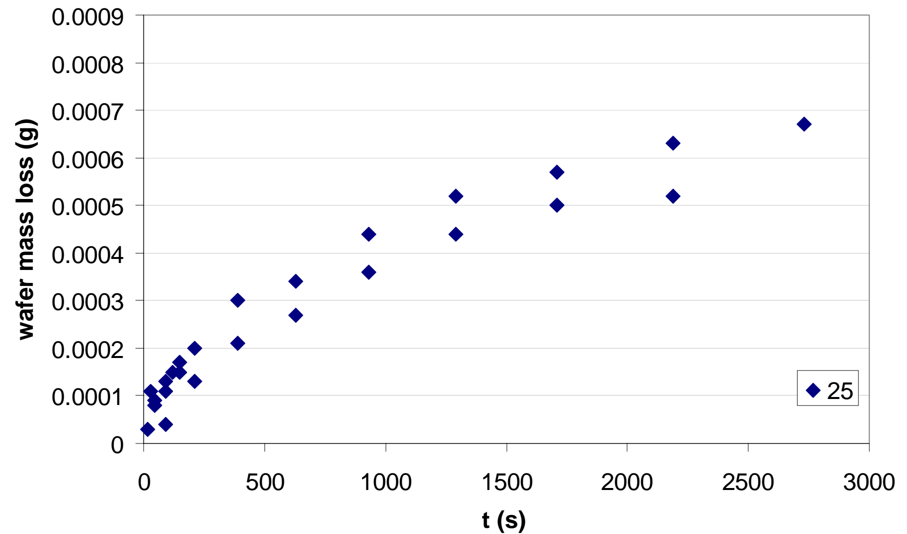


- CMP before each test to remove native oxides
- Cu/TaN/SiO_2/Si stacked wafers
- 170 A oxide grown using H_2O_2
- Oxidized wafers were submerged into stirred slurry solution ***without*** H_2O_2 to monitor etching characteristics

Copper Oxide Dissolution Profiles

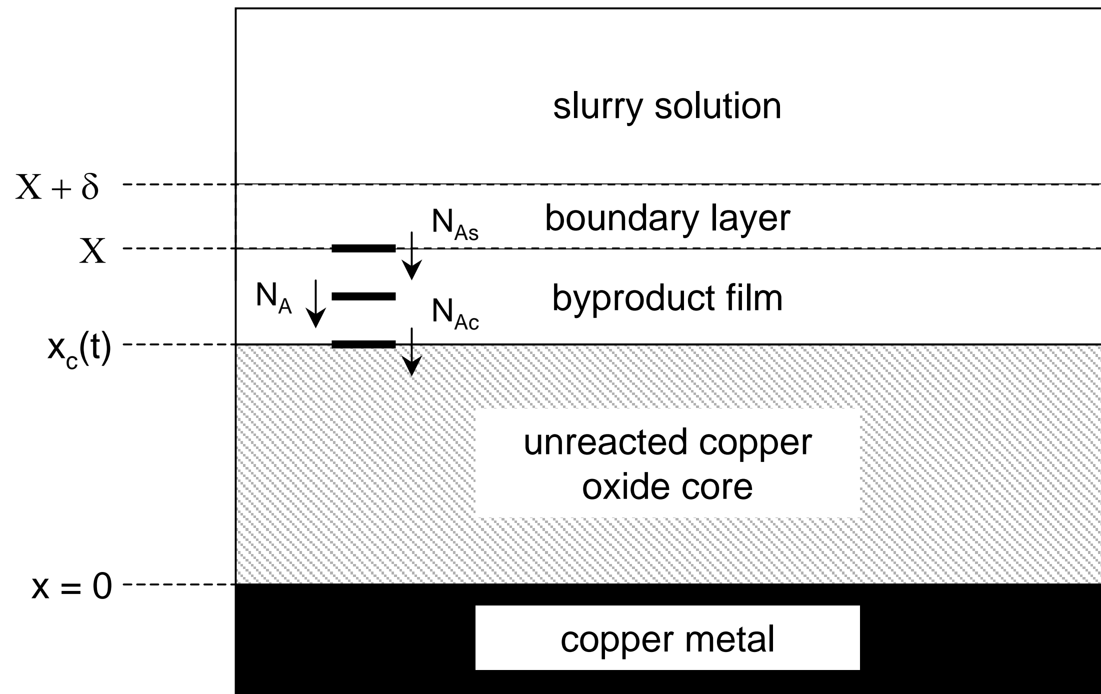


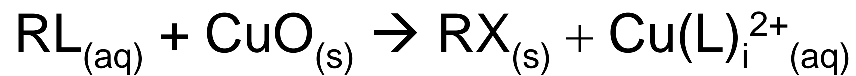
All etchable oxide reacts in 90s for 60°C



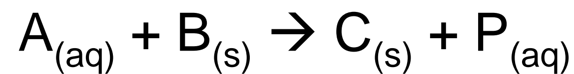
At long times low T profiles approach saturation

Dissolution Process





$$RL_{(aq)} + CuO_{(s)} \rightarrow RX_{(s)} + Cu(L)_i^{2+}{}_{(aq)}$$



$$A_{(aq)} + B_{(s)} \rightarrow C_{(s)} + P_{(aq)}$$

- A soft byproduct film was observed on wafer surface
- Film was present after long times
- Controlling Mechanisms
  - Surface reaction
    - Linear profile
  - Diffusion through BL
    - Reported that profiles are not a function of stirring speed
  - **Diffusion through byproduct**

Model Development

QSS Assumption:

Diffusion of A through the byproduct layer is fast compared to dx/dt

Flux of A at any x: $N_A = -D\frac{dC_A}{dx}$

$$\frac{dn_A}{dt} = \frac{\pi d^2}{4} N_A$$

General mol balance: $dn_B = dn_A = \rho_B dV = \frac{\rho_B \pi d^2}{4} dx_C$

Dissolution time: $t = \frac{\rho_B X^2}{2DC_{AS}}\left(\frac{x_C}{X} - 1\right)^2$

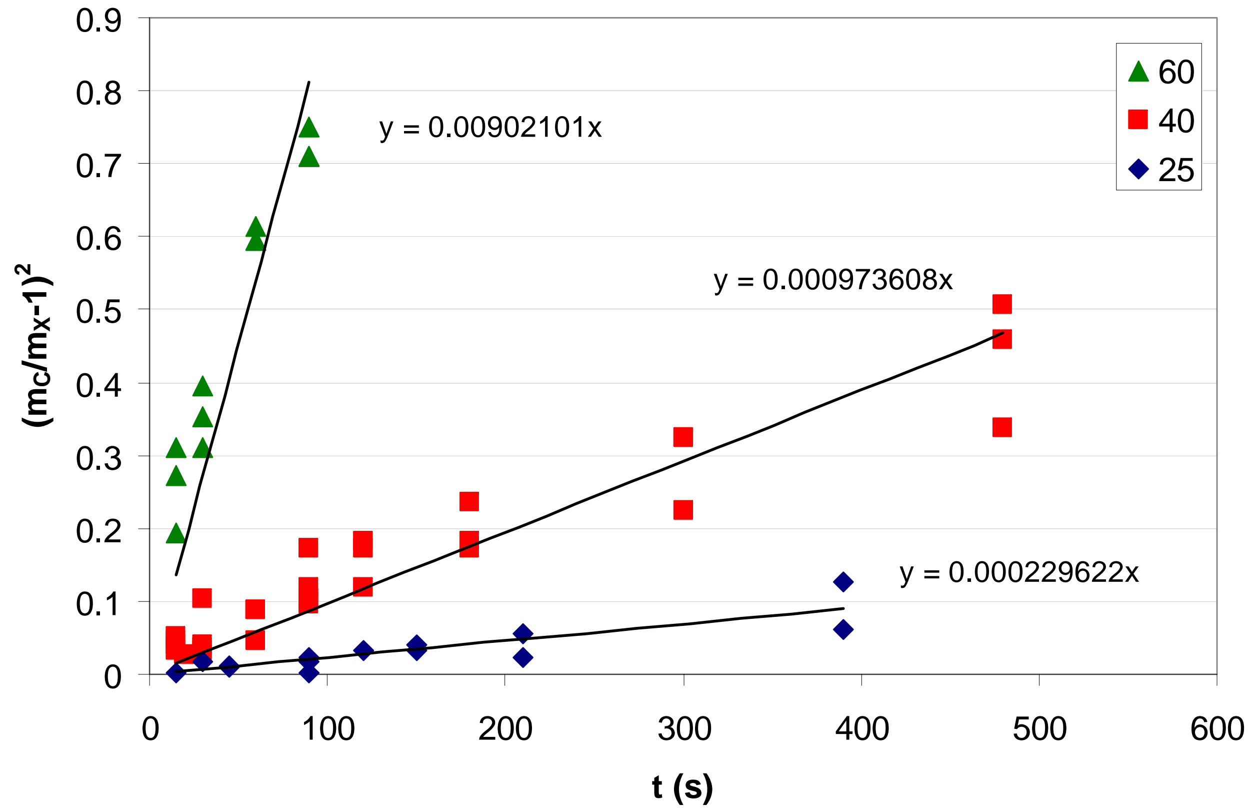
$$\tau = \frac{\rho_B X^2}{2DC_{AS}}$$

$$DC_{AS} = A\exp\left(-\frac{E_a}{RT}\right)$$

$$m_{wi} - m_{wf} \cong m_X - m_C = m_X\left(\frac{t}{\tau}\right)^{0.5}$$

Application of Model

$$t = \tau\left(\frac{m_C}{m_X} - 1\right)^2$$



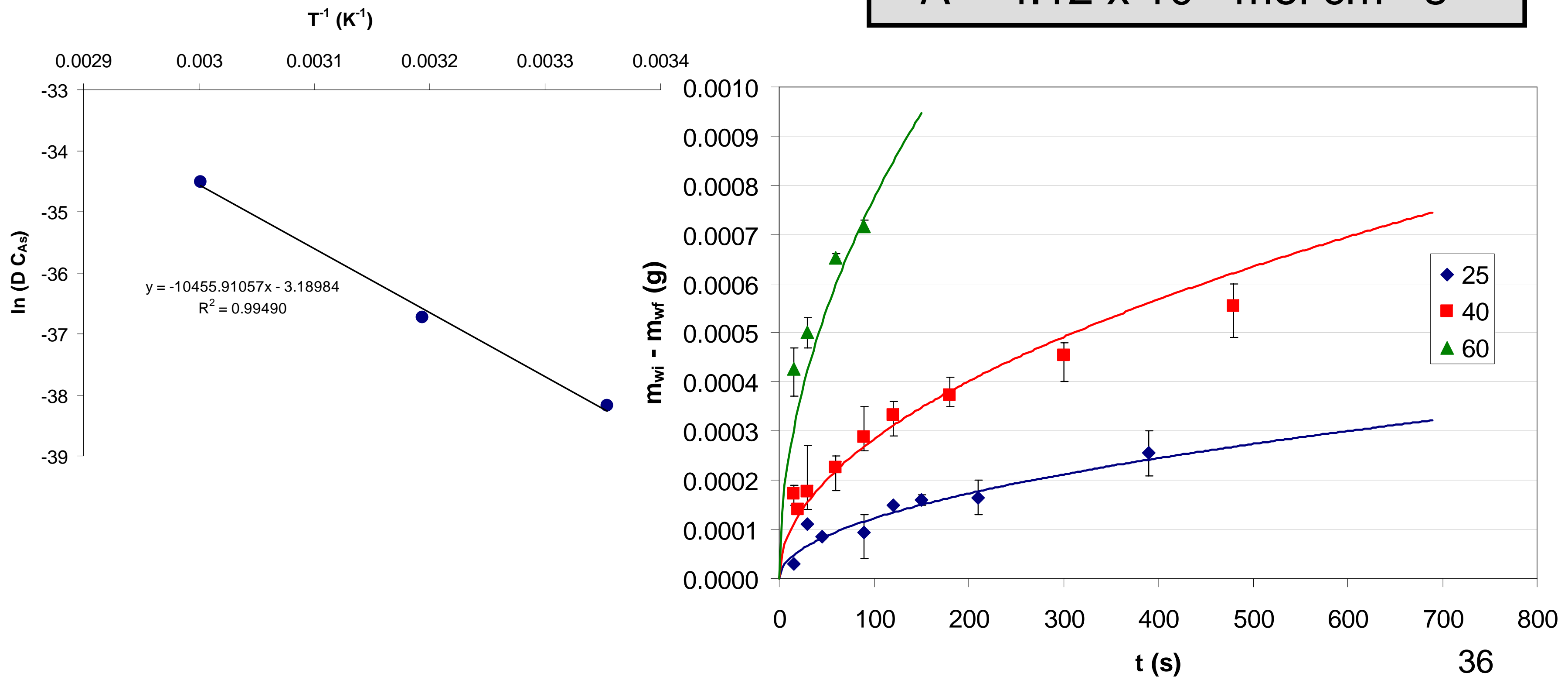
Model Comparison

T (°C)	$1/\tau$ (s^{-1})	τ (s)	D C_{As} (mol cm^{-1} s^{-1})
25	2.30E-04	4.35E+03	2.63E-17
40	9.74E-04	1.03E+03	1.12E-16
60	9.02E-03	1.11E+02	1.03E-15

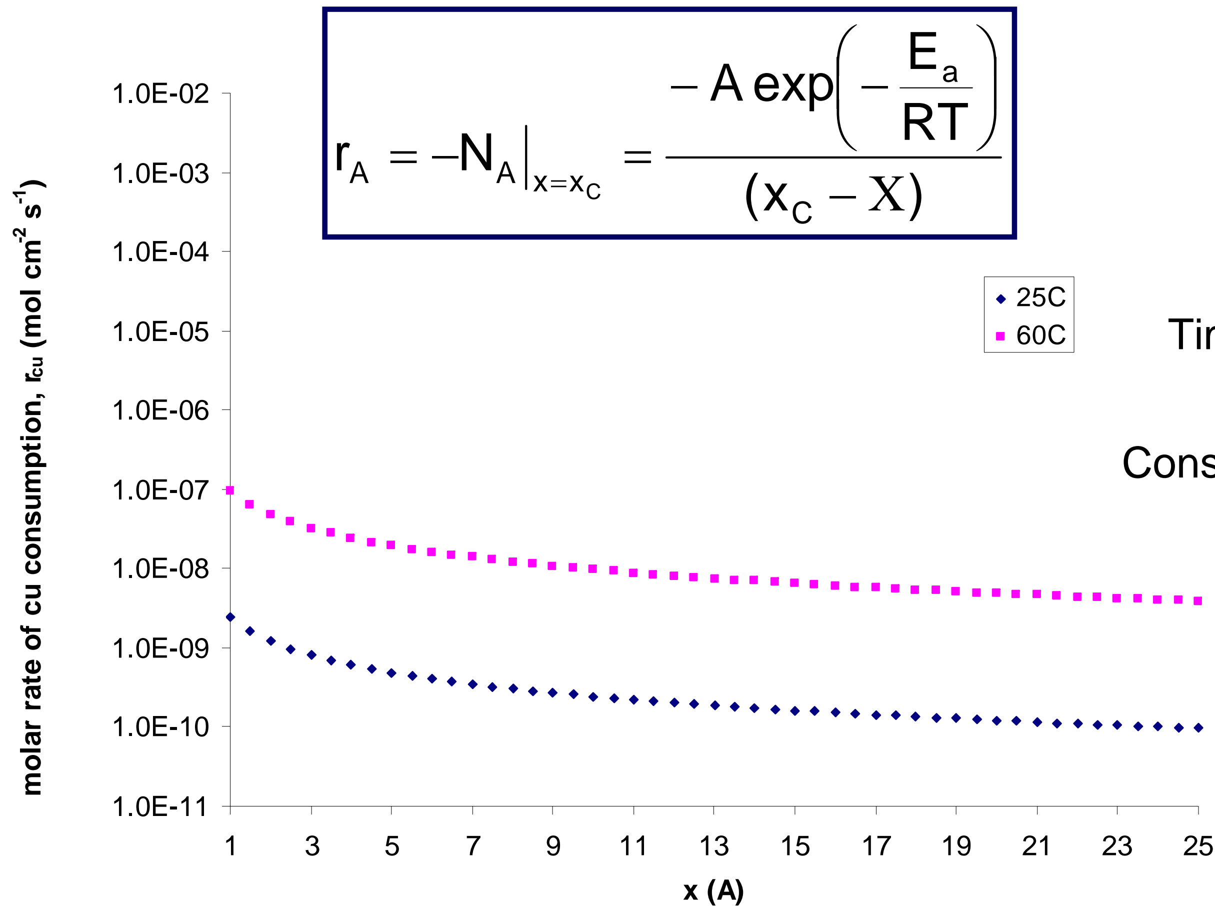
Model Parameters:

$E_a = 86.9$ kJ mol^{-1}

$A = 4.12 \times 10^{-2}$ mol cm^{-1} s^{-1}



Incorporation into Proposed RR Model

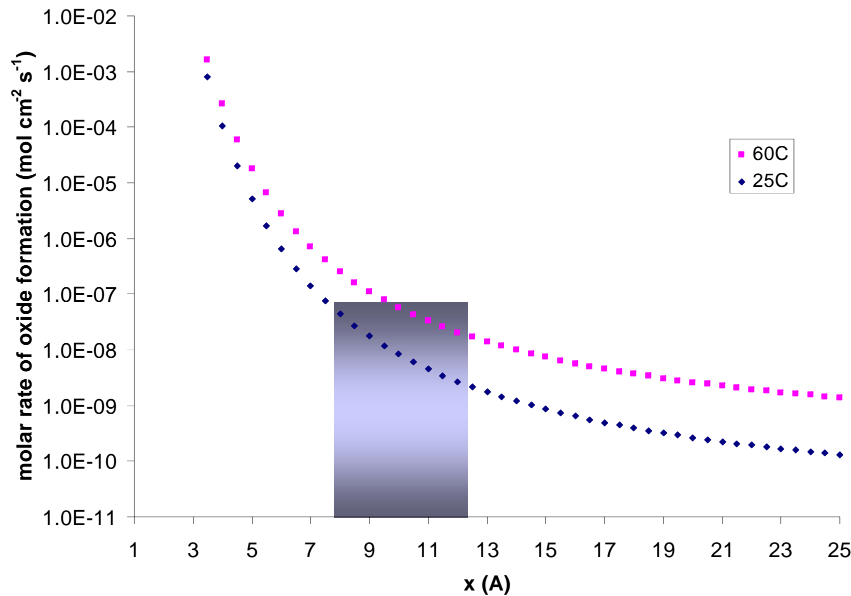


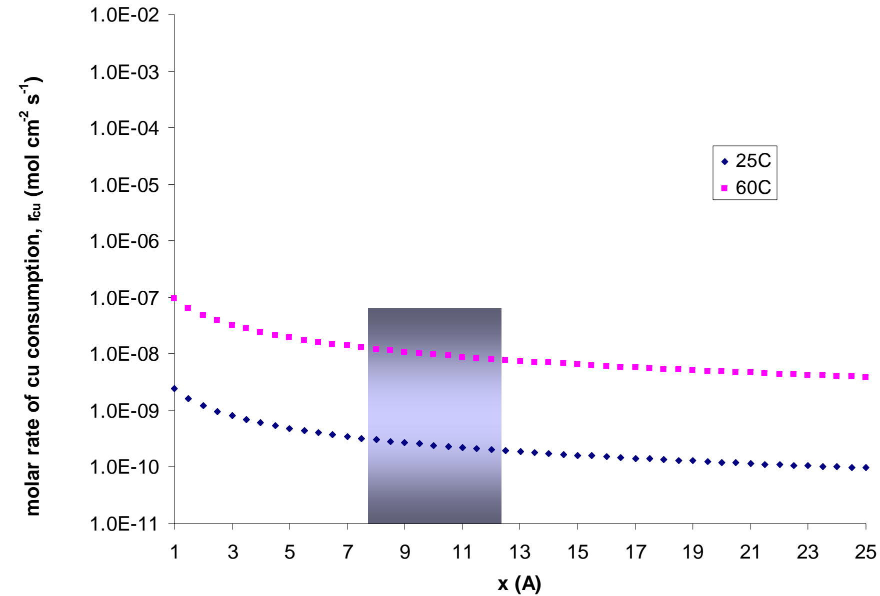
QSS Check

Time required for A to diffuse through 100 A = **1s**

Consumption time for 100 A oxide = **80s**

Rate Comparison of Steps 1 and 3

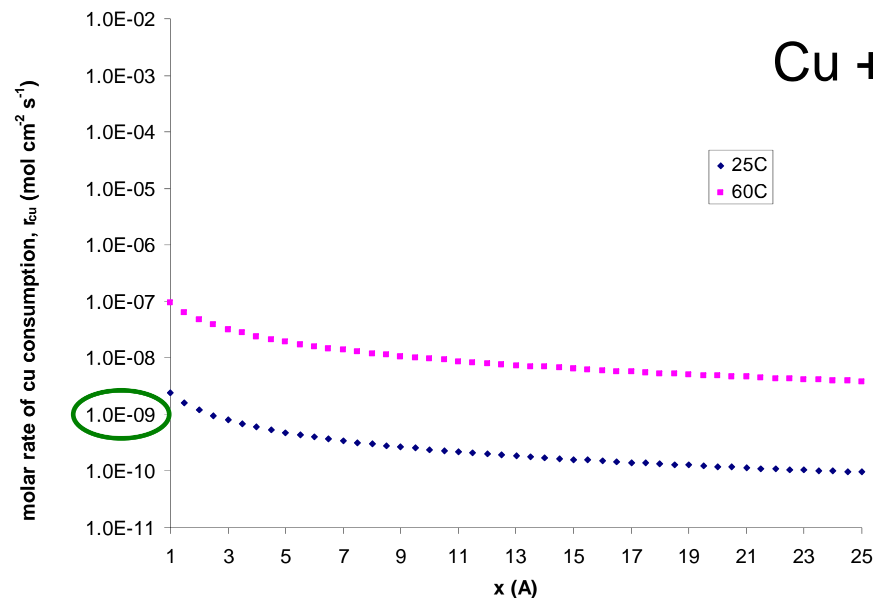


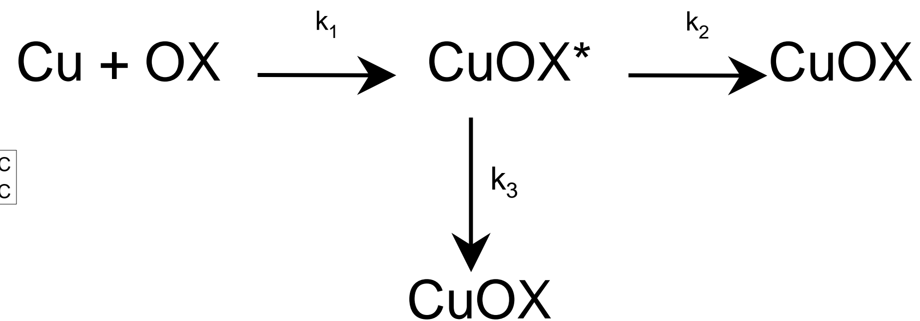


- Oxidation is faster than dissolution for oxide thicknesses of interest, which should be the case
  - Ox. rates must be high enough to facilitate CMP RR of 10000 A min^{-1}
- Dissolution could be considered constant
- Oxidation is a strong function of thickness
- How do these de-coupled steps compare to a process with oxidation and dissolution taking place simultaneously?

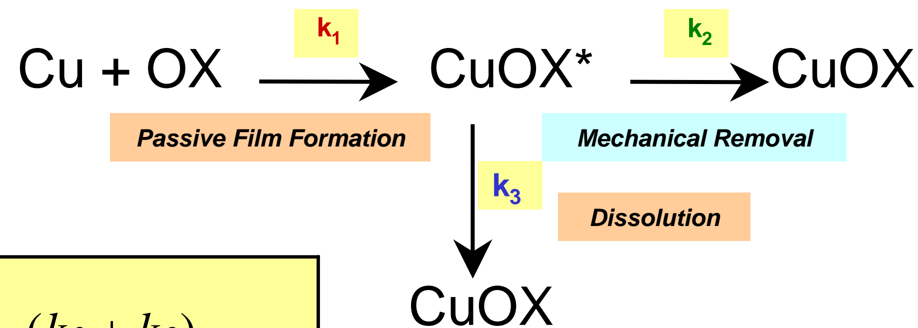
Combined Oxidation and Dissolution

- Copper wafers were exposed to **CMP slurry solution + 1 wt% H_2O_2**
- Observed static etch rates are on the order of **10^{-9} mol Cu cm^{-2} s^{-1}** (150 A min^{-1}), which compare well with the dissolution model
- Verifies that the oxidation and dissolution processes can be decoupled





3-Step Model

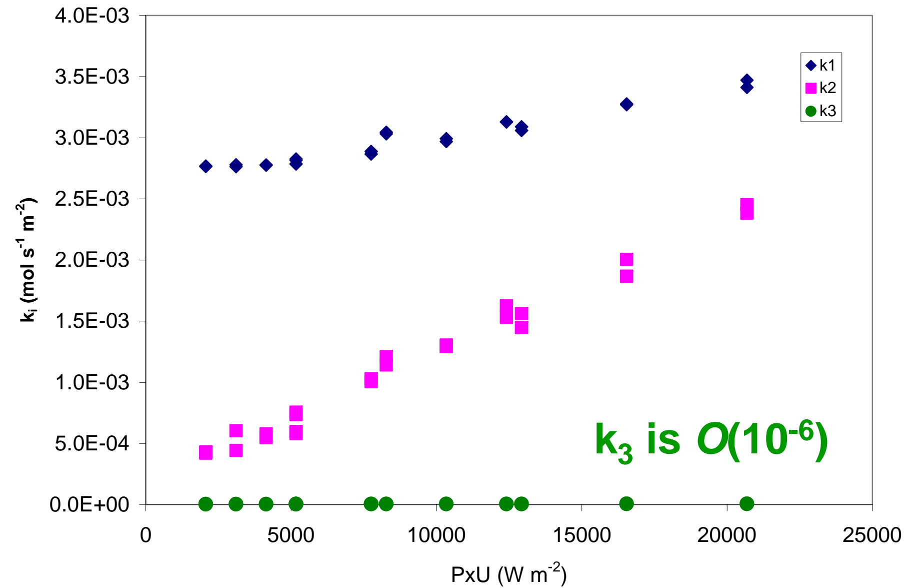


$$RR = \frac{M_w}{\rho} \cdot \frac{k_1 \cdot (k_2 + k_3)}{k_1 + k_2 + k_3}$$

$$k_1 = \frac{\rho_{ox}}{MW_{ox}} \cdot (N \cdot \Omega \cdot f) \cdot \exp\left(\frac{-W}{k \cdot \overline{\overline{T_p}}}\right) \cdot \exp\left(\frac{q \cdot a}{2 \cdot k \cdot \overline{\overline{T_p}} \cdot x} \cdot \mathrm{E}\right)$$

$$k_2 = c_p \cdot \mu_k \cdot (p \cdot V)$$

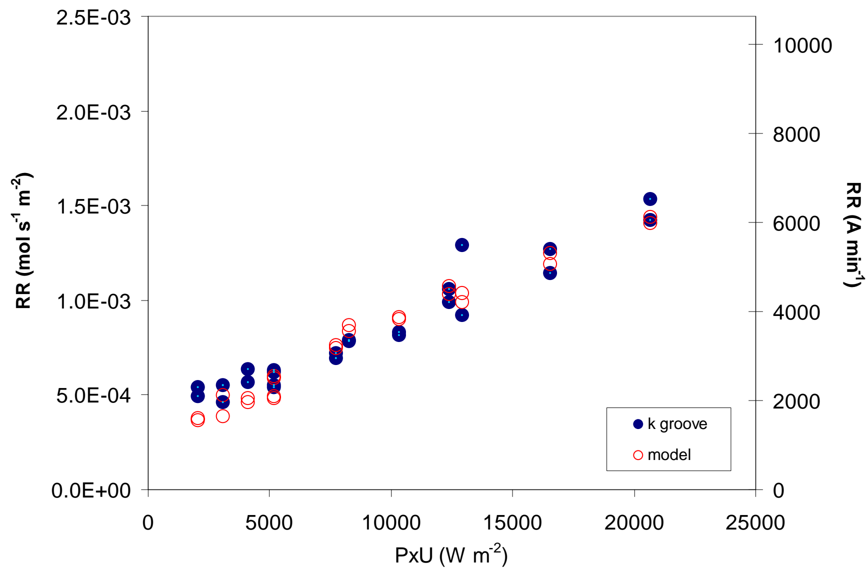
$$k_3 = \frac{-A \cdot \exp\left(-\frac{E_a}{R \cdot \overline{\overline{T_p}}}\right)}{(x_C - \mathrm{X})}$$

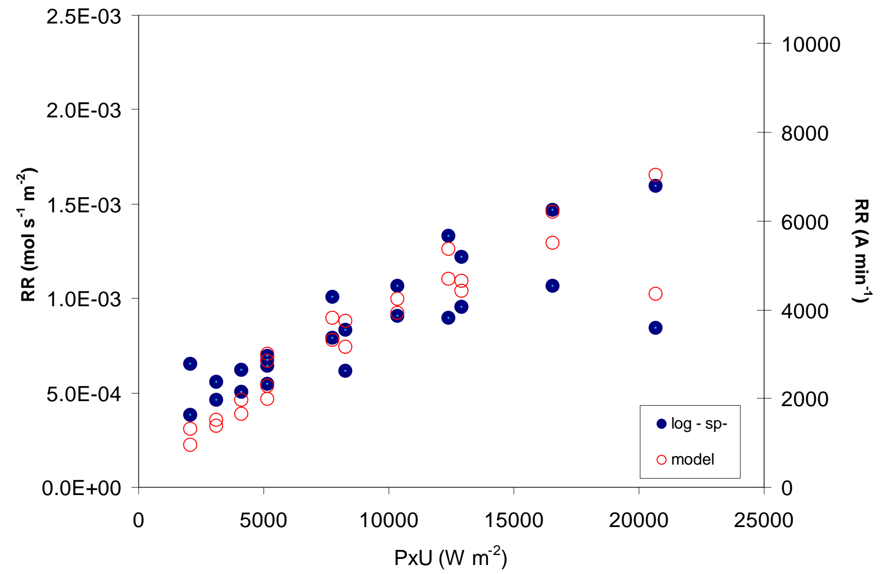


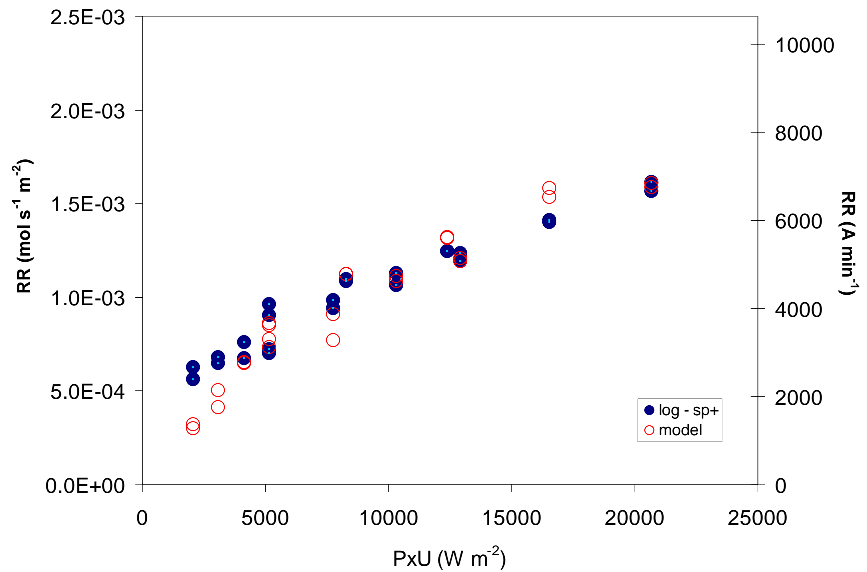
Dissolution rate (k_3) was found to be negligible for Fujimi PL-7102 system at the *pressure* and *velocity* conditions used in this study

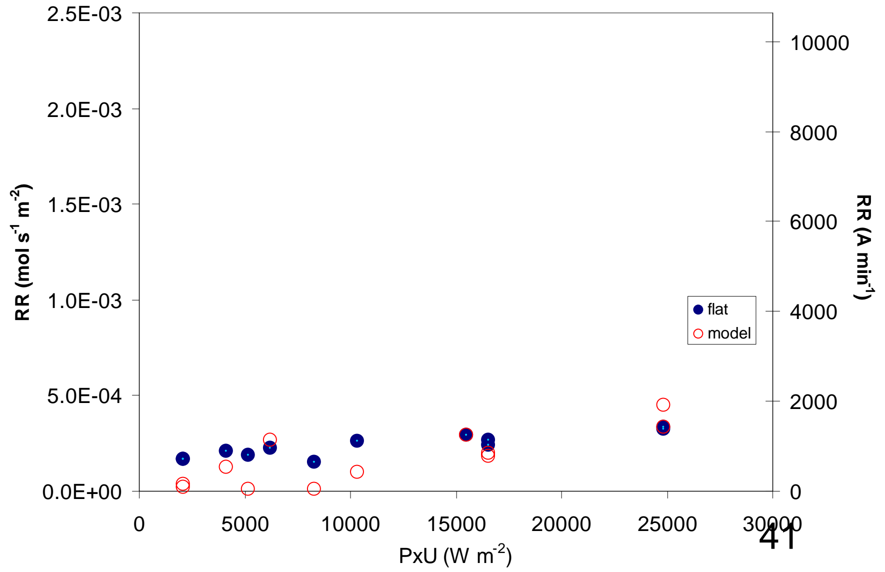
However it becomes more important as *pressure x velocity* approaches zero

Comparison of RR Data to Model



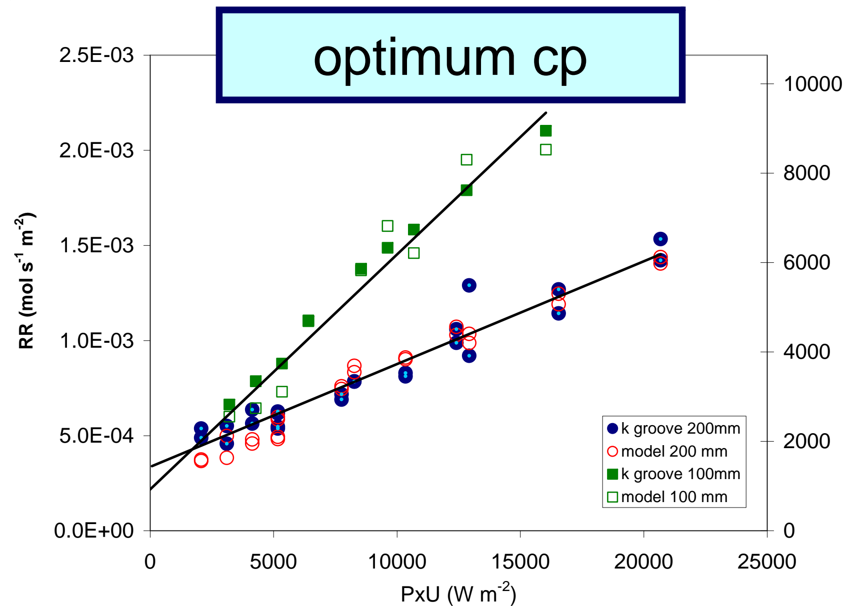


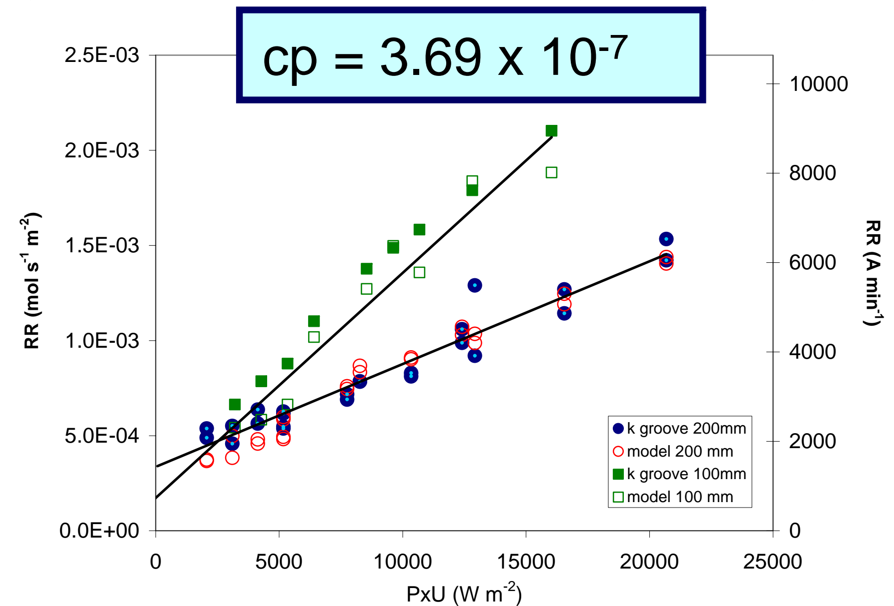




RMS Error and Sensitivity

	3 - Step Model *(Eqs. 6.5.1, 3-5)*		2 - Step Flash Heating	Prestonian Fit	Repeatibility
No. Fitting Parameters	*1*		*5*	*2*	
	cp x 10^7 (mol J^{-1})	RMS (A min^{-1})	RMS (A min^{-1})	RMS (A min^{-1})	RMS (A min^{-1})
IC1000 k - groove 200mm	3.69	397	314	332	340
IC1000 k - groove 100mm	4.19	471		283	
Log (-) Spiral (-)	2.84	591	416	768	1103
Log (-) Spiral (+)	3.24	545	340	290	172
IC1000 flat	4.80	470	440	108	





CMP Model Summary

Preston's Model

$$RR = K \cdot (PU) + b$$

- 2 Fitting parameters.
- No real-time measurements can be used to predict the removal rate of a wafer being polished.
- The intercept does not predict RR in the absence of applied P and U

2-Step with Flash Heating Model

$$RR = \frac{M_w}{\rho} \cdot \frac{k_2 \cdot k_1}{k_2 + k_1}$$

$$k_1 = A \cdot \exp\left(\frac{-E_a}{R \cdot T_w}\right)$$

$$k_2 = c_p \cdot \mu_k \cdot (PU)$$

$$\Delta \bar{T}_f = \frac{\beta}{V^{1/2+e}} \cdot \mu_k \cdot (PU)$$

- Real-time measurements can be used to predict the removal rate of a wafer being polished.
- 5 Fitting parameters.
- Characterization of k_1 using an Arrhenius is over-simplified
- Not applicable at PxU = 0

3-Step Model

$$k_1 = \frac{\rho_{ox}}{MW_{ox}} \cdot (N \cdot \Omega \cdot f) \cdot \exp\left(\frac{-W}{k \cdot T}\right) \cdot \exp\left(\frac{q \cdot a}{2 \cdot k \cdot T \cdot x} \cdot E\right)$$

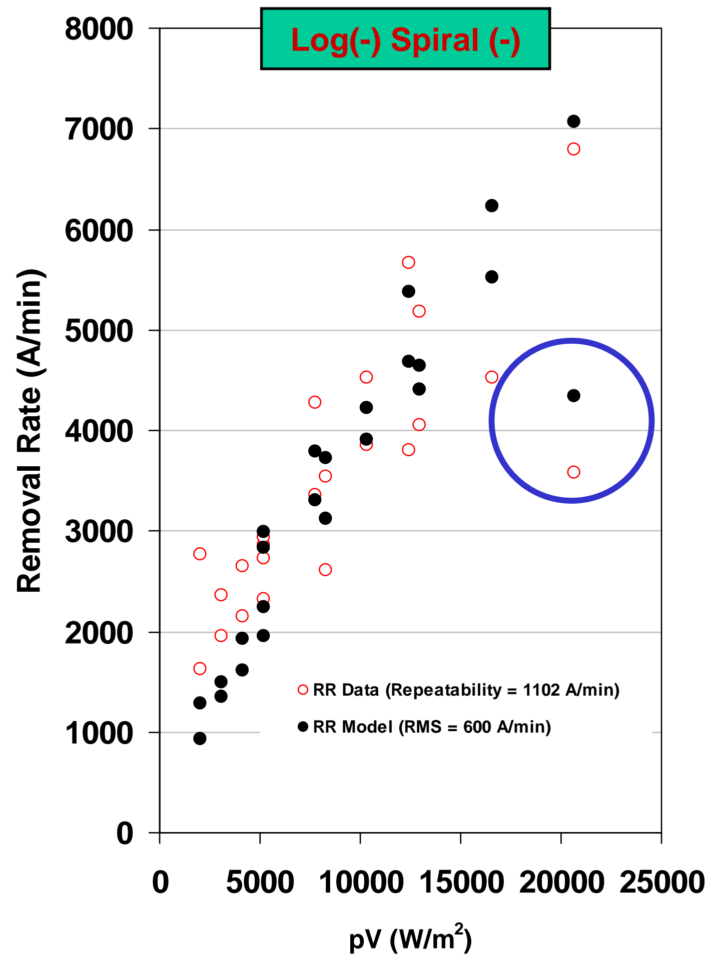
$$RR = \frac{M_w}{\rho} \cdot \frac{k_1 \cdot (k_2 + k_3)}{k_1 + k_2 + k_3}$$

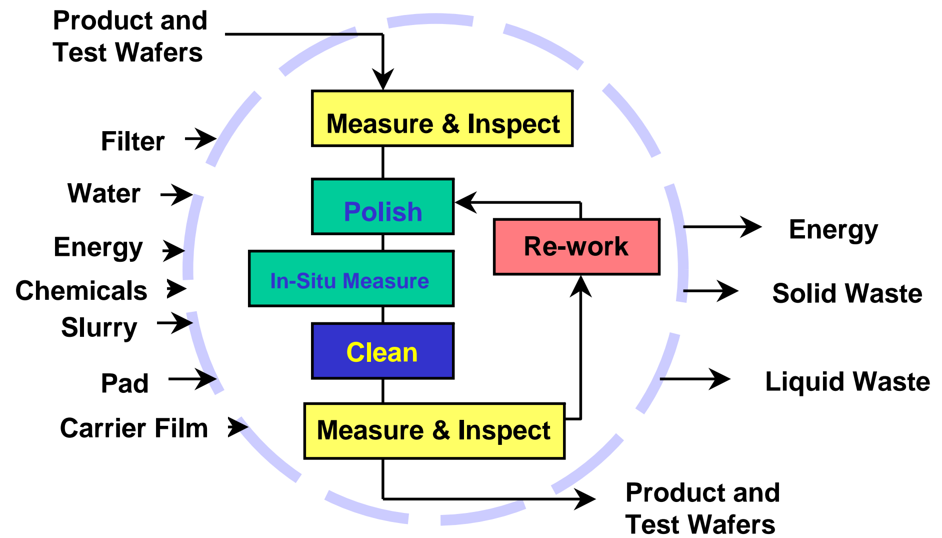
$$k_2 = c_p \cdot \mu_k \cdot (PU)$$

$$k_3 = \frac{-A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right)}{(x_C - X)}$$

- Real-time measurements can be used to predict the removal rate of a wafer being polished.
- 1 Fitting parameter.
- Characterization of k_1 shows dependence of oxide growth on oxide thickness.
- Applicable at PxU = 0.
- Oxide dissolution is controlled by diffusion of complexant agent through by-product film.

Applicability of 3-Step Model in copper CMP





Prediction of process failure with in-situ measurement of temperature and COF

Overall Conclusions

- A 3-step RR mechanism has been developed which separates chemical and mechanical contributions to removal
  - Very useful for evaluating ‘how chemical or mechanical’ a given consumable set is
- The Cu oxidation process using 1 wt% H_2O_2 has been characterized
  - Two modeling parameters relating to the potential across the oxide film and the energy required for cation migration have been determined.
  - The oxidation process may be a weak function of $[H_2O_2]$ allowing results from this study to be applied to other $[H_2O_2]$
- The copper oxide dissolution process has been characterized for Fujimi PL7102 Cu CMP slurry
  - Two Arrhenius parameters have been determined that adequately describe the process found to be controlled by diffusion of the aqueous reacting species through a reaction byproduct film
- The dissolution process is controlling in static (no mechanical abrasion by pad or slurry particles) systems
- Rates predicted using the de-coupled oxidation and dissolution models developed here agree well with measured results of the combined system where dissolution and oxidation occur simultaneously

Overall Conclusions (cont.)

- With Steps 1 and 3 characterized, the only parameters that need to be extracted from RR data are those associated with Step 2 (mechanical removal)
- Oxidation model suggests that passivation layers formed during CMP are 8 to 12 A thick to facilitate removal rates on the order of 1000 to 6000 A min^{-1}
- The novel method outlined here for separately determining chemical contributions to the CMP process is crucial in slurry development and commercial slurry evaluation
- These methods could be easily implemented in determining the removal rate contributions of surfactants, inhibitors, and other additives to the CMP process
- The three-step model agrees well with removal rate data demonstrating slightly higher RMS error than using models that have a higher number of parameters
- The form of the three-step model has been shown to be very sensitive to changes in experimentally measured temperature and COF, but relatively insensitive to changes in c_p

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