Lecture 5
Electrochemical Deposition of Metals
Lecture 5

- Metals in CMOS.
- Operation of Electrochemical Cell.
- Deposition Rates.
- Reaction Potentials.
- Generalizations
Metals in CMOS
Metals in CMOS

- Start with your (doped) semiconductor wafer.
Metals in CMOS

- Oxide is grown over entire substrate (Lecture 7)
Metals in CMOS

• Oxide is etched in certain regions to allow contact with doped regions (Lecture 16).
Metals in CMOS

- Metal is deposited everywhere on wafer (this lecture).
Metals in CMOS

- Metal is selectively etched (Lecture 14-16).
Metals in CMOS

- Wafer is covered everywhere with SiN₃ (Lecture 14-15).
Metals in CMOS

- SiN$_3$ is selectively etched (Lecture 14-16).
 Metals in CMOS

• Metal is deposited everywhere on wafer (this lecture).

![Diagram of Metals in CMOS with substrate, oxide, SiN₃, n⁺, p⁺, and n⁺ regions.]
Metals in CMOS

- Metal is selectively etched.
Metals in CMOS

- 6 metal level copper process cross-section at 0.18μm node:

Metals in CMOS

- 3D SEM of 9 metal level Cu process:

Deposition of Metals

- Evaporation (Lectures 8, 10, 11).
- Sputtering (Lectures 8, 10, 11).
- Chemical Vapor Deposition (Lectures 8, 10, 11).
- Electrochemical Deposition (this lecture).
Electrochemical Deposition

- Used for metals such as copper, gold and nickel.
- Film thickness can be varied easily (<1μm to >100 μm)
- Control of deposition achieved by using external electric potential.
- It requires electrical contact to the substrate while immersed in a liquid bath.
- The surface of the substrate must have an electrically conducting coating (seed layer).
Operation of Electrochemical Cell
Electrochemical Cell

• Used to deposit metal onto an electrode.

• Galvanic or Voltaic:
  • The ‘spontaneous’ reaction. Produces electrical energy.

• Electrolytic:
  • Non-spontaneous reaction. Requires electrical energy to occur.
Galvanic Cell

- Basically a battery (that deposits metal onto electrode).
  - Aqueous electrolyte solution 1.
    - H₂O
    - Zn²⁺
    - SO₄²⁻
  - Solution 1 is ~neutral at start of process.
  - Zn metal is placed in solution 1.
Galvanic Cell

• Basically a battery (that deposits metal onto electrode).

• The **oxidation** half reaction occurs at the **anode**, where electrons are donated by reacting species:

\[
Zn(S) \rightarrow Zn^{2+} (L) + 2e^{-}
\]

• Solid zinc is converted to liquid \(Zn^{2+}\) and enters the solution.

• 2 electrons per zinc atom are added to the anode.
Galvanic Cell

- Basically a battery (that deposits metal onto electrode).

- Aqueous electrolyte solution 2.
  - $\text{H}_2\text{O}$
  - $\text{Cu}^{2+}$
  - $\text{SO}_4^{2-}$

- Solution 2 is ~neutral at start of process.

- A metal (to be coated) is placed in solution 2.

- Metal (cathode) connected to anode via conductor.
**Galvanic Cell**

- Basically a battery (that deposits metal onto electrode).

- Electrons flow from anode, through wire to cathode.

- The **reduction** half reaction occurs at the cathode, where electrons are transferred to the reacting species.

\[ Cu^{2+} (L) + 2e^- \rightarrow Cu(S) \]

- Ionic $Cu^{2+}$ in the electrolyte combines with electrons to form solid copper.
Galvanic Cell

- Basically a battery (that deposits metal onto electrode).

- Over time, solution 1 will become more positive, and solution 2 will become more negative.

- Build up of charge will reduce rate of half-reactions.

- Eventually the process will stop.

\[
\text{Zn}(S) \rightarrow \text{Zn}^{2+}(L) + 2e^- \\
\text{Cu}^{2+}(L) + 2e^- \rightarrow \text{Cu}(S)
\]
Galvanic Cell

- Basically a battery (that deposits metal onto electrode).

- A “salt bridge” is used to enable solutions to remain neutral for much longer.

- It allows a net charge to be transferred from one electrolyte solution to the other, but does not allow undesired mixing of the electrolytes.

- It can be a simple porous disc or a gel saturated with a strong electrolyte such as NaCl.
Galvanic Cell

- Basically a battery (that deposits metal onto electrode).

- As solutions become positive / negative ions diffuse into / out of salt bridge.

- Will help to neutralize solutions.

- But will not replenish reaction components.
Shorthand Notation

• Rather than drawing an entire cell, a type of shorthand can be used.

• For the zinc-copper cell we described, this would be:

\[
\text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Cu}^{2+} (0.01\text{M}) | \text{Cu}
\]

• The anode is always on the left.
  \mid = \text{boundaries between phases}
  \parallel = \text{salt bridge}

• Other conditions like concentration are listed just after each species.
Deposition Rates
Charge Transfer

• We are concerned with the rate at which copper is deposited:

\[ \text{Cu}^{2+} (L) + 2e^- \rightarrow \text{Cu} (S) \]

• We can use Faraday Constant to determine the charge (in Coulombs) that is transferred in this half-reaction, in terms of the number of moles of copper deposited:

\[ Q = nNF \]

• \( Q \) = Charge transferred.
• \( n \) = Electrons transferred per atom.
• \( N \) = Moles of atoms deposited.
• \( F \) = Faraday Constant (9.65×10⁴ C/mol).
Example

• Consider our reduction half-reaction:

\[ \text{Cu}^{2+}(L) + 2e^- \rightarrow \text{Cu}(S) \]

• If 1mg of copper is deposited on our metal, how much charge was transferred in this half reaction?

• We need to know:
  • Faraday Constant, \( F = 9.65 \times 10^4 \text{ C/mol} \).
  • Mass of copper atom, \( m_{\text{Cu}} = 63.546 \text{ amu} \).
Example

• First determine number of moles of copper in 1mg.
• One mole of copper has a mass of: 63.546g.
  • From the definition of atomic mass units.

\[ N = \frac{0.001}{63.546} = 1.57 \times 10^{-5} \text{ mol} \]

• Can now determine charge deposited:

\[ Q = nNF \]

\[ Q = 3.04 \text{ C} \]

\[ Cu^{2+}(L) + 2e^- \rightarrow Cu(S) \]
Current Flow

- We are concerned with the rate at which copper is deposited:
- We know the amount of charge transferred in growing a certain number of atoms on our electrode:
  \[ Q = nNF \]
- It would be more useful to know the growth rate:
  \[ I = \frac{dQ}{dt} = nF \frac{dN}{dt} \]
- Define reaction rate (moles/s): \( \mathcal{R} \)
  \[ \mathcal{R} = \frac{dN}{dt} \]
Example

- Consider our galvanic cell.
- If we measure the current flowing between the electrodes to be constant at 1mA, how long would it take to deposit 5 μg of copper onto the cathode?

$$\text{Cu}^{2+} (L) + 2e^- \rightarrow \text{Cu} (S)$$

- We need to know:
  - Faraday Constant, $F = 9.65 \times 10^4$ C/mol.
  - Mass of copper atom, $m_{\text{Cu}} = 63.546$ amu.
Example

- Since current is constant, we approximate our reaction rate as constant:
  \[ R = \frac{dN}{dt} \approx \frac{N}{t} \]

- So:
  \[ I = \frac{nFN}{t} \]
  \[ t = \frac{nFN}{I} \]

- As before, determine number of moles of copper in 5 μg.
- One mole of copper has a mass of: 63.546g.

  \[ N = \frac{5 \times 10^{-6}}{63.546} = 7.87 \times 10^{-8} \text{ mol} \]
Example

• Just put the numbers in:

\[
t = \frac{nFN}{I}
\]

\[2 \quad 7.87 \times 10^{-8} \text{ mol}
\]

\[9.65 \times 10^4 \text{ C/mol}
\]

\[1 \times 10^{-3} \text{ A}
\]

\[t = 15s
\]
Example 2

- Consider our same galvanic cell.
- But we are told the cathode is cylindrical with a diameter of 0.5cm and a *submerged* length of 10cm.
- We are going to conduct a reaction for 10 minutes.
- If we want to deposit a 100 μm layer of copper on the cathode in this time, what constant current should be flowing in the cell for this to occur?

We need to know:

- Faraday Constant, \( F = 9.65 \times 10^4 \) C/mol.
- Mass of copper atom, \( m_{Cu} = 63.546 \) amu.
- Density of copper, \( \rho = 8.96 \) g/cm\(^3\).
- Electrons per half-reaction, \( n = 2 \).
Example 2

- Consider our galvanic cell again.
- But, now we must consider geometry of our cathode:
Example 2

- We need to determine surface area for reaction:
  - The length of the electrode that is submerged is 10 cm.
  - The diameter of the electrode is 0.5 cm.
  - Area of bottom of electrode:

\[
A_{bottom} = \pi \left( \frac{d}{2} \right)^2
\]

\[
A_{bottom} = 0.196 \text{ cm}^2
\]
Example 2

- We need to determine surface area for reaction:
  - Circumference of electrode:
    \[ L_{circ} = \pi d \]
    \[ L_{circ} = 1.57 \, \text{cm} \]
  - Surface area of sides of cylinder:
    \[ A_{side} = L_{side} L_{circ} \]
    \[ A_{side} = 15.7 \, \text{cm}^2 \]
Example 2

- So total surface area in contact with electrolyte:

\[ A = A_{\text{bottom}} + A_{\text{side}} \]

\[ A = 0.196 + 15.7 \]

\[ A = 15.9 \text{ cm}^2 \]

- We want a \( d = 100 \mu\text{m} \) thick coating.

- Volume of copper deposited:

\[ V \approx dA \]

\[ V = 0.01 \times 15.9 \]

\[ V = 0.159 \text{ cm}^3 \]
Example 2

- We are told the density of copper is $\rho = 8.96 \text{ g/cm}^3$.
- Therefore the mass is:

$$m = \rho V$$

$$m = 1.425 \text{ g}$$

- As before, determine number of moles of copper:
- One mole of copper has a mass of: 63.546 g.

$$N = \frac{1.425}{63.546} = 0.0224 \text{ mol}$$
Example 2

Now we can determine the current:

\[ I = \frac{nFN}{t} \]

\[ n = 2 \]
\[ F = 9.65 \times 10^4 \text{ C/mol} \]
\[ N = 0.0224 \text{ mol} \]
\[ t = 600 \text{ s} \]

\[ I = 7.21 \text{ A} \]
Current Density

- In electrochemical deposition, rates are normally referred to per unit area, e.g. cm\(^{-2}\)s\(^{-1}\).
- Current density is normally labelled as \( J \):
  \[
  J = \frac{I}{A}
  \]
  - \( I \) = current.
  - \( A \) = area reaction takes place over.
- So, our rate equation is:
  \[
  J = \frac{nFR}{A}
  \]
Example 2 (Again)

• If we know the current density we don’t need to work out the area.

\[ J = \frac{nFR}{A} \]

• Again, approximate rate as constant:

\[ R = \frac{dN}{dt} \approx \frac{N}{t} \]

\[ J = \frac{nFN}{At} \]

• One mole depends on mass of material deposited, \( m \):

\[ N = \frac{m}{m_{Cu}} \]
Example 2 (Again)

- From

\[ J = \frac{nFN}{At} \quad \text{and} \quad N = \frac{m}{m_{Cu}} \]

- We get:

\[ J = \frac{nFm}{Atm_{Cu}} \]

- Mass in terms of density is:

\[ m = \rho V \]

\[ J = \frac{nF\rho V}{Atm_{Cu}} \]
Example 2 (Again)

\[ J = \frac{nF \rho V}{Atm_{Cu}} \]

- If we are depositing a thickness \( d \), the volume is:

\[ V = Ad \]

\[ J = \frac{nF \rho Ad}{Atm_{Cu}} \]

\[ J = \frac{nF \rho d}{tm_{Cu}} \]
Example 2 (Again)

- Putting in the numbers from our previous example:

\[ J = \frac{nF \rho d}{tm_{\text{Cu}}} \]

-\( 9.65 \times 10^4 \text{ C/mol} \)
-\( 2 \)
-\( 8.96 \text{ g/cm}^3 \)
-\( 600 \text{ s} \)
-\( 100 \mu\text{m} \)
-\( 63.546 \text{ g/mol} \)

\[ J = 0.453 \text{ Acm}^{-2} \]
Reaction Potentials
Half Cell Potentials

<table>
<thead>
<tr>
<th>Reduction half-reaction</th>
<th>$E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Au^+ + e^- \rightarrow Au$</td>
<td>+1.692</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow H_2O$</td>
<td>+1.229</td>
</tr>
<tr>
<td>$Ag^+ + e^- \rightarrow Ag$</td>
<td>+0.800</td>
</tr>
<tr>
<td>$Cu^+ + e^- \rightarrow Cu$</td>
<td>+0.521</td>
</tr>
<tr>
<td>$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$</td>
<td>+0.401</td>
</tr>
<tr>
<td>$Cu^{2+} + 2e^- \rightarrow Cu$</td>
<td>+0.342</td>
</tr>
<tr>
<td>$Cu^{2+} + e^- \rightarrow Cu^{+}$</td>
<td>+0.153</td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightarrow H_2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$Zn^{2+} + 2e^- \rightarrow Zn$</td>
<td>-0.762</td>
</tr>
<tr>
<td>$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$</td>
<td>-0.828</td>
</tr>
<tr>
<td>$Al^{3+} + 3e^- \rightarrow Al$</td>
<td>-1.662</td>
</tr>
</tbody>
</table>

Relative to a Standard Hydrogen Electrode (SHE):

$H_2 \rightarrow 2H^+ + 2e^-$
Standard Cell Potential

- Consider our galvanic cell:
- Impose **standard conditions**.
  - Soluble species are at a concentration of 1M.
  - Slightly soluble species must be at saturation
  - Any gas is at 1 atm partial pressure.
Standard Cell Potential

- Consider our galvanic cell:
- Impose standard conditions.
- Determine difference in potentials of our half reactions:

$$E^0_{cell} = E^0_{reduction} - E^0_{oxidation}$$

Zn(S) → Zn$^{2+}$(L) + 2e$^-$

$$E^0_{oxidation} = -0.762 \text{ V}$$

Cu$^{2+}$(L) + 2e$^-$ → Cu(S)

$$E^0_{reduction} = +0.342 \text{ V}$$

$$E^0_{cell} = 1.104 \text{ V}$$
Nernst Equation

- What if the concentrations are not equal?
- The potential will be modified.
- The Nernst Equation:

\[ E = E^0 - \frac{RT}{nF} \ln Q \]

- \( E^0 \) = Standard cell potential.
- \( R \) = Gas Constant = 8.314 Jmol\(^{-1}\)K\(^{-1}\).
- \( n \) = Electrons transferred per atom.
- \( F \) = Faraday Constant (9.65\( \times \)10\(^4\) C/mol).
- \( Q \) = Reaction quotient.

\[ Q = \frac{[product]}{[reactant]} \]
Example 1

- Consider our galvanic cell again.

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{Zn}^2+ \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{H}_2\text{O} \quad \text{Zn}^2+ & \quad \text{SO}_4^{2-} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{Cu}^2+ & \quad \text{SO}_4^{2-} \\
\text{H}_2\text{O} & \quad \text{Cu}^2+ \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O}
\end{align*}
\]

- Use shorthand notation:

\[
\text{Zn} \mid \text{Zn}^2+ (1\text{M}) \mid\mid \text{Cu}^2+ (0.01\text{M}) \mid \text{Cu}
\]

\[
[Zn^2+] = 1\text{M} \\
[Cu^2+] = 0.01\text{M}
\]
Example 1

Zn | Zn$^{2+}$ (1M) || Cu$^{2+}$ (0.01M) | Cu

- What is the potential of this cell at 300K?
- We need to know:
  - Cell potential:
    \[ E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0 = 0.342 - (-0.762) \, V = 1.104 \, V \]
  - Gas Constant, \( R = 8.314 \, \text{Jmol}^{-1}\text{K}^{-1} \).
  - Faraday Constant, \( F = 9.65 \times 10^4 \, \text{C/mol} \).
  - \( n = \) Electrons transferred per atom = 2
Example 1

Zn | Zn$^{2+}$ (1M) || Cu$^{2+}$ (0.01M) | Cu

- What is the potential of this cell?
- Determine reaction quotient:

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.01} = 100$$

- Enter values:

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = 9.65 \times 10^4 \text{ C/mol}$$

$$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$300 \text{ K}$$

$$1.104 \text{ V}$$

$$2$$

$$E = 1.04 \text{ V}$$
Example 2

- Consider a different problem. If for the same cell we have a constant concentration of \( \text{Zn}^{2+} \), what concentration of \( \text{Cu}^{2+} \) is required for the cell to stop reacting all together?

\[
\begin{align*}
\text{Zn}^{2+} & \quad \text{H}_2\text{O} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{Zn}^{2+} & \quad \text{SO}_4^{2-} \\
\text{H}_2\text{O} & \quad \text{Zn}^{2+} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{Zn}^{2+} & \quad \text{H}_2\text{O} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{Cu}^{2+} & \quad \text{SO}_4^{2-} \\
\text{H}_2\text{O} & \quad \text{Cu}^{2+} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{Cu}^{2+} & \quad \text{SO}_4^{2-} \\
\text{H}_2\text{O} & \quad \text{Cu}^{2+} \\
\end{align*}
\]

\[ [\text{Zn}^{2+}] = 1 \text{M} \]

\[ [\text{Cu}^{2+}] = ? \]
Example 2

\[
\text{Zn} \mid \text{Zn}^{2+} (1\text{M}) \parallel \text{Cu}^{2+} (x) \mid \text{Cu}
\]

• We require a cell that produces no potential:

\[
E = E^0 - \frac{RT}{nF} \ln Q = 0
\]

• Therefore:

\[
E^0 = \frac{RT}{nF} \ln Q
\]

\[
\ln Q = \frac{E^0 nF}{RT}
\]

\[
Q = \exp \left[ \frac{E^0 nF}{RT} \right]
\]
Example 2

Zn | Zn²⁺ (1M) || Cu²⁺ (x) | Cu

\[ Q = \exp \left( \frac{E^0 nF}{RT} \right) \]

\[ \frac{1}{X} = \exp \left( \frac{E^0 nF}{RT} \right) \]

\[ x = \exp \left( -\frac{E^0 nF}{RT} \right) \]

- Enter values:
  - \( E^0 = 1.104 \text{ V} \)
  - \( n = 2 \)
  - \( F = 9.65 \times 10^4 \text{ C/mol} \)
  - \( E = 8.314 \text{ J mol}^{-1} \text{K}^{-1} \)
  - \( T = 300 \text{ K} \)

\[ x = 7.9 \times 10^{-38} \text{ mol} \]

- So a very low concentration indeed!
Example 3

- Finally, let's consider a different cell:

\[
\text{Cu} | \text{Cu}^{2+} (1\text{M}) || \text{Cu}^{2+} (0.01\text{M}) | \text{Cu}
\]

- In this case we are attempting two identical half reactions:

\[
\begin{align*}
\text{Cu}^{2+}(L) + 2e^- & \rightarrow \text{Cu}(S) \\
E^0_{\text{reduction}} & = +0.342\text{V} \\
E^0_{\text{cell}} & = 0\text{V}
\end{align*}
\]

- So we are relying on just differences in concentration to drive the reaction.

\[
E = E^0 - \frac{RT}{nF} \ln Q = -\frac{RT}{nF} \ln Q
\]
Example 3

- Determine reaction quotient:

\[ Q = \frac{[Cu^{2+}]}{[Cu^{2+}]} = \frac{1}{0.01} = 100 \]

- Enter values:

\[ E = -\frac{RT}{nF} \ln Q \]

- \( 8.314 \text{ Jmol}^{-1}\text{K}^{-1} \)
- \( 300\text{K} \)
- \( 9.65 \times 10^4 \text{ C/mol} \)

\[ E = -59.5 \text{ mV} \]

- I.e. this cell produces a tiny driving force on its own.
Generalizations
Overpotential

• The potential observed experimentally is not always identical to what is predicted from thermodynamics (Nernst Equation) alone.

• Reasons for this include:
  • **Resistance overpotential.**
    Arising from the ohmic drop between electrodes due to the fact that the electrolyte solution and connections have finite conductivity;

\[
\begin{align*}
\text{Zn}^{2+} & \quad \text{H}_2\text{O} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{H}_2\text{O} \quad \text{Zn}^{2+} & \quad \text{SO}_4^{2-} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{Cu}^{2+} \\
\text{SO}_4^{2-} & \quad \text{H}_2\text{O} \\
\text{SO}_4^{2-} & \quad \text{Cu}^{2+} \\
\end{align*}
\]
Overpotential

- The potential observed experimentally is not always identical to what is predicted from thermodynamics (Nernst Equation) alone.
- Reasons for this include:
  - **Concentration or diffusion overpotential.** Due to the presence of concentration gradients in the vicinity of the electrode surface.
Overpotential

- The potential observed experimentally is not always identical to what is predicted from thermodynamics (Nernst Equation) alone.

- Reasons for this include:
  - **Concentration or diffusion overpotential.** Due to the presence of concentration gradients in the vicinity of the electrode surface.

![Diagram showing the relationship between potential and position.](image)
Overpotential

- The potential observed experimentally is not always identical to what is predicted from thermodynamics (Nernst Equation) alone.

- Reasons for this include:
  - **Activation overpotential.** Arising from kinetic inhibition of one of the steps involved in the electrode reaction (desolvation of the reactive ion, chemisorption of the reaction product, etc.).
Activation Overpotential

- Reactions often have to overcome some energetic barrier:

\[ \mathcal{R} = \frac{dN}{dt} = k_0 \exp \left( -\frac{E_a}{RT} \right) \]

Arrhenius relationship
Activation Overpotential

• The activation energy for the cathodic (reduction) reaction increases the activation energy from thermodynamic prediction by:

\[ \Delta E = \alpha_c nFE \]

• \( \alpha_c \) = transfer coefficient for anode.

Quantifies change in energy barrier for reduction
Activation Overpotential

- The activation energy for the anodic (oxidation) reaction decreased the activation energy from thermodynamic prediction by:

\[ \Delta E = (1 - \alpha_a) nFE \]

- \( \alpha_a \) = transfer coefficient.

Quantifies change in energy barrier for oxidation
Butler-Volmer Equation

- [Not examinable]
- Is a way to take account of the overpotential for known transfer coefficients:

\[ J = J_0 \left[ \exp \left( \frac{\alpha_a n F \eta}{RT} \right) - \exp \left( \frac{\alpha_c n F \eta}{RT} \right) \right] \]

- \( J \) = Current density observed.
- \( J_0 \) = Exchange current density.
- \( \eta \) = Overpotential = \( E - E^0 \).