Question 3 [7 marks]:

a) Aluminum oxide is a wide-band gap insulating metal oxide, formed via ionic bonding. By assuming that all outer shells are filled / empty, determine the chemical formula of a stable aluminum oxide compound, and explain your reasoning. You will need to use the fact that aluminum (Al) is a Group 13 element and oxygen (O) is a Group 16 element.[2 marks]

We are told that aluminum (Al) is a Group 13 element and hence has 3 electrons in its outer shell.

We are told that oxygen (O) is a Group 16 element and hence has 6 electrons in its outer shell.

The question is then which combination of Al and O will ensure that all shells are filled. Oxygen has 6 electrons out of 8 in its outer shell so we know it needs two electrons per atom. Aluminum has 3 electrons in its outer shell, so therefore we know that there must be an even number of Al atoms.

Start by considering 2 Al atoms. In this case there will be a total of 6 electrons in outer shells that can participate in bonding. Oxygen needs 2 electrons per atom. Therefore we can conclude that there should be 3 O atoms for the 2 Al atoms:

\[ \text{Al}_2\text{O}_3 \]

Alternatively, we could have used the periodic table to identify that both indium and gallium are in the same group as aluminum, and hence have the same number of electrons in their outer shell. We know (from Lecture 8) that indium oxide and gallium oxide have the formulae: \( \text{In}_2\text{O}_3 \) and \( \text{Ga}_2\text{O}_3 \) respectively, and therefore aluminum should be analogous.

b) Provide one reason why the on/off ratio of TFTs formed of oxides such as ZnO or \( \text{In}_2\text{O}_3 \) are so high compared to silicon.[1 mark]

The band gap is much higher in ZnO and \( \text{In}_2\text{O}_3 \) compared to silicon. This means the intrinsic carrier concentration is much lower, and the off-current is much lower, in ZnO and \( \text{In}_2\text{O}_3 \).

c) Explain briefly why films of indium-gallium-zinc oxide (IGZO) are normally amorphous.[1 mark]

IGZO is essentially a mixture of binary oxides: \( \text{In}_2\text{O}_3 \), \( \text{Ga}_2\text{O}_3 \) and ZnO. These compounds each have different crystal structures. Zinc oxide (predominantly) forms a wurzite crystal structure, indium oxide crystallizes into either the bixbyite or corundum crystal structure. \( \text{Ga}_2\text{O}_3 \) has several polymorphs. When mixed together the film is unable to crystallize into a single structure and hence becomes amorphous. The crystallization is said to be frustrated.

d) Explain briefly why semiconductors that have transport states typically consisting of \( s \)-type orbitals are attractive for TFTs.[3 marks]
**Question 2** [13 marks]

Pentacene is an organic semiconductor formed of 5 fused benzene rings. Figure 1 shows the molecular structure of pentacene, in shorthand notation. The internal lines in this diagram represent double bonds.

![Figure 1 Molecular structure of pentacene, drawn in shorthand notation.](image)

a) Using Figure 1, determine the chemical formula of a pentacene molecule. Do not just quote an answer: you need to show your reasoning to get all marks. [3 marks]

This is basically a question of knowing what shorthand organic chemistry notation means, and then counting atoms.

The first thing to know about shorthand notation is that all vertices are carbon atoms. We can therefore count the atoms as shown below:

In total you should count 22 carbon atoms.

The next rule of shorthand notation is that all the hydrogens are implicit. I.e. they are where they should be. We know that carbon has 4 outer electrons, so each carbon should have 4 bonds. This is made slightly more complicated in pentacene since it is conjugated, i.e. it is formed of alternating single and double bonds. If you look at the molecular structure you will see that each carbon atom is involved in one double bond with an adjacent carbon atom. This means...
that we need only 3 “lines” drawn from every carbon vertex to satisfy bonding (the 4th is always involved in a double bond). If you go through each atom and identify which ones are missing bonds, you should add a hydrogen atom. The structure should look like:

In total you should count 14 hydrogen atoms.

Hence the chemical formula for pentacene is: \( \text{C}_{22}\text{H}_{14} \).

b) What is meant if an organic compound is said to be conjugated?[1 mark]

A conjugated molecule is formed of alternating single and double bonds.

c) Charge transport in pentacene thin-film transistors (TFTs) can be described by the Vissenberg and Maters model. A pentacene TFT is known to have a characteristic width of transport states: \( T_0 = 385\text{K} \). When measured at a temperature of 300K with an applied gate voltage of 20V, the mobility of the transistor was found to be \( \mu = 0.5 \text{ cm}^2/\text{Vs} \). What would you expect the mobility of this TFT to be when measured at a temperature of 300K with an applied gate voltage of 50V, assuming all other parameters remain constant? Use this result to make a statement on the consistency of mobility values reported in the pentacene TFT literature.[7 marks]

At first glance this appears to be a lot more complex than it is. We are asked to use the Vissenberg and Matters model, which involves this equation:

\[
\mu = \frac{\sigma_0}{e} \left( \frac{\pi (T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1 - T/T_0) \Gamma(1 + T/T_0)} \right)^{T_0/T} \left[ \frac{(C_{0\times}V_G)^2}{2k_B T_0 \varepsilon_0 \varepsilon_r} \right]^{(T_0/T-1)}
\]

Luckily we do not need evaluate every parameter here, nor evaluate the \( \Gamma \)-functions. The question tells you that the mobility is \( \mu = 0.5 \text{ cm}^2/\text{Vs} \) at \( T = 300\text{K} \), when we apply \( V_G = 20\text{V} \), and asks you to evaluate the mobility when \( V_G = 50\text{V} \), and all other parameters are the same. Since most of the parameters are constant, we can wrap most of this equation into a single constant (call it \( A \)). Say:

\[
A = \frac{\sigma_0}{e} \left( \frac{\pi (T_0/T)^3}{(2\alpha)^3 B_c \Gamma(1 - T/T_0) \Gamma(1 + T/T_0)} \right)^{T_0/T} \left[ \frac{(C_{0\times}V_G)^2}{2k_B T_0 \varepsilon_0 \varepsilon_r} \right]^{(T_0/T-1)}
\]

This leaves:

\[
\mu = A [(V_G)^2]^{(T_0/T-1)}
\]

Or:
\[
\mu = AV_G^{\left(\frac{2T_0}{T-T_0}\right)^{-2}}
\]

Notice we are given both \(T\) and \(T_0\) in the question. This means we have all the information we need to evaluate this constant \(A\):

\[
A = \frac{\mu}{V_G^{\left(\frac{2T_0}{T-T_0}\right)^{-2}}}
\]

We will work with cm as our spatial unit since we are not using any fundamental constants here.

Putting in the numbers:

\[
A = \frac{0.5}{20^{\left(\frac{2\times385}{300}\right)^{-2}}}
\]

\[
A = \frac{0.5}{20^{0.566}}
\]

\[
A = 0.916
\]

(we will ignore units of \(A\) because this is quite complicated, and we don’t need to worry about it to answer the question)

We now have a value for \(A\) under our measurement conditions. Now we just need to evaluate the mobility (with the same \(A\), \(T\), and \(T_0\)) if \(V_G\) is now 50V. Return to the Vissenberg and Matters Equation:

\[
\mu = AV_G^{\left(\frac{2T_0}{T-T_0}\right)^{-2}}
\]

We have everything we need to evaluate \(\mu\), so we can just put in the numbers:

\[
\mu = 0.916 \times 50^{\left(\frac{2\times385}{300}\right)^{-2}}
\]

The exponent is just the same as before:

\[
\mu = 0.916 \times 50^{0.566}
\]

\[
\mu = 0.840 \text{ cm}^2/\text{Vs}
\]

This shows us that under the Vissenberg and Matters model, when we increase the applied gate voltage, and leave all other parameters the same, we will observe an increase in mobility. This is important because we typically extract \(\mu\) at different applied voltages. Since the applied voltage affects the measured mobility, it means that reported mobilities are likely to be inconsistent between research groups.

d) What is meant by the highest occupied molecular orbital (HOMO) in organic semiconductors, and what is it analogous to in conventional (inorganic) semiconductors?[2 marks]
In an organic semiconductor the highest occupied molecular orbital (HOMO) is the electronic orbital that is highest energy while still being occupied, under equilibrium conditions. I.e. the state above it in energy will be not be occupied by electrons under equilibrium conditions. By removing an electron from this otherwise-full HOMO state, we can create a hole than can participate in transport in the same way as in an otherwise-full valence band in a conventional semiconductor.

The HOMO can be considered an organic-semiconductor analog of the valence band.