Role of Glycine-H$_2$O$_2$ in Chemical Mechanical Polishing of Copper

V. R. Gorantla, Z. Lu, S. Hegde, E. Matijević, and S. V. Babu

Center for Advanced Material Processing
Clarkson University, NY-13699

Center for Advanced Material Processing, Clarkson University, NY 13699
CMP-UG Conference, San Jose, CA. 4 Feb 2004
Outline

- Introduction
- Cu-H₂O₂-glycine interactions
- Packed bed column technique to study chemical and Cu interactions
- Summary
- Acknowledgments
For effective integration of low-k materials with copper interconnects:

Copper CMP has to become a more chemically driven process rather than mechanically driven process
Fundamental understanding of chemicals and copper film interactions are necessary to develop slurries that provide:

• High removal rates

• Fewer defects – Corrosion pits, Galvanic effects

Chemical factors that play important role during Cu CMP

✓ Chemical interactions between various chemical additives
✓ pH of the slurry
✓ Nature and properties of the modified surface layer during Cu CMP
Mechanism of Cu removal in glycine-H$_2$O$_2$ system

(M. Hariharaputhiran et al; J. of Electrochem. Soc. 147 (10) 3820-3826 (2000))

- **Cu**
- **Cu$^{2+}$**
- **Cu$^{2+}$-(gly)$_2$**
- **Gly**
- **H$_2$O$_2$**
- **[*OH]**

✓ **Cu-(Gly)$_2$** complex catalyzes the decomposition of H$_2$O$_2$ to [*OH] radicals.

✓ [*OH] radicals are powerful oxidizing agents than H$_2$O$_2$.

✓ Hydroxyl radicals enhance the removal rates of copper during CMP in glycine-H$_2$O$_2$ based slurries.
• \(*OH\) trapping experiments were performed at pH \sim 8.0

• Increase in Cu\(^{2+}\) ion concentration in glycine-H\(_2\)O\(_2\) system at pH \sim 8 showed an increase in [\(*OH\)]

• Cu dissolution rates also increased with increase in Cu\(^{2+}\) concentration in glycine-peroxide solution at pH \sim 8

• However, the mechanism at other pH values was not tested
Effect of pH on Cu dissolution rates

pH has a strong effect on Cu dissolution rates

1 wt% glycine + 5 wt% H$_2$O$_2$
### Effect of Cu\(^{2+}\) concentration on Cu dissolution rates

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>pH of the solution</th>
<th>Cu dissolution rates (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% glycine + 5 wt% H(_2)O(_2) + 0.06 wt% Cu(NO(_3))(_2)</td>
<td>3.7</td>
<td>225 ± 3</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H(_2)O(_2) + 0.125 wt% Cu(NO(_3))(_2)</td>
<td>3.4</td>
<td>245 ± 7</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H(_2)O(_2) + 1.0 wt% Cu(NO(_3))(_2)</td>
<td>2.6</td>
<td>365 ± 9</td>
</tr>
</tbody>
</table>

Cu dissolution rates increased with increase in [Cu\(^{2+}\)] in glycine-H\(_2\)O\(_2\) system

However, there is change in the pH of the solution (decrease in pH with increasing Cu\(^{2+}\) concentration)

Which factor controls Cu dissolution? pH / *OH radicals
### Cu dissolution experiments

pH adjusted to that in column-2

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>Natural pH of the solution in Column-1</th>
<th>Cu dissolution rates in the solutions of Column-1</th>
<th>Cu dissolution rates in 1 wt% glycine + 5 wt% H$_2$O$_2$ without Cu(NO$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% glycine + 5 wt% H$_2$O$_2$ + 0.06 wt% Cu(NO$_3$)$_2$</td>
<td>3.7</td>
<td>225 ± 3</td>
<td>205 ± 3</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H$_2$O$_2$ + 0.125 wt% Cu(NO$_3$)$_2$</td>
<td>3.4</td>
<td>245 ± 7</td>
<td>250 ± 3</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H$_2$O$_2$ + 1.0 wt% Cu(NO$_3$)$_2$</td>
<td>2.6</td>
<td>365 ± 9</td>
<td>340 ± 42</td>
</tr>
</tbody>
</table>

pH of the solution controls Cu dissolution rates in acidic conditions
Comparison of copper dissolution rates in glycine-\(\text{H}_2\text{O}_2\) system containing \(\text{Cu}^{2+}\) ions at pH 4.0 and pH 8.0

Addition of \(\text{Cu}^{2+}\) ions has an effect on copper dissolution rates at pH 8, but not at pH 4.
Effect of pH on Cu$^{2+}$ and glycine reactivity in aqueous solutions

$pK_{a1} = 2.350$

$\begin{align*}
+H_3NCH_2COOH & \rightleftharpoons +H_3NCH_2COO^- \\
(H_2L^+) & \text{cation} & (HL) & \text{zwitterion} & H_2NCH_2COO^- & \text{anion}
\end{align*}$

$pK_{a2} = 9.778$

Calibrated concentration profiles of [0.002 M] Cu(II) and 0.5 M Glycine

UV/Vis spectroscopy of (Cu\(^{2+}\)-glycine) in aqueous solutions in the absence of H\(_2\)O\(_2\) as a function of pH

Different Cu\(^{2+}\)-glycine species at pH 4 and 8 in the absence of H\(_2\)O\(_2\)

DI water as reference; Solution composition: [0.01 M Cu\(^{2+}\) + 0.1 M Glycine]
UV/Vis spectroscopy of (Cu$^{2+}$ - Glycine - H$_2$O$_2$) in aqueous solution as a function of H$_2$O$_2$ concentration at pH = 4

- Cu(Gly)$_2$ complex prevails at pH = 4 in the presence of H$_2$O$_2$
- Increase in the absorbance at 360 nm with increase in H$_2$O$_2$ concentration
- The absorbance at 360 nm represents Cu$^{2+}$-peroxy-glycine complex

DI water as reference; Solution composition: [0.01 M Cu$^{2+}$ + 0.1 M Glycine + x wt% H$_2$O$_2$]
UV/Vis spectroscopy of (Cu\textsuperscript{2+} - Glycine - H\textsubscript{2}O\textsubscript{2}) in aqueous solution as a function of H\textsubscript{2}O\textsubscript{2} concentration at pH = 8

- Increase in the absorbance at 360 nm with increase in H\textsubscript{2}O\textsubscript{2} concentration
- Absorbance intensity at 360 nm, at pH 8 higher than that at pH 4
- No change in the intensity of the peak at 640 nm (Cu(Gly)\textsubscript{2})

DI water as reference; Solution composition: [0.01 M Cu\textsuperscript{2+} + 0.1 M Glycine + x wt\% H\textsubscript{2}O\textsubscript{2}]
Literature on Cu – complexing agent interactions in aqueous solutions containing H₂O₂

T. Kaden, and H. Sigel, Helvita Chimica Acta, 50 (4), p: 947 (1968) and,

1. Cu²⁺ and complexing agents (CA) like (ethylenediamine /bipyridine) in the presence of H₂O₂ in alkaline solutions form (Cu-peroxy- CA) complex species. Increase in the absorbance intensity at 360 nm indicates the formation of this species.

2. (Cu-peroxy- CA) reacts with H₂O₂ to form O₂ and H₂O and Cu-compounds.


Copper(II)-glycine complexes activate H₂O₂ for oxidation of organic substrates through formation of Cu-peroxy complexes.

M. S. Sastry et. al., J. Inorganic Biochemistry, 45, pp: 159-167 (1992)

The blue precipitate in the system CuO + Glycine + H₂O₂ was shown by element analysis and ESR to be [Cu(O₂²⁻)(H₃N⁺CH₂COO⁻)₂(H₂O)] Peroxy group
Experimental techniques?

Techniques usually used to investigate interactions between chemical and Cu films:

- Electrochemical experiments (In situ and/or ex situ)
- XPS analysis of the films after CMP and dissolution expts

These techniques give us limited information. For example, chemical byproducts formed and their effects on Cu CMP are not observed.

In this study we used packed column technique to investigate the interactions between chemicals of the slurry and Cu films.

This packed column technique was used by us to investigate the interactions (adhesion and detachment) between abrasives and metal/dielectric films*.

(* Z. Lu, S.V. Babu, and E. Matijević, in MRS spring meeting proceedings, 2003)
Particle deposition and detachment Studies: Packed column technique

Suspensions: SiO$_2$, CeO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$

Additives: surfactants, oxidizers, chelating agents, pH regulation agents

Control temperature and flow rate

Beads: Cu, Ta, SiO$_2$
Experimental details

- Height of packed column = ~ 1 cm.
- Avg. Size of copper beads = 80 µm.
- Flow rate = 5 cm³/min
- Enough void space in the column.
  - No filtration effect
  - Effluent represents chemical byproducts due to the interactions of chemical additives with Cu film

Center for Advanced Material Processing, Clarkson University, NY 13699
Experiments with Cu Beads

5 wt% H₂O₂ + 1 wt% glycine, at Natural pH ~5

(1) Dark blue color effluent
(2) It turns into green color with aggressive bubbling finally forming a green color precipitate, all within 30 sec
(3) pH of the effluent (~7.7) is greater than the influent (~5.0)
(4) The effluent is also hot (reactions appear to be exothermic)

Effluent with green precipitate
Experiments with Cu beads

5 wt% $\text{H}_2\text{O}_2$ + 1 wt% glycine, at pH 8.

The green precipitate is generated with in 5-10 seconds.
Reaction mechanism (Hypothesis)

Reactions taking place inside the column

Cu²⁺ → Cu²⁺-(gly)₂

??

??

*OH

Reactions taking place in the bottle

Gly

[Cu²⁺-(HO₂⁻)-(gly)₂]

+ H₂O₂ (Excess)

Green precipitate + O₂

More HO₂⁻ generated with increase in pH

What impact does {Cu²⁺-(HO₂⁻)-(gly)₂} complex have on CMP of Cu?
CMP experiments on Cu blanket films

Blanket Cu films were polished with 1 wt% glycine + 5 wt% H₂O₂ solutions at pH 5 and 8

Experimental conditions:

Polisher: Westech 372
Wafer size: 6 inch.
Polishing conditions: (Time, Down Pressure (psi), Platen/carrier speed (RPM))
(5 sec, 2, 40/40) → (30 sec, 4, 75/75) → (5 sec, 2, 40/40)

Ramp up  Polish cycle  Ramp down
Case 1: No DI water rinse
Case 2: DI water rinse
## CMP of Cu blanket films

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>Avg. copper polish rate (nm/min)</th>
<th>Avg. surface roughness (nm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% glycine + 5 wt% H₂O₂ at pH = 5</td>
<td>225</td>
<td>0.9</td>
<td>No rinse during the polish ramp down step</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H₂O₂ at pH = 8</td>
<td>280</td>
<td>2.0</td>
<td>(Reddish brown patches)</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H₂O₂ at pH = 5</td>
<td>180</td>
<td>0.9</td>
<td>5 sec DI water rinse during the polish ramp down step</td>
</tr>
<tr>
<td>1 wt% glycine + 5 wt% H₂O₂ at pH = 8</td>
<td>245</td>
<td>1.0</td>
<td>(No patches)</td>
</tr>
</tbody>
</table>

Corrosion patches on the wafer polished at pH 8. These patches not observed when rinsed with DI water (instead of polish solution) during ramp down step.

Chemical byproducts (Cu-peroxy-glycine complex) generated are corrosive!
Summary

- pH of the solution controls Cu dissolution rates in acidic conditions and strongly alkaline conditions
- Hydroxyl radicals are important at intermediate pH values
- Cu-peroxy-glycine complex concentration increases with increase in pH and H₂O₂ concentration
- The chemical byproducts (Cu-peroxy-glycine complex) may be responsible for corrosion defects during CMP
  - Effective transportation of these chemical byproducts away from the wafer could reduce defects
Acknowledgment

This work is supported by INTEL Corporation and SRC.