Chemistry and Electrochemistry of Copper CMP – Capturing their Influence at the Feature and Bulk Levels

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Outline

- Introduction – objective of FLCC effort in CMP
- Passive layers and their importance
  - Anomalous passivity induced by hydrogen peroxide
- EQCM studies of passive films
  - Relationship to other literature
  - Capturing behavior in models
- Galvanic interactions
  - How best to apply in feature scale models
- Conclusions
Aim

- Insure uniform, global planarization with no defects by means of optimized process recipes and consumables
- Idealized single-phase CMP processes are now well understood in terms of the fundamental physical-chemical phenomena controlling material removal
- The challenge is to extend this to heterogeneous structures that are encountered when processing product wafers with device features
Approach

• Our approach is to develop integrated feature-level process models linked to basic process mechanics

• These models will drive process optimization and the development of novel consumables to minimize feature-level defects and pattern sensitivity

• For this, we will require the capability of faithfully predicting defects and non-idealities at feature boundaries.
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Passive films, or corrosion inhibitors, are key to attaining planarization.

Kaufman’s Model for Planarization

For effective planarization, must maintain higher removal at protruding regions and lower removal at recessed regions on the wafer.

1- removal of passivating film by mechanical action at protruding areas
2- wet etch of unprotected metal by chemical action. Passivating film reforms
3- planarization by repetitive cycles of (1) and (2)
Chemistry of Copper-Water System

Potential-pH diagram, with \( \{\text{Cu}_T\} = 10^{-4} \) or \( 10^{-6} \), 4% \( \text{H}_2\text{O}_2 \) or 0.5M hydroxylamine

Tamilmani, Huang, Raghavan & Small, JECS, 2002

Potential-pH diagram, with \( \{\text{Cu}_T\} = 10^{-5} \)

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Chemistry of Glycine-Water System

\[ \text{pK}_{a1} = 2.350 \]
\[ \text{pK}_{a2} = 9.778 \]

\[ +\text{H}_3\text{NCH}_2\text{COOH} \rightleftharpoons +\text{H}_3\text{NCH}_2\text{COO}^- \]
\[ \text{Cation: } \text{H}_2\text{L}^+ \]
\[ \text{Zwitterion: } \text{HL} \]
\[ \text{Anion: } \text{L}^- \]

Cu(II) glycinate complexes
- \( \text{Cu(H}_3\text{NCH}_2\text{COO})^{2+} : \text{CuHL}^{2+} \)
- \( \text{Cu(H}_2\text{NCH}_2\text{COO})^+ : \text{CuL}^+ \)
- \( \text{Cu(H}_2\text{NCH}_2\text{COO})_2 : \text{CuL}_2 \)

Cu (I) glycinate complexes
- \( \text{Cu(H}_2\text{NCH}_2\text{COO})^-_2 : \text{CuL}^-_2 \)

Potential-pH diagram, with \( \{\text{Cu}_T\} = 10^{-5}, \{L_T\} = 10^{-2} \)

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FLCC
Mechanisms for copper passivation and removal

- The “wet etch” of copper is an electrochemical corrosion process
  - Redox reaction in which oxidation occurs at sites separated (albeit at microscopic or nanoscopic scale) from sites where reduction occurs
  - \( \text{Cu} = \text{Cu}^{2+} + 2e^- \) - oxidation, anodic reaction
  - \( \text{Ox} + ne = R \) - reduction, cathodic reaction
- The Cu(II) may form a solid phase that passivates the underlying metal. This would be the layer that is removed mechanically – copper itself is very ductile
- Regardless, slurry must contain some oxidant, Ox, that is reduced while oxidizing copper
Consider the dissolution of copper in a slurry containing hydrogen peroxide:

\[ \text{Cu} + \text{H}_2\text{O}_2 + 2\text{H}^+ = \text{Cu}^{2+} + 2\text{H}_2\text{O} \]

Reaction occurs as two separate reactions, at different locations:
- Oxidation of the metal - called anodic dissolution:
  \[ \text{Cu} = \text{Cu}^{2+} + 2\text{e} \]
- Reduction of the hydrogen peroxide - called cathodic reduction:
  \[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O} \]
Electrochemical mechanisms of metal dissolution

- Oxidation is more favorable at high energy surface defects, such as emergent dislocations and grain boundaries
  - The electrons lower the electrical potential of these sites
- Reduction is “forced” to dominate at other areas, where surface sites are available for sorption of hydrogen peroxide and hydrogen ions, and any reaction intermediates
  - The utilization of electrons in the reduction process tends to raise the electrical potential of cathodic sites
- The potential difference draws electrons from anodic sites to cathodic sites to maintain the reaction

Electrochemical mechanisms of metal dissolution

\[
\text{Polycrystalline copper} \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 + 2\text{H} \rightarrow 2\text{H}_2\text{O} + 2\text{e}^- \]

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Kinetics of Electrochemical Reactions
– Crucial for Reaction Control

- For both the anodic and cathodic reactions, the rate of reaction depends upon the potential relative to the equilibrium potential
  - potential is a measure of the chemical activity of electrons, one of the participants in the reaction
- When the kinetics are dominated by the electron transfer process, the Butler-Volmer equation applies:

\[
\therefore i = i_o \{\exp\left(\frac{-\alpha n F \eta}{RT}\right) - \exp\left(\frac{(1 - \alpha) n F \eta}{RT}\right)\}
\]

- May also see kinetics affected by transport and the availability of reactants

System settles at point where anodic and cathodic currents are equal (electroneutrality), with distinctive corrosion current density and corrosion potential

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Obtain information on electrochemical processes with polarization studies

Measure current passing between counter electrode and working copper electrode. This is the net difference between the anodic and cathodic curves, as shown.
More complex polarization behavior

- In aerated solutions used in some of our experiments, cathodic reaction principally reduction of oxygen:
  \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e = 4\text{OH}^- \]
  current limited by transport of oxygen
- Anodic reactions are oxidation of copper to \( \text{Cu}^{2+} \), \( \text{Cu}_2\text{O} \), \( \text{Cu(OH)}_2 \) or \( \text{CuO} \) – current may be limited by transport, blockage of sites or presence of passivating films
- Behavior complex if there are multiple anodic or cathodic reactions
Polarization Curves in Cu-Glycine-H$_2$O

\[ \{\text{Cu}_T\} = 10^{-5}, \{\text{L}_T\} = 10^{-2} \]

\[ \{\text{L}_T\} = 10^{-2} \]
**In-situ** Electrochemical Polarization While Polishing

- **Magnetic stirrer**
- **Pt Counter Electrodes**
- **Luggin Probe & Reference Electrode**
- **Copper Working Electrode**
- **Polish pad**
- **Slurry pool**
- **Rotator Frame**

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In-situ Polarization

pH 4

- No abrasion
- Polishing with pad only
- Polishing with pad and 5% alumina particles

pH 9

Aqueous $10^{-2}$ M glycine, 27.6 kPa, 200 rpm

pH 12

- No abrasion
- Polishing with pad only
- Polishing with pad and 5% alumina particles

FLCC
Kinetic Experiments Using H$_2$O$_2$

**Dissolution**
- Cleaned, weighed, copper coupons (50 x 25 x 1 mm, 99.999%) suspended in stirred solutions
- After tests, dried and weighed
- Copper removal rate determined by weight loss

**Polishing**
- Used same equipment used for *in-situ* polarization tests
- Electrochemical information unstable with peroxide
- Polishing rates determined from weight loss measurements
Effect of H₂O₂ on Dissolution and Polish Rates

**pH 4**

Aqueous 10⁻² M glycine, 27.6 kPa, 200 rpm

**pH 9**

Dissolution Rate
Polish Rate
Effect of $\text{H}_2\text{O}_2$ on Open Circuit Potential in Aqueous, $10^{-2}$ M Glycine

Nernst Equation: $E = E^\circ + \frac{2.303RT}{nF} \log \frac{\Pi a_{\text{ox}}}{\Pi a_{\text{red}}}$
Effect of H$_2$O$_2$ on Open Circuit Potential in Aqueous, $10^{-2}$ M Glycine

$pH 4$

$y = 166.03 \log(x) + 518.76$

$R^2 = 0.948$

$pH 9$

$y = 59.31 \log(x) + 395.801$

$R^2 = 0.996$
Equivalent Polarization Curves

Polarization in the absence of H\textsubscript{2}O\textsubscript{2}
Dissolution in the presence of H\textsubscript{2}O\textsubscript{2}
Polishing in the presence of H\textsubscript{2}O\textsubscript{2}

pH 4

pH 9
Polarization Curves in Cu-Glycine-H$_2$O

{Cu$_T$} = 10$^{-5}$, {L$_T$} = 10$^{-2}$

{L$_T$} = 10$^{-2}$
Why the unexpected passivation?

- Passivation induced by $\text{H}_2\text{O}_2$ at moderate concentrations cannot be due to colloidal effects altering abrasive-substrate interactions, because this effect is seen for dissolution, in the absence of abrasives.
- Not due to a thermodynamically stable phase.
- $\text{Cu}_2\text{O}_3$ or $\text{CuO}_2$ (Pourbaix, 1965) – unlikely.
- The pH at the surface, is much higher than in the bulk: $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$ – difficult to envisage such a dramatic difference.
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Quartz Crystal Microbalance

- The changes in frequency of a piezoelectric quartz crystal, $\Delta f$, are related to changes in mass, $\Delta m$, of a substrate (e.g. Cu) that is attached to the quartz crystal:

$$\frac{\Delta m}{\Delta f} = -\frac{\left(\mu_q \rho_q\right)^{1/2}}{2 f_0^2}$$

where $\mu_q$ is the shear modulus of the quartz crystal, $\rho_q$ the density, and $f_0$ the resonant frequency.

- for an AT-cut quartz crystal with a resonant frequency of 5 MHz gives that $\Delta m/\Delta f$ is $-1.77 \times 10^{-8}$ g/cm$^2$/Hz.
MaxTek, Inc., PM-700 Series Etching Products

Measurement resolution:
Frequency: 0.5 Hz
Weight: 0.01 µg/cm²
Thickness: 0.001 µm/min (0.1 Å/s)

Teflon holder
EQCM
1 inch AT-cut polished
5 MHz Cr/Cu crystal
pH 4, OCP, 0.01 M glycine premixed in acetate buffer

Temporary loss in weight, followed by significant gain in weight, more pronounced at higher concentration of H$_2$O$_2$.  

[Graph showing mass change over time with different concentrations of H$_2$O$_2$.]
pH 9, OCP, 0.01 M glycine added to carbonate buffer after stabilization

Slow loss in weight upon adding glycine. Temporary sharp loss in weight after adding peroxide, followed by significant gain in weight.
Effect of adding additional glycine, after adding 2.09% hydrogen peroxide

Deionized water

pH 9
Open circuit potential of copper, pH 9, 0.01 M glycine and 2.09% hydrogen peroxide.

No passivation without H$_2$O$_2$. See that behavior is strongly dependent on history of glycine additions; oxidized layers must resist dissolution.
Potential application in CMP

Polarize copper sample to oxidizing potential, to allow protective film to develop, then add glycine - little effect

1- removal of protective film by mechanical action at protruding areas

2- freshly created surface will dissolve actively in glycine solution. Recessed regions remain protected
Effect of glycine and $\text{H}_2\text{O}_2$ additions at different potentials, pH 9, 0.01 M glycine

Iron disk-Au ring electrode. $\text{H}_2\text{O}_2$ produced during reduction of $\text{O}_2$ is rapidly reduced at high and low potentials, but can escape electrode at intermediate potentials

At controlled potentials, either oxidizing or reducing, $\text{H}_2\text{O}_2$ does NOT lead to weight increase. Protective film must be sensitive to potential

However, this is not consistent with passivation at high concentrations of $\text{H}_2\text{O}_2$

We know that chemical/electrochemical material removal rates are relatively slow compared to rates measured while polishing.

So is chemistry important at all?

Dornfeld group has successfully modeled various aspects of mechanical behavior.

Talbot group has added colloidal behavior to the Luo and Dornfeld model for material removal rates; accounts for effect of solution chemistry on agglomeration of abrasive particles.

Would there be large errors from ignoring chemistry?

Yes!
Chemistry also interacts synergistically with mechanical/colloidal phenomena.

Chemistry affects degree of aggregation of abrasive particles.

Mechanical forces on copper introduce defects, increasing reactivity.

Copper nanoparticles have dramatic effect.

Mechanical properties of films appear to be strongly dependent on chemistry, and probably potential.
Adding chemistry/electrochemistry to models

• Obtain quantitative information on mechanical properties of surface films under different chemical conditions
  – Add to models

• Use curve-fitting to capture major chemical details
  – add to models as additive material removal rate over and above mechanical phenomena

• Model material removal with “chemical tooth” approach, and add kinetic data to estimate rates for reforming passive films
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How are electrode kinetics affected by multiple half-cell reactions?

- Metal A, which is more active, corrodes at \( E'_{corr} \)
- Metal N, which is more noble, corrodes at a higher potential, \( E_{corr} \)
- When metals A and N are in electrical contact, they develop a common corrosion potential, \( E''_{corr} \)
- At \( E''_{corr} \), the corrosion current of N is lower than for the isolated metal, but the corrosion current of A is greater than for the isolated metal
- This effect is called galvanic corrosion
Motivation

- Galvanic cells may form when polished patterned copper wafers with Ta or Ti-based barriers are immersed in CMP slurries; either copper or the barrier layer is corroded preferentially by galvanic corrosion.
- Galvanic corrosion may impair the quality and reliability of copper interconnects. This effect will become increasingly pronounced with smaller-scale features.
- Galvanic corrosion can be observed microscopically, measured by electrochemical techniques and controlled by modifying the slurry chemistry, temperature etc.
- Therefore, it is becoming increasingly important to understand the galvanic cells that develop during copper CMP, and incorporate this understanding into models.
What is the effect of different electrode areas?

- Total anodic CURRENT must equal total cathodic current
- A small anode:cathode area ratio causes more severe galvanic corrosion, because
- The total anodic current is concentrated over a smaller area
- Hence the anodic dissolution rate increases

This effect could be really problematic in CMP if diffusion barriers are more active than copper

Jones, Denny A., Principles and prevention of corrosion, 2nd ed.
Galvanic Series and Sensitivity to Solution Chemistry

- A galvanic series is a series in which the corrosion potential of different metals and alloys is placed in ascending order.
- Comprehensive galvanic series have been published for a large number of metallic materials in sea water and aerated fresh water.
- Much less information is available for copper and barrier materials in solution chemistries representative of CMP slurries.
- Anticipate significant variations in potentials of copper and barrier materials according to the precise complexing agents and oxidants.
Polarization tests in solutions containing \( \text{H}_2\text{O}_2 \) and glycine

- **Electrodes**: Cu, Ti, Ta polished down to 0.25 µm using diamond paste

- **Electrolytes**:
  - Solution containing \( \text{H}_2\text{O}_2 \) and 0.01M glycine
  - Solution pH controlled using buffer solution
    - Acetate buffer pH=3
    - Carbonate buffer pH=9
    - KOH solution pH=12
  - Varying \( \text{H}_2\text{O}_2 \) concentration

- **Potentiodynamic polarization measurements** were made on the Ta and Cu rotating disk electrodes, scanning at 1mV/s, rotating at 650 rpm
Ta-Cu, Ti-Cu, pH 3 buffer + 0.01M glycine + 0.65 M H₂O₂

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 Reminder – what you are seeing with polarization curves

Potential, V (SHE)

Cathodic

Anodic

E_{oc}

E_{corr}

log i

Net anodic

Net cathodic

Potential, V (SHE)

log i
Polarization tests – commercial slurry

- **Electrodes:** Ta rotating disk electrode (6.25mm in diameter) and Cu rotating disk (10mm in diameter), polished down to 0.25 μm using diamond paste
- **Electrolytes:**
  - Mixture of commercial slurry A + H$_2$O$_2$ (final concentration: 1.0%wt H$_2$O$_2$ or 6.0%wt H$_2$O$_2$), referred to as Cu-1.0%H$_2$O$_2$, Cu-6.0%H$_2$O$_2$, Ta-1.0% H$_2$O$_2$, Ta-6.0% H$_2$O$_2$
  - 50 times dilution of the above mixture, referred to as Cu-1.0%-diluted, Cu-6.0 %-diluted, Ta-1.0 %-%-diluted, Ta-6.0 %-%-diluted
  - The above electrolytes had a measured pH of 4.00
- **Potentiodynamic polarization measurements were made on the Ta and Cu rotating disk electrodes, scanning at 1mV/s, rotating at 650 rpm**
Ta-Cu: Commercial slurry + 1% H\textsubscript{2}O\textsubscript{2}

E vs SCE, mV

Log\textsubscript{l}, A/cm\textsuperscript{2}

Cu-1.0% H\textsubscript{2}O\textsubscript{2}

Ta-1.0% H\textsubscript{2}O\textsubscript{2}

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Ta-Cu: Commercial slurry + 6% \( \text{H}_2\text{O}_2 \)

**Graph:**

- **Axes:**
  - Y-axis: Evs SCE, mV
  - X-axis: Logl, A/cm^2

**Lines:**

- **Cu-6.0%H\(_2\)O\(_2\):**
- **Ta-6.0%H\(_2\)O\(_2\):**

**Additional Information:**

- **Cu-0.6%-diluted**
- **Ta-6.0%-diluted**
Results of electrochemical measurements

Area ratio effect, without polishing

Start with DI water, then add buffer, then glycine, then H$_2$O$_2$ to create pH=9 carbonate buffer, 0.01M glycine and 0.3%H$_2$O$_2$
Results of electrochemical measurement

Effects of $[\text{H}_2\text{O}_2]$, pH=9, without polishing

in pH=9 carbonate buffer, 0.01M glycine and varying $[\text{H}_2\text{O}_2]$
Galvanic currents and potentials will be measured with or without polishing, to investigate the effects of surface modification by chemicals and mechanical force on the polarity and galvanic current; area ratio of Cu:Ta is to be varied using different sample assemblies with different area ratios.
How to model galvanic effects

- Modest galvanic currents can have devastating effects on quality if localized
  - Need to focus on feature level
- Basic electrochemical theory suggests that the corrosion current in a galvanic couple can be predicted
  - Relative areas of anodic and cathodic metals can then be invoked to predict damage due to galvanic interactions
- But the corrosion potentials of Cu, Ta and Ti differ in different solution chemistries; in some cases the relative nobility changes
  - Hence the polarization behavior of each material must be determined for different slurries to provide input for modeling copper CMP
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Conclusions

• The chemical and electrochemical mechanisms in copper CMP are complex
  – Sometimes the behavior is not fully understood

• However, the subtleties of chemical behavior alone may be of second order, compared to synergism between mechanical, chemical and colloidal behavior
  – A mechanistic understanding is invaluable in tackling modeling of this synergism

• Galvanic effects are different; here models must focus on feature scale effects