Lecture 4: Electrochemical Deposition of Metals

Announcements

Homework 1/4:
- The first homework is online now.
- Total of 25 marks.
- Each homework contributes an equal weight.
- All homework contributes to 40% of overall grade.
- Each homework contributes 10% of overall grade.
- A physical copy is due Tuesday 15th October at the start of the lecture (10:00 am).
- I will return it one week later (22nd October).
- I will post solutions online when I return the homework.
- Homework 1 will consist of content covered in Lectures 2-4.
Announcements

Homework 1/4:

- One the questions requires you to download some data:
  - [http://classes.engr.oregonstate.edu/eecs/fall2019/ece611/downloads/ECECHE611%20Fall%202019%20-Homework%20Data.csv](http://classes.engr.oregonstate.edu/eecs/fall2019/ece611/downloads/ECECHE611%20Fall%202019%20-Homework%20Data.csv)
  - The data is in .csv (comma separated) format.
  - If you open it in Excel it looks like this:
  - Any problems, let me know.

Last Time

- We have covered the basics of gas theory and some real vacuum systems.
Lecture 4

• Metals in CMOS.
• Operation of Electrochemical Cell.
• Deposition Rates.
• Reaction Potentials.
• Generalizations.
• Plating Additives.
Metals in CMOS

• Start with your (doped) semiconductor wafer.
• We will talk about doping (Lectures 7 and 8) and laterally defining features (Lectures 13 and 14) later in the course.

Metals in CMOS

• Oxide is grown over entire substrate (Lecture 6).
Metals in CMOS

- Oxide is etched in certain regions to allow contact with doped regions (Lecture 15).

Metals in CMOS

- Metal is deposited everywhere on wafer (this lecture).
Metals in CMOS
• Metal is selectively etched (Lectures 13-15).

Metals in CMOS
• Wafer is covered everywhere with SiN₃ (Lecture 11).
Metals in CMOS

• SiN$_3$ is selectively etched (Lectures 13-15).

Metals in CMOS

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

- Metal is selectively etched.

![Diagram of Metals in CMOS]

- Metal is selectively etched.
Deposition of Metals

- There are a number of different techniques to deposit metals in integrated circuits:
  - Evaporation.
  - Sputtering.
  - Chemical Vapor Deposition (CVD) – Lecture 11.
  - Electrochemical Deposition – this lecture.
    - Is primarily used to deposit copper (an excellent conductor).
    - This has only really been routine since ~2000.

Electrochemical Deposition

- Electrochemical deposition has been used in printed circuit boards (PCB) for a while.
- Its use inside of integrated circuits requires much greater precision.
- In particular, infilling trenches and openings with very small (∝ μm) sizes is challenging.
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:

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:

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

- Solid zinc is converted to liquid \( \text{Zn}^{2+} \) 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.

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

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.
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

- 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:

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

- The anode is always on the left.
  - \mid = \text{boundaries between phases}
  - \| = \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:
  \[ Cu^{2+} (L) + 2e^- \rightarrow Cu(S) \]

- 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 (9.65×10^4 C/mol).

Example

- Consider our reduction half-reaction:
  \[ Cu^{2+} (L) + 2e^- \rightarrow Cu(S) \]

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

  - We need to know:
    - Faraday Constant, \( F = 9.65 \times 10^4 \) C/mol.
    - Mass of copper atom, \( m_{Cu} = 63.546 \) 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:
  \[
  Q = nNF
  \]

\[
\begin{align*}
\text{Cu}^{2+}(L) + 2e^{-} & \rightarrow \text{Cu}(S) \\
2 & \quad 1.57 \times 10^{-5} \text{ mol} \\
Q & \quad 9.65 \times 10^4 \text{ C/mol} \\
Q & \quad 3.04 \text{ C}
\end{align*}
\]

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): \( \mathcal{R} \)
  \[
  \mathcal{R} = \frac{dN}{dt}
  \]
  \[
  I = nF \mathcal{R}
  \]
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, \( F = 9.65 \times 10^4 \text{ C/mol.} \)
  - Mass of copper atom, \( m_{\text{Cu}} = 63.546 \text{ amu.} \)

Since current is constant, we approximate our reaction rate as constant:

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

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:

\[ t = \frac{2 \times nF}{7.87 \times 10^{-8} \text{ mol}} \times \frac{9.65 \times 10^4 \text{ C/mol}}{1 \times 10^{-3} \text{ A}} \]

\[ t = 15 \text{s} \]

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:

\[ J = \frac{nFR}{A} \]
**Reaction Potentials**

**Half Cell Potentials**

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

Relative to a Standard Hydrogen Electrode (SHE): $H_2 \rightarrow 2H^+ + 2e^-$

Pt black plate
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.

\[ E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}} \]

\[ Zn(S) \rightarrow Zn^{2+}(L) + 2e^- \]
\[ E_{\text{oxidation}}^0 = -0.762 \text{V} \]

\[ Cu^{2+}(L) + 2e^- \rightarrow Cu(S) \]
\[ E_{\text{reduction}}^0 = +0.342 \text{V} \]

\[ E_{\text{cell}}^0 = 1.104 \text{V} \]

\[ V = 1.104 \text{V} \]
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.

\[
\begin{align*}
\text{Zn} & | \text{Zn}^{2+} (1 \text{M}) || \text{Cu}^{2+} (0.01 \text{M}) | \text{Cu} \\
\text{H}_2\text{O} & | \text{SO}_4^{2-} \\
\text{SO}_4^{2-} & \text{Zn}^{2+} \\
\text{H}_2\text{O} & \text{Cu}^{2+} \\
\text{H}_2\text{O} & \text{SO}_4^{2-} \\
\end{align*}
\]

- Use shorthand notation:

\[ \text{Zn} | \text{Zn}^{2+} (1 \text{M}) || \text{Cu}^{2+} (0.01 \text{M}) | \text{Cu} \]
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:
    \[ E_{cell}^0 = E_{reduction}^0 - E_{oxidation}^0 = 0.342 - (-0.762) = 1.104 \text{V} \]
  • 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 2

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

\[
\begin{align*}
\text{Zn} | \text{Zn}^{2+} (1M) \parallel \text{Cu}^{2+} (x) | \text{Cu}
\end{align*}
\]

We require a cell that produces no potential:

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

Therefore:

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

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

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

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

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

\[ \frac{1}{X} = \exp \left[ \frac{E^0 nF}{RT} \right]^2 \]

- Enter values:
  \[ x = \exp \left[ -\frac{E^0 nF}{RT} \right] \]
  \[ x = 7.9 \times 10^{-38} \text{ mol} \]

- So a very low concentration indeed!

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;

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

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.

- **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:

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

- Reaction rates are described in terms on an activation energy:

\[ \Delta E = \alpha_c nFE \]

- 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

- The Butler-Volmer Equation is a way to take account of the overpotential for known transfer coefficients:

\[ J = J_0 \left[ \exp \left( \frac{\alpha_anFE\eta}{RT} \right) - \exp \left( \frac{\alpha_canFE\eta}{RT} \right) \right] \]

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

- To get a full description of how an ionic liquid moves in a concentration gradient and an electric field, you need to use the Nernst–Planck Equation.

\[ \frac{\partial c}{\partial t} = \nabla \cdot \left[ D \nabla c - uc \frac{Dze}{k_B T} cE \right] \]

- \( c \): Concentration of species.
- \( t \): Time.
- \( D \): Diffusion coefficient.
- \( u \): Fluid velocity vector.
- \( T \): Temperature.
- \( z \): Valence of the ionic species.
- \( k_B \): Boltzmann Constant.
- \( E \): Electric field vector.

This equation describes how the concentration of an ionic species \( c(r, t) \), changes as a function of position and time, due to concentration gradients (\( \nabla c \)), fluid flow (\( u \)) and electric fields (\( E \)).

If the flow and electric field go to zero, this reduces to the Diffusion Equation (Fick’s 2nd Law):

\[ \frac{\partial c}{\partial t} = \nabla \cdot \left[ D \nabla c - \frac{Dze}{k_B T} cE \right] \]

See Lecture 7

\[ \frac{\partial c}{\partial t} = D \nabla^2 c \]
Nernst–Planck Equation

\[
\frac{\partial c}{\partial t} = \nabla \cdot \left[ D \nabla c - uc + \frac{Dze}{k_BT} cE \right]
\]

- In reality, even Fick's 2nd law can only be solved analytically in a handful of situations.
- This equation will almost always be solved numerically.
  - E.g. using finite-difference methods:
    \[
    \frac{\partial c}{\partial t} \rightarrow \frac{\Delta c}{\Delta t} = \frac{c_{i+1} - c_{i-1}}{t_{i+1} - t_{i-1}}
    \]
- You will not be expected to use the Nernst–Planck Equation, or finite difference methods, for this course.

Plating Additives
**Trenches and Openings**

- While plating a planar surface using electrochemical deposition is routine, filling trenches and openings with very small (≪ μm) sizes is challenging.
- Interconnects can be ≫ μm thick, but trenches are typically very small (< 100 nm).

If the rate is the same everywhere across the wafer this can cause issues for small features.

**Superfill**

- The objective is to fill the entire feature, without it closing at the top first. This is called superfill by the community.
- This is achieved by attaching additives to certain regions of the trenches.
### Superfill

- The objective of superfill is to deposit suppressors near the top of a trench, and accelerators near the bottom.

![Diagram of Superfill](image)

- We will not worry how additives work or how we deposit them inhomogenously.


### Mounding

- Another issue is “mounding”, where accelerators can result in unwanted excess growth over trenches (after superfill has been achieved).

![Diagram of Mounding](image)

- This results in more complex (hence expensive) planarization and chemical mechanical polishing (CMP) steps being necessary.
Mounding

- A leveler molecule can be used to solve this issue.

- Again, you don’t need to know the mechanism for the this course, just that they are used.

Summary

- We have studied the electrochemical deposition of metals.
Next Time...

- We will look at the generation and application of plasmas.