Electrochemistry of Copper in Aqueous Ethylenediamine Solutions

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2001 GOAL: to delineate specific roles of a range of complexing agents and oxidizers in copper CMP by 9/30/2001.
Motivation and Methods

• Ethylenediamine is one of the candidate complexing agents for the metal chemical mechanical planarization (CMP) slurries

• Potential-pH equilibria and potentiodynamic polarization studies over a wide pH range were used to examine the electrochemical behavior of copper in aqueous ethylenediamine solutions

• Polarization experiments were conducted using a copper disk electrode rotating at 200 rpm and a scan rate of 1 mV/sec
Ethylenediamine

\[ \text{pK}_a^1 = 6.848 \quad \text{pK}_a^2 = 9.928 \]

\[ \begin{align*}
+H_3N-CH_2-CH_2-NH_3^+ & \rightleftharpoons +H_3N-CH_2-CH_2-NH_2 & \rightleftharpoons H_2N-CH_2-CH_2-NH_2
\end{align*} \]

\( (H_2\text{En}^2+) \quad (\text{HEn}^+) \quad (\text{En}) \)

Cu(II) En complexes

- \( \text{Cu}(H_2N-CH_2-CH_2-NH_2)_2^{2+} : \text{CuEn}^2+ \)
- \( \text{Cu}(H_2N-CH_2-CH_2-NH_2)_2^{2+} : \text{CuEn}_2^{2+} \)
- \( \text{CuOH}(H_2N-CH_2-CH_2-NH_2)^+ : \text{CuOHEn}^+ \)

Cu (I) En complexes

- \( \text{Cu}(H_2N-CH_2-CH_2-NH_2)_2^+ : \text{CuEn}_2^+ \)
Potential-pH Diagrams

- Diagram 1: \( [\text{En}_T] = 10^{-2} \) and \( [\text{Cu}_T] = 10^{-3} \)
  - pH range: 0 to 16
  - Redox species: \( \text{Cu}^{2+} \), \( \text{Cu}^{\text{En}_2^{2+}} \), \( \text{CuO}^{2-} \), \( \text{Cu}_2\text{O} \)

- Diagram 2: \( [\text{En}_T] = 10^{-1} \) and \( [\text{Cu}_T] = 10^{-4} \)
  - pH range: 0 to 16
  - Redox species: \( \text{Cu}^{2+} \), \( \text{Cu}^{\text{En}_2^{2+}} \), \( \text{CuOH}^{\text{En}_2^{2+}} \), \( \text{Cu}_2\text{O} \)

- Diagram 3: \( [\text{En}_T] = 10^{-2} \) and \( [\text{Cu}_T] = 2 \times 10^{-4} \)
  - pH range: 0 to 16
  - Redox species: \( \text{Cu}^{2+} \), \( \text{Cu}^{\text{En}_2^{2+}} \), \( \text{Cu}^{\text{En}_2^{2+}} \), \( \text{Cu}_2\text{O} \)

- Diagram 4: \( [\text{En}_T] = 10^{-4} \) and \( [\text{Cu}_T] = 10^{-5} \)
  - pH range: 0 to 16
  - Redox species: \( \text{Cu}^{2+} \), \( \text{Cu}^{\text{En}_2^{2+}} \), \( \text{Cu}_2\text{O} \), \( \text{CuO}^{2-} \)
Polarization Experiments in De-aerated 10^{-2} M En and 10^{-3} M CuSO_4 Solutions
Polarization Experiments in Aerated 10^{-2} M En and 10^{-3} M CuSO_4 Solutions
Polarization Experiments in De-aerated 10^{-4} M En and 10^{-5} M CuSO_{4} Solutions
Polarization Experiments in Aerated $10^{-4}$ M En and $10^{-5}$ M CuSO$_4$ Solutions
Conclusions

• Due to its complexation action, ethylenediamine increased the solubility range of copper to lower potentials and higher pH’s.

• The stability regions of CuO and Cu\textsubscript{2}O contracted with increasing amounts of ethylenediamine.

• The polarization behavior agreed well with the thermodynamic potential-pH diagrams.