Lecture 7: Diffusion
Chapter 8 Wolf and Tauber

Last Time
• We looked at growth of oxides (mainly SiO$_2$).
Lecture 7

- Diffusion in Applications
- Diffusion in Crystals
- The Diffusion Equation
- The Diffusion Equation in Literature

Useful Links

MIT:

Clarkson University:
- [http://people.clarkson.edu/~isuni/Chap-6.pdf](http://people.clarkson.edu/~isuni/Chap-6.pdf)
Diffusion

- A general term to describe the movement of material from a region of high density to a region of low density due to random motion.

- Diffusion coefficient is defined as:

\[ J = D \left( -\frac{\partial C}{\partial z} \right) \]

Flux (#/m²s⁻¹)  Diffusion Coefficient (m²s⁻¹)  Concentration gradient (m⁻⁴)

Concentration

Position
Diffusion

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• Diffusion coefficient is defined as:

\[ J = D \left( -\frac{\partial C}{\partial z} \right) \]

Flux (#/m\(^2\)s\(^{-1}\))
Diffusion Coefficient (m\(^2\)s\(^{-1}\))
Concentration gradient (m\(^{-3}\))
Diffusion

- A general term to describe the movement of material from a region of high density to a region of low density due to random motion.
- Diffusion coefficient is defined as:

\[ J = D \left( -\frac{\partial C}{\partial z} \right) \]
Diffusion in Silicon Processing

- In solids $D$ is thermally activated:
  
  $D = D_0 \exp\left(-\frac{E_A}{k_B T}\right)$

- So it is usual to talk about a diffusion coefficient at a certain temperature $T$.

- Fick’s 1st Law in 3-dimensions:
  
  $J = D \left(-\frac{\partial C}{\partial z}\right) \quad \Rightarrow \quad J = -\nabla C$

Early IC Fabrication (~1960s)

- Historically, diffusion was the process by which n-type (P, As) and p-type (B) dopants were introduced into Si.

- Wafer was exposed to gas containing the dopant (pre-deposition).

- Remove dopant source, anneal to allow dopant to diffuse deeper into the wafer (drive in).
Early IC Fabrication (~1960s)

Modern Fabrication

- Perform pre-deposition by ion implantation: high energy dopant ions are fired into the wafer.
- Perform anneal to repair damage to crystal, also causes dopant to diffuse.
- Many fabrication facilities still have “Diffusion” groups which can include a range of activities: from high $T$ processes (thermal CVD, oxidation and anneal) to ion implant.
Modern Fabrication

- Ion-implantation apparatus:

Modern Fabrication

- Silicon is doped with boron, phosphorous and arsenic by ion implantation.
- Ions from the ion beam damage the lattice.
Modern Fabrication

- Annealing is a process where the wafer is heated to repair the damage to the lattice.
- The dopant ions become part of the crystal lattice (Activation).
- The ions also spread out during anneal (Diffusion).

Annealing Tool

- Heating lamps (Cross wise)
- Heating lamps (Length wise)
- Wafer
- Inert atmosphere
- Robot arm
Diffusion in Crystals

Vacancy Diffusion

- Initial and final states have same energy:

\[ D = D_0 \exp \left( -\frac{E_A}{k_B T} \right) \]
Direct Exchange

- Bonds are broken and re-formed.
  
  ![Broken bonds diagram]

- This has a higher energy barrier because more bonds are broken → even lower value of $D$.
- In Si, substitutional impurities are P, B, As, Al, Ga, Sb, Ge.

Interstitial Diffusion

- Very fast process with low activation energy.
  
  ![Interstitial diffusion diagram]

- Common with small atoms.
- Examples in Si: H, Li, Na, O, Au, Fe, Ni, Cu, Zn, Mn.
- No vacancy needed.
Interstitialcy diffusion

- Combination of interstitial and vacancy.
- A dopant atom is “kicked out” by an interstitial Si.
- The dopant diffuses interstitially until it falls into a vacancy (Frank-Turnbull mechanism).
- Or until the dopant kicks out a Si atom.
- In Si, interstitial diffusion is important for P, B, Al, Ga.

Effective Diffusivity

- If there are several diffusion mechanisms occurring at once: each contributes to the effective diffusivity: $D_{eff}$.
- E.g. Au diffuses by both interstitial and substitutional mechanisms, so we can say:
  $$ J = D_{int} \frac{\partial C_{int}}{\partial z} + D_{sub} \frac{\partial C_{sub}}{\partial z} $$
  $$ J = D_{eff} \frac{\partial C_{eff}}{\partial z} $$
- Significant (anisotropic) diffusion can occur along grain boundaries and dislocations to affect diffusivity.
Vacancy Diffusion: More Detail

- Step 1: Create vacancy:
  \[ n_V = \exp \left[ -\frac{E_V}{k_B T} \right] \]
  Concentration of vacancies

- To energy required to create a vacancy is \( E_V = 2 \text{–} 3 \text{ eV} \).

- Step 2: Jump over barrier:
  \[ \nu_V = \nu_0 \exp \left[ -\frac{E_a}{k_B T} \right] \]
  Frequency of jump attempts

- Jump of a vacancy involves breaking 1-2 bonds, requiring energy \( E_a \).

- The diffusion coefficient is then:
  \[ D \approx d^2 \times \text{rate} \]
  \[ D = d^2 n_V \nu_V \]
  \[ D = d^2 \nu_0 \exp \left[ -\frac{E_V}{k_B T} \right] \exp \left[ -\frac{E_a}{k_B T} \right] \]
  \[ D = d^2 \nu_0 \exp \left[ -\frac{(E_V - E_a)}{k_B T} \right] = D_0 \exp \left[ -\frac{E_{VD}}{k_B T} \right] \]

- Vacancy diffusion activation energy \( E_{VD} = E_a + E_V \) is 3.5 → 4.0 eV for most dopants.

- \( D_0 \sim 1 \text{ cm}^2/\text{s} \) typically → \( D \sim 10^{-17} \text{ cm}^2/\text{s} \) at 1000 K.
Diffusion of Impurities in Si

Substitutional

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$D_0$ (cm$^2$/s)</th>
<th>$E_{VD}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>3.85</td>
<td>3.66</td>
</tr>
<tr>
<td>B</td>
<td>0.037</td>
<td>3.46</td>
</tr>
<tr>
<td>As</td>
<td>0.066</td>
<td>3.44</td>
</tr>
<tr>
<td>Sb</td>
<td>0.214</td>
<td>3.65</td>
</tr>
</tbody>
</table>

Interstitial

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$D_0$ (cm$^2$/s)</th>
<th>$E_{VD}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.0011</td>
<td>1.12</td>
</tr>
<tr>
<td>Cu</td>
<td>0.04</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0062</td>
<td>0.87</td>
</tr>
<tr>
<td>O</td>
<td>0.21</td>
<td>2.44</td>
</tr>
</tbody>
</table>

$$D = D_0 \exp \left[ -\frac{E_{VD}}{k_B T} \right]$$
Solubility Limits

- The maximum amount of a dopant that can dissolve in the Si is given by the solid solubility limits $C_0$.

![Solubility Limits Graph](image)

The Diffusion Equation
The Diffusion Equation

- Fick’s 1\textsuperscript{st} and 2\textsuperscript{nd} Law.
- Defining Boundary Conditions.
- Converting PDE into ODEs.
- Solving ODEs.
- Determining Constants.
- Example Solution.
- Some Example Data.

Mathematics of Diffusion

- We want a mathematical toolset to quantify how concentration in different parts of our system changes over time.

- Knowing the concentration of impurities (e.g. dopants) is important for electronic properties.
Fick’s Law’s

- Fick’s 1\textsuperscript{st} Law describes the movement of material due to a driving force (we won’t derive it):

\[ J = D \left(- \frac{\partial C}{\partial z}\right) \]

Flux (describes movement of material through surface)

Diffusion Coefficient (describes mobility of material through medium)

Concentration gradient (driving force)

- Everything is quantified by the diffusion coefficient \( D \).

Fick’s 2\textsuperscript{nd} Law

- We can derive Fick’s 2\textsuperscript{nd} law through conservation of # of particles:

\[ J_{in} - J_{out} = \int_{z}^{z+\Delta z} \left(- \frac{\partial C}{\partial z}\right) \, d\Delta z \]

- In a period of time \( \Delta t \) the mobile material with move from position \( z \) to position \( z + \Delta z \).

- During this time the flux has changed from \( J_{in} \) to \( J_{out} \):

\[ \Delta J = J_{in} - J_{out} = J(z) - J(z + \Delta z) \]
Fick's 2nd Law

\[ \Delta J = J(z) - J(z + \Delta z) \]

- Consider the change in the number of particles in time \( \Delta t \) from this change in flux: \( J(z) \rightarrow J(z + \Delta z) \):

\[ \Delta \# = A \Delta t \Delta J = A \Delta t [J(z) - J(z + \Delta z)] \]

Fick's 2nd Law

- For the flux to have changed in \( \Delta t \), the concentration must have changed.
- The change in concentration in this box in this time:

\[ \Delta C = C(t) - C(t + \Delta t) \]

- Again, think of this in terms of change in numbers:

\[ \Delta \# = A \Delta C \Delta z = A \Delta z [C(t) - C(t + \Delta t)] \]
Fick’s 2\textsuperscript{nd} Law

$$\Delta \# = A \Delta z [C(t) - C(t + \Delta t)]$$
$$\Delta \# = A \Delta t [J(z) - J(z + \Delta z)]$$

- The change in $\#$ is equivalent.
- The change flux leads to a change in concentration (or vice-versa).

---

\[ A \Delta z [C(t) - C(t + \Delta t)] = A \Delta t [J(z) - J(z + \Delta z)] \]
\[ \Delta z [C(t) - C(t + \Delta t)] = \Delta t [J(z) - J(z + \Delta z)] \]

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**Fick’s 2\textsuperscript{nd} Law**

$$\Delta z [C(t) - C(t + \Delta t)] = \Delta t [J(z) - J(z + \Delta z)]$$

- Re-arrange:

\[ \frac{C(t) - C(t + \Delta t)}{\Delta t} = \frac{J(z) - J(z + \Delta z)}{\Delta z} \]

- Take the infinitesimal limit:

\[ \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial z} \]
Fick’s 2\textsuperscript{nd} Law

- Combine: \( \frac{\partial C}{\partial t} = -\frac{\partial J}{\partial z} \)
- With Fick’s 1\textsuperscript{st} Law: \( J = D \left( -\frac{\partial C}{\partial z} \right) \)
- Gives us: \( \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) \)
- If \( D \) is a constant in space:
  \[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \]

How to Solve Fick’s 2\textsuperscript{nd} Law?

- Fick’s 2\textsuperscript{nd} Law is a 2\textsuperscript{nd} order partial differential equation (PDE):
  \[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \]
- In general this is tough to solve.
- For certain situations it can be solved analytically however.
- It all comes down to how we define the problem, and the boundary conditions we choose.
How to Solve Fick’s 2\textsuperscript{nd} Law?

- We want to describe how material moves from a region of high concentration, to a region of low concentration, by thermal (random) motion.
- Define a “container” from $z = 0 \rightarrow z_t$.
- Say initially ($t = 0$) some material with concentration $C_0$ is confined between $z = z_0 \rightarrow z_t$.

Why These Conditions?

- This description appears throughout science (and in VLSI).
- We often have heterostructures in research / industry.
- Combining two materials can often result in inter-diffusion (even at room temperature):
The Diffusion Equation

• Fick’s 1\textsuperscript{st} and 2\textsuperscript{nd} Law.
• Defining Boundary Conditions.
• Converting PDE into ODEs.
• Solving ODEs.
• Determining Constants.
• Example Solution.
• Some Example Data.

Boundary Conditions

• We define the edges of the container as impenetrable, i.e. no material can flow across the boundaries:

\[
\frac{\partial C(0, t)}{\partial z} = 0 \quad \frac{\partial C(z_t, t)}{\partial z} = 0
\]
Boundary Conditions

\[ \frac{\Delta C(z_t, t)}{\Delta z} = 0 \]

As \( \Delta z \to 0 \):

\[ \frac{\partial C(z_t, t)}{\partial z} = 0 \]

The Diffusion Equation

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PDE $\rightarrow$ ODEs

- We will use our boundary conditions later.
  \[
  \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}
  \]

- The first thing we need to do is tackle this equation as ordinary differential equations (ODEs):

- To do this we use separation of variables:

  \[C(z, t) = Z(z)T(t)\]

  Concentration as a function of both \(z\) and \(t\)

  Function of position \((z)\) only

  Function of time \((t)\) only

PDE $\rightarrow$ ODEs

- Put this into Fick’s 2nd Law:
  \[
  \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}
  \]

- Gives:

  \[
  \frac{\partial}{\partial t} (Z(z)T(t)) = D \frac{\partial^2}{\partial z^2} (Z(z)T(t))
  \]

  \[
  Z(z) \frac{\partial T(t)}{\partial t} = DT(t) \frac{\partial^2 Z(z)}{\partial z^2}
  \]
PDE → ODEs

\[ Z(z) \frac{\partial T(t)}{\partial t} = DT(t) \frac{\partial^2 Z(z)}{\partial z^2} \]

• Collect terms:

\[ \frac{1}{DT(t)} \frac{\partial T(t)}{\partial t} = \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} \]

• If this is true for all \( z \) and all \( t \) we can set each side equal to a constant:

\[ \frac{1}{DT(t)} \frac{\partial T(t)}{\partial t} = \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -\lambda^2 \]

• Why use \(-\lambda^2\) instead of \(\lambda\), will become apparent later.
• Basically we don’t want loads of \(\sqrt{\lambda}\)’s later on.

PDE → ODEs

\[ \frac{1}{DT(t)} \frac{\partial T(t)}{\partial t} = \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -\lambda^2 \]

• We can then write this as two ODEs:

\[ \frac{dT(t)}{dt} = -\lambda^2 DT(t) \]
\[ \frac{d^2 Z(z)}{dz^2} = -\lambda^2 Z(z) \]

• We can now solve these equations analytically.
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Solving spatial ODE

- We start with the spatial ODE:
\[
\frac{d^2 Z(z)}{dz^2} = -\lambda^2 Z(z)
\]
- Since we are engineers and not mathematicians, we just use known solutions.
- The solution to this equation depends on the type of variable our constant ($\lambda^2$) is.
  - $\lambda^2$ can be real ($\lambda > 0$).
  - $\lambda^2$ can be zero ($\lambda = 0$).
  - $\lambda^2$ can be imaginary ($\lambda < 0$).
Solving spatial ODE
\[ \frac{d^2Z(z)}{dz^2} = -\lambda^2 Z(z) \]

- If \( \lambda < 0 \):
  \[ Z(z) = \phi e^{-\lambda z} + \psi e^{\lambda z} \]
- If \( \lambda = 0 \):
  \[ Z(z) = \phi z + \psi \]
- If \( \lambda > 0 \):
  \[ Z(z) = \phi \sin(\lambda z) + \psi \cos(\lambda z) \]
- Where \( \phi \) and \( \psi \) are constants, to be determined.
- This is all the mathematics can tell us.
- Our job is to determine the nature of \( \lambda \), from our physical situation (given our boundary conditions).
- We need to eliminate non-physical situations (*reductio ad absurdum*).

If \( \lambda < 0 \)

- First consider the case that \( \lambda < 0 \):
  \[ Z(z) = \phi e^{-\lambda z} + \psi e^{\lambda z} \]
- Use our first boundary condition:
  \[ \frac{\partial C(0, t)}{\partial z} = 0 \]
- Recall:
  \[ C(z, t) = Z(z)T(t) \]
  \[ \frac{\partial C(0, t)}{\partial z} = \frac{\partial}{\partial z} (Z(0)T(t)) = T(t) \frac{\partial Z(0)}{\partial z} \]
  \[ T(t) \frac{\partial Z(0)}{\partial z} = 0 \]
  Divide by \( T(t) \):
  \[ \frac{dZ(0)}{dz} = 0 \]
If \( \lambda < 0 \)

\[
\frac{dZ(0)}{dz} = 0
\]

- Differentiate our solution for \( \lambda < 0 \):
  
  \[
  Z(z) = \phi e^{-\lambda z} + \psi e^{\lambda z}
  \]
  
  \[
  \frac{dZ}{dz} = -\lambda \phi e^{-\lambda z} + \lambda \psi e^{\lambda z}
  \]

- Our boundary condition applies at \( z = 0 \):

  \[
e^0 = 1
  \]

  \[
  \frac{dZ(0)}{dz} = \lambda (\psi - \phi) = 0
  \]

  Divide by \( \lambda \):

  \[
  \phi = -\psi
  \]

If \( \lambda < 0 \)

\[
\phi = -\psi
\]

- Our equation is valid everywhere (including boundaries).
- Applying boundary conditions, restricts the behavior of our equation to our physical description.

\[
Z(z) = \phi e^{\lambda z} + \psi e^{\lambda z}
\]

\[
Z(z) = \psi e^{\lambda z} - \psi e^{-\lambda z}
\]

\[
Z(z) = \psi (e^{\lambda z} - e^{-\lambda z})
\]
If $\lambda < 0$

$$Z(z) = \psi(e^{\lambda z} - e^{-\lambda z})$$

• Now apply our second boundary condition:

$$\frac{\partial C(z_t, t)}{\partial z} = 0$$

Material cannot flow out the top of our container.

• For the same reason as before:

$$dZ(z_t) = 0$$

$$\frac{dZ}{dz} = \psi \lambda (e^{\lambda z} + e^{-\lambda z})$$

$$\frac{dZ(z_t)}{dz} = \psi \lambda (e^{\lambda z_t} + e^{-\lambda z_t}) = 0$$

If $\lambda < 0$

$$\psi \lambda (e^{\lambda z_t} + e^{-\lambda z_t}) = 0$$

• Now, we know that:
  • $z_t > 0$, because of our container:
  • $\lambda < 0$, because the solution depends on it.
  • There is no combination of $z_t$ and $\lambda$, that leads to:

$$e^{\lambda z_t} + e^{-\lambda z_t} = 0$$

• So if $e^{\lambda z_t} + e^{-\lambda z_t} \neq 0$ and $\lambda < 0$, we are forced to conclude: $\psi = 0$

$$Z(z) = \psi(e^{\lambda z} - e^{-\lambda z}) = 0$$

$Z(z) = 0$ Everywhere
If $\lambda = 0$

• Since $\lambda < 0$ leads to an unphysical result, we are forced to try other types of $\lambda$ for our solution to the ODE:

$$\frac{d^2Z(z)}{dz^2} = -\lambda^2 Z(z)$$

• Next consider the case that $\lambda = 0$:

$$Z(z) = \phi z + \psi$$

• This solution is a lot more easy to disprove.

If $\lambda = 0$

$$Z(z) = \phi z + \psi$$

• Just consider one boundary condition:

$$\frac{\partial C(0, t)}{\partial z} = 0 \quad \Rightarrow \quad \frac{dZ(0)}{dz} = 0$$

$$\frac{dZ(0)}{dz} = \phi = 0$$

• If $\phi = 0$ then: $Z(z) = \psi$

• This means that the concentration is constant everywhere.

• $\lambda \neq 0$. 
\[ \lambda > 0 \]

- So far we know that \( \lambda < 0 \) and \( \lambda \neq 0 \).
- Therefore we know: \( \lambda > 0 \).

\[ \frac{d^2Z(z)}{dz^2} = -\lambda^2Z(z) \]

- So we can say for sure that:
  \[ Z(z) = \phi \sin(\lambda z) + \psi \cos(\lambda z) \]
- We will determine the variables \( \phi \) and \( \psi \) in a bit.
- With \( \lambda > 0 \), we can also solve the time-dependent ODE:
  \[ \frac{dT(t)}{dt} = -\lambda^2 DT(t) \]

\[ \lambda > 0 \]

\[ \frac{dT(t)}{dt} = -\lambda^2 DT(t) \]

- If \( \lambda > 0 \), the solution is:
  \[ T(t) = \beta e^{-\lambda^2 Dt} \]
- We can then put this back into our equation for concentration:
  \[ C(z, t) = \beta e^{-\lambda^2 Dt} (\phi \sin(\lambda z) + \psi \cos(\lambda z)) \]
- We are making progress towards an equation describing the concentration at any position \( z \) and any time \( t \).
- But we do have some unknown constants: \( \beta, \phi, \psi, \lambda \).
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Determining Constants

\[ C(z, t) = \beta e^{-\lambda^2 D t} (\phi \sin(\lambda z) + \psi \cos(\lambda z)) \]

- We apply boundary conditions to determine constants.

\[ \frac{\partial C(0, t)}{\partial z} = 0 \quad \text{Material cannot flow out the bottom of our container} \]

\[ \frac{\partial C}{\partial z} = \beta e^{-\lambda^2 D t} (\lambda \phi \cos(\lambda z) - \psi \lambda \sin(\lambda z)) \]

- At \( z = 0 \):

\[ \cos(\lambda z) = 1 \quad \sin(\lambda z) = 0 \]

\[ \frac{\partial C(0, t)}{\partial z} = \lambda \phi \beta e^{-\lambda^2 D t} = 0 \]
Determining Constants

\[ \lambda \phi \beta e^{-\lambda^2 Dt} = 0 \]

- Consider how this can be true.
- The only way for \( e^{-\lambda^2 Dt} = 0, \ t \to \infty \).
  - So this isn’t generally true, \( e^{-\lambda^2 Dt} \neq 0 \).
- We know that \( \lambda > 0 \). So \( \lambda \neq 0 \).
- What if \( \beta = 0? \)
- Our equation for concentration is:
  \[
  C(z, t) = \beta e^{-\lambda^2 Dt} (\phi \sin(\lambda z) + \psi \cos(\lambda z))
  \]
- If \( \beta = 0, \ C(z, t) = 0 \) everywhere.

Again, this can’t be true.

Therefore for \( \lambda \phi \beta e^{-\lambda^2 Dt} = 0, \ \phi = 0 \).

\[
C(z, t) = \beta e^{-\lambda^2 Dt} (\phi \sin(\lambda z) + \psi \cos(\lambda z))
\]

\[
C(z, t) = \beta \psi e^{-\lambda^2 Dt} \cos(\lambda z)
\]

- We can define a new constant \( \alpha = \beta \psi \).
  \[
  C(z, t) = \alpha e^{-\lambda^2 Dt} \cos(\lambda z)
  \]
- So we are now down to 2 constants: \( \alpha \) and \( \lambda \).
Determining Constants

\[ C(z, t) = \alpha e^{-\lambda^2 D t} \cos(\lambda z) \]

- We then apply our second boundary condition:

\[ \frac{\partial C(z_t, t)}{\partial z} = 0 \]

Material cannot flow out the top of our container

\[ \frac{\partial C(z_t, t)}{\partial z} = -\alpha \lambda e^{-\lambda^2 D t} \sin(\lambda z_t) = 0 \]

- For the same reasons as before, the only non-trivial solution is:

\[ \sin(\lambda z_t) = 0 \]

• We see for this to be true:

\[ \lambda z_t = \pi n \]

\[ \lambda = \frac{\pi n}{z_t} \]
Determining Constants

\[ C(z, t) = \alpha e^{-\lambda^2 Dt} \cos(\lambda z) \]

- We can now substitute in \( \lambda \):
  \[ \lambda = \frac{\pi n}{z_t} \]

  \[ C(z, t) = \alpha \exp \left( - \frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

- We are now down to one unknown constant: \( \alpha \).
- This constant is determined by the initial concentration \( C(z, 0) \).

Determining \( \alpha \)

- To determine \( \alpha \) we use a trick.

  \[ C(z, t) = \alpha \exp \left( - \frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

- We can write this as a linear superposition of many solutions:

  \[ C(z, t) = \sum_{n=0}^{\infty} \alpha_n \exp \left( - \frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

- Notice \( \alpha_n \neq \alpha \).
- Let’s briefly explain why this is valid.
### Determining $\alpha$

\[ C(z, t) = \alpha \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

- E.g. Let $\alpha_0 = \alpha / 2$, $\alpha_1 = \alpha / 2$:

\[
C(z, t) = \alpha_0 \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) + \alpha_1 \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)
\]

\[
C(z, t) = \frac{\alpha}{2} \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) + \frac{\alpha}{2} \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)
\]

\[
C(z, t) = \alpha \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)
\]

- The same principle can be applied to an infinite number of constants.

### Determining $\alpha$

\[ C(z, t) = \sum_{n=0}^{\infty} \alpha_n \exp \left( -\frac{n^2\pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

- Why would we do this?
- Because, we can now define any initial distribution...

\[ C(z, 0) = f(z) = \sum_{n=0}^{\infty} \alpha_n \exp \left( -\frac{n^2\pi^2 D \times 0}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right) \]

\[ f(z) = \sum_{n=0}^{\infty} \alpha_n \cos \left( \frac{n\pi z}{z_t} \right) \]

\[ e^0 = 1 \]
Determining $\alpha$

- ...And we can identify this series as a cosine Fourier Series for $f(z)$ over $0 \leq z \leq z_t$:

$$f(z) = \sum_{n=0}^{\infty} \alpha_n \cos \left( \frac{n\pi z}{z_t} \right)$$

This is just from the definition of a Fourier Series.

$$\alpha_n = \begin{cases} 
\frac{1}{z_t} \int_0^{z_t} f(z) dz & \text{if } n = 0 \\
2 \int_0^{z_t} f(z) \cos \left( \frac{n\pi z}{z_t} \right) dz & \text{otherwise}
\end{cases}$$

Initial Distribution

- We are basically there now.
- We have our equation for concentration as a function of time and position:

$$C(z, t) = \sum_{n=0}^{\infty} \alpha_n \exp \left( -\frac{n^2\pi^2Dt}{z^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$

- We also know how to determine $\alpha = \Sigma_{n=0}^{\infty} \alpha_n$ from our initial distribution: $f(z)$.

$$\alpha_n = \begin{cases} 
\frac{1}{z_t} \int_0^{z_t} f(z) dz & \text{if } n = 0 \\
\frac{2}{z_t} \int_0^{z_t} f(z) \cos \left( \frac{n\pi z}{z_t} \right) dz & \text{otherwise}
\end{cases}$$
The Diffusion Equation

- Fick’s 1\textsuperscript{st} and 2\textsuperscript{nd} Law.
- Defining Boundary Conditions.
- Converting PDE into ODEs.
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- Determining Constants.
- Example Solution.
- Some Example Data.

Initial Distribution

- We can now choose any initial distribution we want.
- We will just use a simple step function:

\[
 f(z) = \begin{cases} 
 0 & \text{for } 0 \leq z \leq z_0 \\
 C_0 & \text{for } z_0 \leq z \leq z_t 
\end{cases}
\]
Evaluation of $\alpha$

- Now we can evaluate $\alpha_n$'s
- Start with $n = 0$:
  \[
  \alpha_0 = \frac{1}{z_t} \int_0^{z_t} f(z) dz
  \]
  \[
  f(z) = \begin{cases} 
  0 & \text{for } 0 \leq z \leq z_0 \\
  C_0 & \text{for } z_0 \leq z \leq z_t
  \end{cases}
  \]
- Therefore:
  \[
  \alpha_0 = \frac{1}{z_t} \int_0^{z_0} 0 \, dz + \frac{1}{z_t} \int_{z_0}^{z_t} C_0 \, dz = \frac{1}{z_t} \int_{z_0}^{z_t} C_0 \, dz
  \]
  \[
  = \frac{1}{z_t} [C_0 z]_{z_0}^{z_t} = \frac{C_0 (z_t - z_0)}{z_t}
  \]

Now look at other $n$'s:

- Again:
  \[
  f(z) = \begin{cases} 
  0 & \text{for } 0 \leq z \leq z_0 \\
  C_0 & \text{for } z_0 \leq z \leq z_t
  \end{cases}
  \]
  \[
  \alpha_n = \frac{2}{z_t} \int_0^{z_0} 0 \times \cos \left( \frac{n \pi z}{z_t} \right) \, dz + \frac{2}{z_t} \int_{z_0}^{z_t} C_0 \cos \left( \frac{n \pi z}{z_t} \right) \, dz
  \]
  \[
  \alpha_n = \frac{2}{z_t} \int_{z_0}^{z_t} C_0 \cos \left( \frac{n \pi z}{z_t} \right) \, dz
  \]
Evaluation of $\alpha$

$$\alpha_n = \frac{2}{z_t} \int_{z_0}^{z_t} C_0 \cos \left( \frac{n\pi z}{z_t} \right) dz$$

$$\alpha_n = \frac{2}{z_t} \left( C_0 \frac{z_t}{n\pi} \sin \left( \frac{n\pi z}{z_t} \right) \right)_{z_0}^{z_t} = 2 C_0 \left[ \sin \left( \frac{n\pi z}{z_t} \right) \right]_{z_0}^{z_t}$$

$$\alpha_n = \frac{2C_0}{n\pi} \left( \sin \left( \frac{n\pi z}{z_t} \right) - \sin \left( \frac{n\pi z_0}{z_t} \right) \right)$$

$$\alpha_n = \frac{2C_0}{n\pi} \sin \left( \frac{n\pi z_0}{z_t} \right)$$

The Solution

- We have our equation for concentration:

$$C(z,t) = \sum_{n=0}^{\infty} \alpha_n \exp \left( - \frac{n^2 \pi^2 D t}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$

- We also know $\alpha_n$'s:

$$\alpha_0 = \frac{C_0(z_t - z_0)}{z_t} \quad \alpha_n = \frac{2C_0}{n\pi} \sin \left( \frac{n\pi z_0}{z_t} \right)$$

$$C(z,t) = C_0 \left( 1 - \frac{z_0}{z_t} \right) - C_0 \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin \left( \frac{n\pi z_0}{z_t} \right) \exp \left( - \frac{n^2 \pi^2 D t}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$
The Solution

- This is the equation that describes the concentration:

\[ C(z, t) = C_0 \left(1 - \frac{z_0}{z_t}\right) - C_0 \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin \left(\frac{n\pi z_0}{z_t}\right) \exp \left(-\frac{n^2\pi^2 D t}{z_t^2}\right) \cos \left(\frac{n\pi z}{z_t}\right) \]

- To evaluate this we need to know:
  - \( C_0 \) (starting concentration).
  - \( z_t \) (thickness of film).
  - \( z_0 \) (position of boundary).
  - \( D \) (Diffusivity of species).
- We need to sum over \( 0 \rightarrow \infty \).
- The series is convergent, so we just need a large number.

The Diffusion Equation

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Examples:

- For $t = 0$s, the concentration profile is flat.
- At $t = 10$s, there is a significant increase in concentration.
- After $t = 10$ min, the profile remains relatively stable.

The diffusion coefficient $D$ is constant.

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Examples:

Steps to Follow:

1). Define your initial concentration:

\[ f(z) = C(z, t = 0) \]

2). Evaluate \( \alpha_0 \) by just integrating the initial concentration over the entire container:

\[ \alpha_0 = \frac{1}{z_t} \int_0^{z_t} f(z)dz \]

This can be tricky sometimes

3). Evaluate \( \alpha_n \) (where \( n > 0 \)):

\[ \alpha_n = \frac{2}{z_t} \int_0^{z_t} f(z) \cos \left( \frac{n\pi z}{z_t} \right) dz \]
Steps to Follow:

4). Substitute $\alpha_0$ and $\alpha_n$ into the equation for concentration:

$$C(z, t) = \sum_{n=0}^{\infty} \alpha_n \exp \left( -\frac{n^2 \pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$

$$C(z, t) = \alpha_0 + \sum_{n=1}^{\infty} \alpha_n \exp \left( -\frac{n^2 \pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$

For our step function this is:

$$C(z, t) = C_0 \left( 1 - \frac{z_0}{z_t} \right) - \sum_{n=1}^{\infty} \frac{2C_0}{n\pi} \sin \left( \frac{n\pi z_0}{z_t} \right) \exp \left( -\frac{n^2 \pi^2 Dt}{z_t^2} \right) \cos \left( \frac{n\pi z}{z_t} \right)$$

The Diffusion Equation in Literature
“Dose” of Impurity

• In most textbooks, the problem is described in a much-simplified way.

• The initial impurity is described as a “dose” at a single position \( z = 0 \).

• Mathematically it is described as a delta-function:

\[
C(z,0) = f(z) = Q\delta(z)
\]

\[
\int_{-\infty}^{\infty} C(z,0)dz = Q
\]

```
\text{No material flows through boundary}
\text{The concentration is initially zero everywhere apart from } z = 0
\text{The sample is very thick}
```

• This leads to the following (we won’t derive it):

\[
C(z,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left[ -\frac{z^2}{4Dt} \right]
\]
"Dose" of Impurity

\[ C(z, t) = \frac{Q}{\sqrt{\pi Dt}} \exp \left[ -\frac{z^2}{4Dt} \right] \]

- We can determine the diffusion length, from the half-width of the Gaussian:

\[ L = 2\sqrt{Dt} \]

Limitless Source of Dopant

- In this case assume there is an infinite supply of impurity.

- We can in this case use the approximation that the concentration at \( z = 0 \) is always \( C_0 \).
Limitless Source of Dopant

- The boundary conditions are then:
  - Limitless source of dopant: \( C(0, t) = C_0 \)
  - The concentration is initially zero everywhere: \( C(z, 0) = 0 \)
  - The sample is very thick: \( C(\infty, t) = 0 \)

In this case, the solution is:

\[
C(z, t) = C_0 \text{erfc} \left( \frac{z}{2\sqrt{Dt}} \right)
\]

- Where:
  \[
  \text{erfc}(x) = 1 - \text{erf}(x)
  \]
- And:
  \[
  \text{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{x} e^{-\xi^2} d\xi
  \]

Normally, in textbooks, a table of values of \( \text{erf}(x) \) is given.
Example Data

- Y-axis is normalized to the surface concentration ($C_0$).
- The x-axis is the distance from the surface (normalized to diffusion length).

Summary

- We studied the physics and mathematics of diffusion.
Next Time...

• We will look at ion implantation.