Insight into Mechanisms for Passivation of Copper in CMP Slurries Containing Peroxide and Glycine

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Small Feature Reproducibility

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Outline

- **Background and approach**
- Chemistry of copper-complexing agents
- Electrochemistry of copper in aqueous glycine
- Weight loss and polishing in presence of hydrogen peroxide
- Mechanisms for observed behavior
- Conclusions
Kaufman’s Model for Planarization of Tungsten

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).
Copper CMP

- Several principles govern desirable attributes of a slurry
  - If Kaufman’s model is applicable, want passivation, not active etching of metallic surfaces
  - However, abraded debris should dissolve to prevent re-deposition, and the resulting ions should stay in solution
  - Also may want selectivity for metal over dielectric (not considered here)
- Oxidizing agent needed
- Expect complexing agents to be beneficial, if there is also passivation
Hypothesis

Since oxidizing agents change potentials in CMP systems, one can characterize and model their action through characterization and modeling of the electrochemical responses.

- Action of individual oxidizing agents can be correlated with their electrochemical effect.

Anode: \[ M = M^{n+} + ne \] Oxidation

Cathode: \[ O + me = R \] Reduction

- Should allow different oxidizing agents to be modeled using a generic approach.
Electrochemical Studies

We have studied and previously reported the electrochemical behavior of copper in the presence of several different model complexing agents.

- The electrochemical behavior has been analyzed in terms of thermodynamic models of the system chemistry.
- Our aim is to develop predictive models based on the thermodynamics of different systems.
Testing our Hypothesis

- Here we report work done to test our hypothesis that electrochemical studies provide information applicable to models describing the effect of different oxidizing agents in CMP.

- Hydrogen peroxide selected as model oxidizing agent.
  - Broadly used, does not introduce extraneous ions.

- Glycine selected as model complexing agent.
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● **Conclusions**
Potential-pH diagram, with $\{Cu_T\} = 10^{-4}$ or $10^{-6}$, 4% H$_2$O$_2$ or 0.5M hydroxylamine
Tamilmani, Huang, Raghavan & Small, JECS, 2002
Chemistry of Glycine-Water System

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

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

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

Potential-pH diagram, with
\[ \{\text{Cu}_T\} = 10^{-5}, \{\text{L}_T\} = 10^{-2} \]
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Polarization Measurements using Rotating Disk Electrode

- Rotating Cu disk electrode
- Fritted glass gas bubbler
- Pt counter electrode
- Magnetic stirrer
- Luggin probe & reference electrode
Polarization Curves

- At any potential, electrode passes both anodic and cathodic currents.
- In aerated solutions used here, cathodic reaction principally reduction of oxygen:
  \[ O_2 + 2H_2O + 4e = 4OH^- \]
  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.
- Record the sum of these:
  - Anodic above \( E_{oc} \)
  - Cathodic below \( E_{oc} \)
- Behavior complex if there are multiple anodic or cathodic reactions.
Polarization Curves in Cu-Glycine-H₂O

{Cuₜ} = 10⁻⁵, {Lₜ} = 10⁻²

{Lₜ} = 10⁻²
In-situ Electrochemical Polarization

- Luggin Probe & Reference Electrode
- Pt Counter Electrodes
- 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

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

pH 9

pH 12
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Kinetic Experiments Using H₂O₂

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**
Effect of $H_2O_2$ on Open Circuit Potential in Aqueous, $10^{-2}$ M Glycine

Nernst Equation: $E = E^o + \frac{2.303RT}{nF} \log \frac{\Pi a_{ox}}{\Pi a_{red}}$

pH 4

pH 9
Effect of \( \text{H}_2\text{O}_2 \) on Open Circuit Potential in Aqueous, \( \text{10}^{-2} \text{ M Glycine} \)

**pH 4**

\[
y = 166.03 \log(x) + 518.76 \\
R^2 = 0.948
\]

**pH 9**

\[
y = 59.31 \log(x) + 395.801 \\
R^2 = 0.996
\]

\( \text{E}_{oc}, \text{mV vs. SHE} \) vs. \( \text{H}_2\text{O}_2 \) wt%
Equivalent Polarization Curves

- Polarization in the absence of H2O2
- Dissolution in the presence of H2O2
- Polishing in the presence of H2O2

**pH 4**

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

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

\[ \{\text{L}_T\} = 10^{-2} \]
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Passivation induced by H$_2$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


- Cu$_2$O$_3$ or CuO$_2$ (Pourbaix, 1965)
Do the different gradients provide insight into the films forming at pH 4 and pH 9?

- Dominant cathodic reaction
  - $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$

$$E = 1.776 + \frac{0.0591}{2} \log \frac{\{\text{H}_2\text{O}_2\} \{\text{H}^+\}^2}{\{\text{H}_2\text{O}\}^2}$$

- Anodic reactions
  - $\text{Cu} + \text{HL} = \text{CuL}^+ + \text{H}^+ + 2\text{e}$ (at pH 4)
  - $\text{Cu} + 2\text{HL} = \text{CuL}_2 + 2\text{H}^+ + 2\text{e}$ (pH 9)
  - $\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{e}$

$$E = 0.682 + \frac{0.0591}{2} \log \frac{\{\text{O}_2\} \{\text{H}^+\}^2}{\{\text{H}_2\text{O}_2\}}$$

- The different copper complexation reactions at pH 4 and 9 are likely to yield different films
- The kinetics of gas evolution (anodic decomposition of $\text{H}_2\text{O}_2$) are strongly substrate dependent

The mixed potential reached in peroxide solutions is expected to be strongly pH dependent.
Weight loss and copper release rates

See that at acidic pH, weight loss measurements suggest lower rate of reaction than do copper concentrations in solution.

At higher pH, two measurements fairly consistent.

Suggests that surface films formed at low pH contain more oxygen/water/glycine than films formed at high pH.
Copper dissolution at pH 3, 10^{-2} M glycine

At short contact times, dissolution rates insensitive to amount of H_2O_2
After longer contact times, see non-linearity in dissolution rates at high H_2O_2 concentrations
Consistent with progressive thickening of a protective layer, rather than with adsorption of an inhibiting species from solution

23x23 mm copper coupons
200 ml solution
Samples withdrawn periodically and analyzed for dissolved copper
At 3% and 5% H_2O_2, copper surfaces turn black
Copper dissolution at pH 4, 10^{-2} M glycine

- 23x23 mm copper coupons
- 200 ml solution
- Samples withdrawn periodically and analyzed for dissolved copper
- At 3% and 5% H$_2$O$_2$, copper surfaces turn black

Even at short contact times, dissolution rates more sensitive to amount of H$_2$O$_2$
After longer contact times, see more pronounced non-linearity in dissolution rates at modest and high H$_2$O$_2$ concentrations
Consistent with progressive thickening of a protective layer, rather than with adsorption of an inhibiting species from solution
Copper dissolution in 10^{-2} M aqueous glycine (no buffer, pH ~ 4.5)

23x23 mm copper coupons
200 ml solution
Samples withdrawn periodically and analyzed for dissolved copper
At 3% and 5% H_2O_2, copper surfaces turn black

Rates an order of magnitude lower than at pH 3 or 4
Even at short contact times, dissolution rates more sensitive to amount of H_2O_2
After longer contact times, see pronounced suppression of dissolution at high H_2O_2 concentrations
Although films contain less oxygen/water/glycine than those formed at pH 3 or 4, highly protective
Copper dissolution at pH 9, $10^{-2}$ M glycine

Rates an order of magnitude lower than at pH 3 or 4
Even at short contact times, dissolution rates sensitive to amount of H$_2$O$_2$
After longer contact times, see pronounced non-suppression of dissolution at all H$_2$O$_2$ concentrations
Although films contain less oxygen/water/glycine than those formed at pH 3 or 4, highly protective
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- Electrochemistry provides useful, quantitative information on behavior of metals in CMP
- However, see that specific oxidants, in this case peroxide, induce unexpected passivation
- Mechanism for passivation
  - Formation of higher oxides
  - Surface perturbation of pH due to peroxide decomposition
  - Does not appear to be sorption of inhibiting species
- For CMP, this passivation is highly desirable
  - Even with passivation, high rates seen at pH 3 and 4 with acetate buffer. Possible that acetate plays an active role
- Emphasizes the need to couple electrochemical studies with chemical studies
- Future work to characterize physical nature of films