ECE 611 / CHE 611 - Electronic Material Processing
Fall 2019
Homework 1 - Solutions
Due at the beginning of class Tuesday October 15th

Question 1 [5 marks]:

a) Like silicon, germanium (Ge) adopts the diamond crystal structure (see Figure 1). The lattice constant of Ge is \( a = 5.66 \text{Å} \). The mass of Ga atoms are 73 amu. You will need to know that 1 amu = \( 1.66 \times 10^{-27} \) kg. Using Figure 1 Determine the mass density of crystalline germanium. Give your answer in g/cm\(^3\).[3 marks]

This is the same approach as we have seen in the lectures, just the mass of atoms is different. We first calculate the number of atoms per cell:

Corner atoms contribute 1/8\(^{th}\) atom per atom:

\[ N_{\text{corner}} = 8 \times \frac{1}{8} = 1 \]

Face atoms contribute 1/2\(^{th}\) atom per atom:

\[ N_{\text{face}} = 6 \times \frac{1}{2} = 3 \]

Internal atoms contribute 1 atom per atom:

\[ N_{\text{internal}} = 4 \times 1 = 4 \]

So the total number of atoms per cell is:

\[ N = N_{\text{corner}} + N_{\text{face}} + N_{\text{internal}} \]

\[ N = 1 + 3 + 4 = 8 \]
We now need to determine the mass in the cell. All atoms are germanium, with mass \( m_{\text{Si}} = 73 \) amu. So the mass in the cell in kg is:

\[
m = 8 \times 73 \times 1.66 \times 10^{-27} \text{ kg}
\]

\[
m = 9.69 \times 10^{-25} \text{ kg}
\]

We are going to express the answer in g/cm\(^3\):

\[
m = 9.69 \times 10^{-22} \text{ g}
\]

To determine the density we need to know the volume \( V \) of the cell. Since the silicon unit cell is cubic \((a=b=c)\) we can then just say:

\[V = a^3\]

We are given the unit cell in Angstroms but we are going to express the result in g/cm\(^3\):

\[a = 5.66 \text{ Å}\]

\[a = 5.66 \times 10^{-10} \text{ m}\]

\[a = 5.66 \times 10^{-8} \text{ cm}\]

\[V = (5.66 \times 10^{-8})^3 \text{ cm}^3\]

\[V = 1.81 \times 10^{-22} \text{ cm}^3\]

So we can finally determine the density:

\[
\rho = \frac{m}{V}
\]

\[
\rho = \frac{9.69 \times 10^{-22} \text{ g}}{1.81 \times 10^{-22} \text{ cm}^3}
\]

\[\rho = 5.35 \text{ g/cm}^3\]

b) Figure 2 shows planes in a cubic crystal structure. Determine the Miller indices for the two crystal planes shown in Figure 2. The tick marks on the axes are evenly spaced. Quote the miller indices in standard form: with the lowest possible, integer values. For example, the plane \((600)\) should be quoted as \((100)\).[2 marks]
As in class, the first thing we do is determine the intercepts with each axis. For (a) this is \(x=y=z=4\).

Next step is to take the reciprocals:

\[
\frac{1}{x} = \frac{1}{y} = \frac{1}{z} = \frac{1}{4}
\]

Next we multiply this reciprocals by the smallest number that makes them all integers. In this case this is 4. Hence the solution is \((hkl) = (111)\).

For (b) this is \(x=1, y=4, z=5\).
Take the reciprocals as before:

\[
\frac{1}{x} = \frac{1}{1}, \quad \frac{1}{y} = \frac{1}{4}, \quad \frac{1}{z} = \frac{1}{5}
\]

We want to make these integers by multiplying by a common factor. The easiest way is to multiply by the product of all intercepts: 1×4×5=20. Giving us:

\[
\left(\frac{20}{1}, \frac{20}{4}, \frac{20}{5}\right) = (20,5,4)
\]

This is the best we can do. There is no common factor we can divide by to give the Miller indices as smaller integers. Therefore the answer is: (hkl) = (20,5,4).

**Question 2 [8 marks]:**

a) Explain why we require single-crystal (rather than polycrystalline or amorphous) silicon for microelectronics. [2 marks]

While the mobility in polycrystalline silicon is lower than in single-crystalline silicon it is not prohibitively low. The main issue with polycrystalline silicon is that the introduction of grain-boundaries cause significant device-to-device variation. This makes devices unpredictable and unreliable.

While amorphous silicon is homogenous, the charge carrier mobility is about 1000 times lower in amorphous silicon compared to single-crystalline silicon. It is far too for processor applications.

b) Figure 3(a) shows a schematic diagram of a silicon boule being withdrawn from a melt. Figure 3(b) shows the measured impurity concentration in this boule as a function of the fraction of the melt solidified. If the impurity concentration in the melt was $10^{19}$ cm$^{-3}$ before the boule was
started to be withdrawn, use the data in Figure 3(b) to determine the segregation coefficient of the impurity element present. [6 marks]

![Diagram](image)

**Figure 3:** (a) Schematic diagram of boule of silicon withdrawn from melt. (b) Impurity concentration in the silicon boule as a function of the fraction of the melt that has been solidified. This data can be downloaded [here](#).

This question requires us to use the normal freezing relation:

\[ C_s = k_0 C_0 (1 - X)^{k_0 - 1} \]

Where:
- \( C_s \) is the impurity concentration in the solid at position \( X \).
- \( k_0 \) is the segregation coefficient of the impurity.
- \( C_0 \) is the impurity concentration in the melt.
- \( X \) is the fraction of the melt solidified.

We are given the impurity concentration as a function of \( X \), are given \( C_0 \), and need to determine the value of \( k_0 \). Unfortunately, because \( k_0 \) appears on the right hand side as both a linear term and an exponent, there is no easy way to re-arrange this equation to give \( k_0 \) as the subject.

We do however have \( C_s \) measured for a range of values of \( X \), so can perhaps use some sort of linear fitting strategy to solve this.

To linearize an equation like this, we first take logarithms. We will work in base-10 but it doesn’t matter which base you use. Start by re-arranging:

\[ \frac{C_s}{k_0 C_0} = (1 - X)^{k_0 - 1} \]

Now take logs:

\[ \log_{10} \left( \frac{C_s}{k_0 C_0} \right) = \log_{10} [(1 - X)^{k_0 - 1}] \]

Using known logarithmic identities, we can bring the exponent out the fronts:

\[ \log_{10} \left( \frac{C_s}{k_0 C_0} \right) = (k_0 - 1) \log_{10} [1 - X] \]
Also use the logarithmic identity for quotients on the left hand side:

\[ \log_{10}[C_S] - \log_{10}[k_0 C_0] = (k_0 - 1)\log_{10}[1 - X] \]

If we re-arrange this, we can get this into the equation for a straight line:

\[ \log_{10}[C_S] = (k_0 - 1)\log_{10}[1 - X] + \log_{10}[k_0 C_0] \]

\[ y = mx + c \]

So if we plot \( y = \log_{10}[C_S] \) against \( x = \log_{10}[1 - X] \) we should get a straight line graph with a gradient of \( m = (k_0 - 1) \) and an intercept of \( c = \log_{10}[k_0 C_0] \).

We can easily do this in Excel:

If we plot this we get something like the following:

I.e. a straight line graph. To get \( k_0 \) we can either extract the gradient \( m = (k_0 - 1) \) or the constant \( c = \log_{10}[k_0 C_0] \). We will just evaluate the gradient. There are many ways you can do this: straight line fitting, drawing on the graph, or simply evaluating the slope of the two end points. Here we carry out a linear fit, but any valid approach will be accepted.
We find the gradient is $m = -0.977$. From above we know that $m = k_0 - 1$. So we can say:

$$k_0 = m + 1$$
$$k_0 = -0.977 + 1$$
$$k_0 = 0.023$$

Alternatively we could just choose a value then solve recursively. The normal freezing relation should hold for all $X \neq 1$, so can choose any value. As an example we will just choose $X = 0.5$. We can either read the corresponding $C_s$ off Figure 3(b), or we could use the data provided. We will here just look in the data:

$$C_s = 4.5 \times 10^{17} \text{ cm}^{-3}$$

You could then re-arrange the normal freezing relation:

$$C_s = k_0 C_0 (1 - X)^{k_0 - 1}$$

$$k_0 = \frac{C_s}{C_0 (1 - X)^{k_0 - 1}}$$

You would then enter a starting guess value of $k_0$ on the right hand side (e.g. $k_0 = 0.5$), then evaluate the left hand side, put it into the right hand side, and so-on until the solution converges.

Full marks will however be given for any reasonable solution where it is made clear how you evaluated $k_0$.

**Question 3 [7 marks]:**

a) Figure 4 shows a pipe through which nitrogen gas ($N_2$) is flowing. The internal diameter of the pipe is 5 cm and the temperature of the gas is 300K. Determine the pressure at which the flow in the chamber makes the transition from viscous to molecular. The molecular diameter of $N_2$ is 3.16Å. Give your answer in Torr.[2 marks]
From Lecture 3 we know that viscous flow occurs when \( \lambda \ll d \) and molecular flow occurs when \( \lambda \gg d \), where \( \lambda \) is the mean free path of particles and \( d \) is the representative dimensions of the chamber. The transition between these types of flow occurs when \( \lambda = d \).

The mean free path of particles was given in the lecture:

\[
\lambda = \frac{1}{\sqrt{2\pi d_0^2 n}}
\]

Note \( d_0 \) is the molecular diameter \((d \neq d_0)\).

So we seek the situation when:

\[
d = \frac{1}{\sqrt{2\pi d_0^2 n}}
\]

The pressure is given by:

\[
P = nk_B T
\]

So:

\[
n = \frac{P}{k_B T}
\]

Therefore we can say:

\[
d = \frac{k_B T}{\sqrt{2\pi d_0^2 P}}
\]

We know the representative dimensions of the pipe \((5 \text{ cm})\), and we need to know the pressure.

\[
P = \frac{k_B T}{\sqrt{2\pi d_0^2 d}}
\]

After we enter the values \(\text{remember to convert to SI}\) we get a pressure of \( P = 0.187 \text{ Pa} \). We need the value in Torr so the answer is therefore: \( 0.187 / 133.3 = 1.4 \times 10^{-3} \text{ Torr} \).

b) A \((111)\) terminated silicon wafer is placed in a chamber containing \( \text{O}_2 \), held at 300K for 5 minutes. What type of pump \(\text{(high vacuum or low vacuum)}\) would be sufficient to ensure a complete monolayer is not formed on the wafer? Approximate \( \text{O}_2 \) molecules as spheres that form a monolayer in a 2D square array, as shown below. Just guessing the answer \((\text{right or wrong})\) will get you zero marks! \([3 \text{ marks}]\)
You will need to know:

- The molecular diameter of O$_2$ is 2.96 Å.
- The mass of an O atom is 15.999 amu.
- The sticking coefficient of O$_2$ on (111) Si is 0.15.
- The Boltzmann constant is $1.38 \times 10^{-23} \text{ m}^2\text{kg} \cdot \text{s}^2\text{K}^{-1}$.
- 1 atomic mass unit = $1.66 \times 10^{-27} \text{ kg}$.

Recall, low vacuum pumps are defined in the range: 760 to $10^{-3}$ Torr, and high vacuum pumps are required to achieve vacuums of 1 to $10^{-10}$ Torr. Hence we need to determine the pressure for the condition to be met.

This is again a similar problem to what was observed in class. If we know the time the wafer is present in the chamber ($t$), the areal (2-dimensional) density of molecules on the monolayer ($n_{2D}$), and the sticking coefficient ($S_c$) we can determine the necessary impingement rate for a monolayer to form in this time:

$$J_A = \frac{n_{2D}}{tS_c}$$

We here approximate the monolayer as a square array of circles, as we did in the lecture:

The areal density of this layer is then simply the reciprocal of the area occupied by each sphere. Since we approximated the packing as a square array, the area occupied by each molecule is just:

$$A = d_0^2$$

$$n_{2D} = \frac{1}{d_0^2}$$

So the impingement rate required can be expressed as:

$$J_A = \frac{1}{tS_c d_0^2}$$

From 5(a) we know the impingement rate as a function of pressure is

$$J_A = P \frac{1}{\sqrt{2\pi mk_BT}}$$
Therefore:

\[ \frac{1}{tS_c d_0^2} = \frac{1}{P \sqrt{2\pi m k_B T}} \]

Re-arrange for \( P \):

\[ P = \frac{n m k_B T}{tS_c d_0^2} \]

Filling in the parameters (in SI units):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>( 15.999 \times 2 \times 1.66 \times 10^{-27} = 5.31 \times 10^{-26} \text{ kg} )</td>
</tr>
<tr>
<td>( k_B )</td>
<td>( 1.38 \times 10^{-23} \text{ m}^2 \text{kg} \text{s}^{-2} \text{K}^{-1} )</td>
</tr>
<tr>
<td>( T )</td>
<td>( 300 \text{ K} )</td>
</tr>
<tr>
<td>( t )</td>
<td>( 5 \times 60 = 300 \text{ s} )</td>
</tr>
<tr>
<td>( S_c )</td>
<td>( 0.15 )</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>( 2.96 \text{ Å} = 2.96 \times 10^{-10} \text{ m} )</td>
</tr>
</tbody>
</table>

We get \( P = 9.43 \times 10^{-6} \text{ Pa} \).

In Torr: \( P = 7.07 \times 10^{-8} \text{ Torr} \). Hence a **high vacuum pump** is required.

c) Explain why cryocondensation of hydrogen and helium is not effective in most cryogenic pumps. [2 marks]

- Cryocondensation is the process by which gas molecules in the chamber condense onto the condenser arrays in the pump.
- The temperature of condenser arrays in the cryogenic pump are normally about 20K.
- This is above (or close to) the boiling point for H and He, so these molecules will not condense on the arrays.
- Instead reduction in H and He concentration is obtained through cryoadsorption.

**Question 4 [5 marks]:**

a) Figure 5 an example galvanic cell. The cathode is a cylinder with a diameter of 0.5cm, and 10cm submerged in the solution. If we were to carry out electrodeposition for 10 minutes and need to deposit 100 μm of copper onto the cathode, approximate what constant current would we need to maintain? Give your answer in amps. [3 marks]

You will need to know:

- The mass of a copper atom is 63.546 amu.
- The mass density of copper is 8.96 g/cm³.
- The electrons per half-reaction is 2.
- Faraday Constant, \( F = 9.65 \times 10^4 \text{ C/mol} \).
- 1 atomic mass unit = \( 1.66 \times 10^{-27} \text{ kg} \).
This is similar to a problem we studied in Lecture 4, but we are not told the mass of the copper being deposited. Instead we are told the density of copper, and the dimensions the copper will be deposited over.

As in class, we can start with the relationship between current and reaction rate:

\[ I = nF \mathcal{R} \]

Where \( I \) is the current that is flowing, \( n \) is the number of electrons per atom, \( F \) is the Faraday Constant, and \( \mathcal{R} \) is the reaction rate in moles / second.

If \( \mathcal{R} \) is the number of moles transferred per second, we can say:

\[ \mathcal{R} = \frac{N}{t} \]

Where \( N \) is the number of moles transferred and \( t \) is the reaction time.

I.e.

\[ I = nF \frac{N}{t} \]

We know the reaction time is 10 minutes, but we need to determine the number of moles deposited. Let’s first determine the volume of copper deposited. We know that copper deposited will be 100 \( \mu \)m thick but the area is a little complicated with this geometry.

Starting with the bottom of the electrode, we know the diameter is 0.5 cm, so the area is:
\[ A_{\text{bottom}} = \pi \left( \frac{d}{2} \right)^2 \]

Hence:

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

Now we also need to consider the sides of the electrode. We are told the submerged length is 10 cm:

To get the area we need to multiple this by the circumference of the circle:

The circumference is just:

\[ L_{\text{circ}} = \pi d \]

\[ L_{\text{circ}} = 1.57 \text{ cm} \]

The area of the side of the cylinder is then:

\[ A_{\text{side}} = 10 \text{ cm} \times L_{\text{circ}} \]

\[ A_{\text{side}} = 15.7 \text{ cm}^2 \]

Finally, the total area is:

\[ A = A_{\text{bottom}} + A_{\text{top}} = 15.9 \text{ cm}^2 \]
Since we are asked for an approximation, and the thickness of the copper is much smaller than the radius of the cathode, we don’t need to worry about changes in circumference with growth. The thickness is \( d = 100 \text{ μm} \), so the total volume deposited is:

\[
V \approx dA \\
V = 0.01 \times 15.9 \\
V = 0.159 \text{ cm}^3
\]

With the density \( \rho \) of copper given, we can determine the total mass deposited:

\[
m = \rho V \\
m = 8.96 \times 0.159 \\
m = 1.425 \text{ g}
\]

We are told the atomic mass of copper is 63.546 g. The atomic mass is the mass of one mole. Hence we can determine the number of moles from:

\[
N = \frac{1.425}{63.546} = 0.0224 \text{ mol}
\]

Now it is simply a case of entering numbers:

\[
I = nF \frac{N}{t} \\
I = 2 \times 9.65 \times 10^4 \times \frac{0.0224}{10 \times 60}
\]

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

b) Explain briefly one way organic additive compounds can be used to avoid voids being introduced when depositing metals into trenches via electrochemical deposition. [2 marks]

Void are established during electrochemical deposition when the top of a trench closes before the bottom. This can be because the original features were not uniform (see below) or another reason.

Additives such as suppressors or accelerators are used to locally change the deposition rates.

A common strategy is to place suppressors at the top of the trench and accelerators at the bottom. This ensures the trench fills from the bottom up.
Accelerator

Suppressors