QUESTION 1: Asked 20/4/2017

Quoting K:

- Q: 2016 Q1 (c) You ask under what condition does $K$ become unity. I realise that this is the Langmuir regime, and I can plot the $\theta = 1 - e^{-rst}$ curve, that is when $s$ is linearly proportional to the coverage. However I can’t think of much more to say for this answer. Would you use the previous equation for $K$ and say it’s when $p_a’ = p_a + p_a$ (where p’s are the relative probabilities) ?
- A: What about migration i.e. $p_m$ or $p_m’$?
- Q: Ah ok so, $K = p_a’/(p_a + p_a)$ which can be re-written as $(1 - p_m’)/(1 - p_m)$ so either the probabilities of migration are equal from occupied and unoccupied sites in Langmuir, or they are zero. Would guess zero since it is said to be an ‘ideal’ case.
- A: Essentially answered by your other reply above - Langmuir case implies also that the migration probabilities from above chemisorbed (filled) sites or from above unfilled sites to neighbouring physisorbed sites are the same. I might note $p_m = p_m’ = 0$ is not necessarily the cause of the “ideal” Langmuir behaviour in each and every case. This observation or the allied observation of $p_a’ = p_a + p_a$ are sufficient to answer the question provided one explicitly discusses the physics of “what happens” i.e. it is helpful to put into words what this equality means.

I should note however that the same probabilities in each case need not necessarily imply the same timescales. To illustrate deviations from the Langmuir case also arise where the timescale for e.g. $p_a$ is very fast i.e. when it is easy for a physisorbed state to lead to a chemisorbed state and the transition probability (or rate) is very high. By comparison it may be slow to desorb, but quick to migrate whether above a filled or unfilled site. In these circumstances $K$ will be very different from 1, and even if the timescale or rate of migration is the same in each case, the probability of $p_m’$ may be much higher than for $p_m$ (that is if $p_a$ is dominant and approaches 1). The above discussion is not necessary (for answering the exam question), but should make you think about the processes involved.

QUESTION 2: Asked 20/4/2017

Quoting K:

- Q: 2016 Q2 (d) I have worked out the first part of the question, to grow a 40 nm layer of GaAs, however I get slightly confused when adding in the Al. Would you use the same equation as before for the Ga flux but then only have 0.75 of the monolayer attributed to it (assuming s for Al =1). And then for the cell parameters equate the ratios of the rates to their stoichiometric ratios?
- A: To determine the time necessary for 10nm of GaAs (you are given temperature, vapour pressure and molecular weight of Ga), this will give you atoms per unit area per second. Don’t forget tooling factor! Using the GaAs unit cell and that the Ga within that cell is an fcc arrangement, you get 2 atoms of Ga for each square area of the real space bulk unit cell (each face has 4 Ga atoms at the corner and one in the Ga centre). Going vertically upwards there are two spacings between three LAYERS of Ga for each 565pm (see bulk unit cell) - so each layer is separated by 283pm. So with a factor of atoms / unit area you can change the flux into a rate of monolayers per second, and then change it again into successive layers (at 283pm spacing) per second giving you a growth rate of nm/second.
BUT THIS WAS NOT YOUR QUESTION …

For the AlGaAs layer you are not changing the rate of the Ga deposition - by implication to get the stoichiometry you wish you only need 3/4 as much Ga for every completed monolayer (the other 1/4 of the atoms in that layer must be aluminium). So provided you have set the rate of Al deposition correctly then the total amount of time for the 40nm AlGaAs growth will be 3/4 that required for the undoped GaAs growth. For a thickness of 10 nm it would thus be 1/4x3/4 = 3/16 of the time for 40nm GaAs.

You are right to point out that an implicit assumption might be that for Al \( s=1 \). Lets run with this later, though this is not likely to be the case! This assumption is not necessary for the calculation on the time (answered above). If for instance for the Al \( s=0.5 \), then one must double the Al flux on the surface in order to get the 1/4 monolayer of Al in \textbf{THE SAME TIME} as the 3/4 monolayer of the Ga. So the answer for the time does not depend on this assumption on sticking ratio of the aluminium.

The parameters necessary for the Al deposition cell, do depend on the assumption (or knowledge) of the sticking coefficient for Al. Let us assume that this is \( s=1 \). (If it is less then we need to increase the rate of flux from the Al cell).

We need a flux from the Al cell that is \( \frac{1}{3} \) the flux of Ga from the Ga cell i.e. a ratio determined by 1/4:3/4.

On that basis and using the calculation of flux for Ga (you are given temperature, vapour pressure and molecular weight of Ga), you then need to divide this by three to get the flux for Al. Rearrange the other factors (mass of Al) to get \( \frac{P^2}{T} \) for the aluminium source.

Look at the graph - pick e.g. \( P_{Al} = 1 \times 10^{-4} \) mbar - look at the \( T \) from the vapour pressure graph - calculate \( \frac{P^2}{T} \) - is it too big or too small than the \( \frac{P^2}{T} \) you need? If so go up or down the curve and trial a new value - you will find an appropriate value quite quickly.

QUESTION 3: Asked 20/4/2017

Quoting K:

- Q: 2015 Q2 (e) You ask how long it takes to grow 10 nm of Si. We have the equation from the previous derivation and then the atomic density of Si. Just wondering does this atomic density value given correspond to the number density \( (Ca) \) of the growth layer?

  Maybe I'm misreading the diagram but I thought they should be the same?

- A: Quick answer in this case they are the same, especially if depositing Si on Si.

Possibly this is a bad choice of words in the question but I will explain why this is phrased in this fashion. Examining the dimensionality of the equation in (c), it should be clear that \( C_a \) has the same dimensions as \( C_g \). Thus \( C_a \) is the volumetric number density \( \text{atoms/m}^3 \).

If Silicon were a simple cubic with atoms only at the corners of the cube, then a monolayer would have the same number density as in the unit cell. If there were 5 layers in the unit cell, then for one layer, the number of atoms in that layer would be 1/5 of as in the whole unit cell, but in only 1.5th the volume, giving the \textbf{SAME} volumetric number density. \textbf{Thus \( C_a \) is EQUAL to the bulk atomic number density of silicon.}

Why then this distinction or awkward phrasing? The reason for the distinction is in the
more general case of epitaxial deposited monolayers with larger lattice spacings due to registry with the substrate atoms, i.e. larger atomic spacings than is normal as compared to their bulk unit cells, and hence a lower number density of the growth layer $(C_a)$ than the bulk atomic number density.

(Perhaps this deserves a further explanatory note next year).

Q: I couldn't find it in the notes, but I think I remember you saying it in lectures....is it correct to say that wet oxidation is faster than dry oxidation because H2O has better bonding to the surface and therefore higher concentration here? However, I always thought Si was hydrophobic when it had a clean surface?

Look at graphs in lecture 8 slide 18 - these are from Sze and Lee chapter 12 - the growth rates for wet vs dry oxidation are almost two orders of magnitude higher. Why? H2O chemisorbs to the Si surface and immediately forms a Si-OH bond. O2 will not chemisorb as readily as it is more difficult to dissociate the O2. This is the simple answer! Thus upon Si exposure to O2 vs H2O, the immediate result is more chemisorption on the H2O exposed surface due to the H2O. You may have also remembered that the Si(111) has a higher surface atom density than Si(100), and thus the difference between the solid and dashed lines (see figures again) for either the wet or the dry oxidation. Your question has conflated the latter fact with the former.

There will always be a native oxide on silicon in atmosphere as it will react very quickly (in fact with water vapour) and it is notoriously difficult from a surface science point of view to keep a clean Si surface clean for even a few hours as it will react with background pressures of $10^{-10}$ mbar of H2O to form an oxidised surface at room temperature, even in UHV chambers. Thus background pressures of $<10^{-10}$ are needed if working with Si surfaces.

Thus in testing the hydrophobicity of a Si surface you are either testing a SiO2 native oxide layer (often <3nm), or a passivated Si layer - perhaps with Si terminated in Si-F bonds if dip-etched in HF acid. The results will be very different. There is in fact also very different results for SiO2 layers when grown in different manners i.e. with a hydrated SiO2 layer (extra H2O in interstices, or OH at lattice sites in place of O) versus oxygen deficient SiO2 layers. So not true in general, or one must limit the applicability of your statement.

**QUESTION 4: Asked 20/4/2017?**

Quoting K:

- 2014 Q2 (a) Two properties of low energy electrons that underpin the LEED technique. I know one is their short mean free path and therefore surface sensitivity. Possibly a second one could be the fact that they are charged so their energies can be effectively separated. However, this is a property of electrons in general and not specifically low energy electrons, so was just wondering if I have missed another important property here.

- A: Wavelength! Low energy electrons will have deBroglie wavelengths that are comparable to the atomic spacing between neighboiring atoms on the surface of most solids i.e. between 1.8 and 3.5 angstroms, thus corresponding to between 20 - 120 eV.

- 2014 Q2 (c) How would one determine whether the (1,1) beam is visible on the screen?

- A: The LEED apparatus, at best, only collects electrons in one hemisphere, i.e. perhaps to a maximum 90° angles from the normal. In practice this may be 80°. The question is straightforward - calculate the needed theta for the (1,1) spot. The fcc(100) LEED pattern
will be a square pattern of diffraction spots in reciprocal space (imaged via the LEED). The (1,1) will be at the diagonal from the (0,0) and above the (1,0) and to the right of the (0,1). Begin by calculating the angle for the (1,0) spot for Ni and for 75eV - perhaps you will get \( n \times \lambda/d = 0.56 = \sin \theta \). The (1,1) spot is observed at a greater angle and has a sin theta that is sqrt(2) greater. Is this angle still small i.e. < 80° - if so you will see it on the screen. Spots whose diffraction angle approaches 90° (or further) cannot be collected by the LEED apparatus.

**QUESTION 5: Asked 20/4/2017?**

**Quoting K:**

- **Q:** 2013 Q1 (d) I was unable to work out how to approach the electrostatic argument. This was an exercise in the notes as well that I was unable to get out fully. I have the equation relating delta E to q and V, however any help with this would be much appreciated.
- **A:** Imagine a sphere of say 1 angstrom, now charge the sphere by removing ONE electron. What is the voltage difference before and after? The voltage on a charged sphere will be \( V = q/(4 \pi \epsilon_0 r) \) One might change \( r \) to a more appropriate atomic radius. Thus the **valence** influences the binding energy. To explain further: removing an electron from a singly positively charged atom is HARDER, and must overcome this additional voltage than removing an electron from a neutral atom. This is the valence effect for the chemical shift
- **Q:** Also in terms of the 'other effect' you ask for that must be taken into consideration. Is this relating to the chemical environment and the valence? Or is there something more to that question?
- **A:** The electron is NOT removed to infinity (as in 1st year electrostatics) - instead in a metal oxide - it is removed from the metal and moved to the oxygen atom which is perhaps located 2.5 Angstroms away. Thus the electrostatic voltage difference is actually more like \( 1/r_1 - 1/r_2 \)

BUT there is now also an electrostatic potential energy in this ionic solid. If simple cubic and a formula unit MO, then every metal is surrounded by 6 oxygens and vice versa (every oxygen surrounded by 6 metals), then each metal site is surrounded by a shell of 6 negatively charged O atoms at 2.5 A distance, and then a second shell of positively charged M atoms at distance of \( 2.5^2 + 2.5^2 \) \( 0.5 \), and further successive negatively and positively charged shells, ad infinitum.

This is evaluated as the Madelung potential.

The **observed chemical shift** is the sum of the electrostatic contribution from the different valences, and the Madelung contribution which itself is dependent upon the valences (the ionic charges on the atoms) and on the atomic arrangement.

**QUESTION 6: Asked 20/4/2017?**

**Quoting K:**

- **Q:** 2009 Q3 (d) It is asked the time to adsorb 0.5 monolayer of CO on a surface. I have worked out the flux from the equation using pressure, and also the surface atoms/cm^2 of the (100) Cu surface. To determine the time to cover half a monolayer do we just divide the Cu surface atoms by 2, or is there more that needs to be taken into account?
A: Part (c) suggests the Langmuir adsorption regime and the functional dependence with time is that it saturates exponentially with time.

Thus \[ \theta = 1 - \exp(-r s_0 t) \] (Slide 12 Lecture 4)

Solve this for \( \theta = 0.5, s_0 \) as given, \( r \) the ratio of flux to surface density of atoms (need to calculate for flux and for surface described). The only unknown is \( t \).

Cannot simply divide by 2 as you suggest - but numerically one would not be far off being correct as for small time the equation above is like \( \theta = r \ast t \) (as for small \( x \) \( \exp(-x) \approx 1 - x \) ), but will deviate by the time we get to half a monolayer i.e. for \( \theta = 0.5 \)

**QUESTION 7: Asked 20/4/2017?**

**Quoting K:**

- **Q:** 2008 Q10 (c) Any help with this question is appreciated. The maximum partial pressure of oxygen that will keep oxygen incorporation into the growth below one part per million...
- **Q:** In principle one can calculate the molecular flux for O$_2$ - use ambient temperature, given molecular mass and partial pressure.

The limit asked in the question, is (assuming the worst case scenario and sticking coefficient for O$_2$ is =1) that for every $10^6$ Ga atoms there is less than one O atom. Thus the flux of Ga must be $10^6$ times the flux of O$_2$ onto the surface. (Note it is O$_2$, but for every Ga there is an As, so no other factor of two is needed). Based on that one can calculate the MAXIMUM allowable background partial pressure.

If the sticking coefficient for oxygen were less than 1, then one could get away with a higher background pressure of O$_2$.

**QUESTION 8: Asked 20/4/2017?**

**Quoting K:**

- **Q:** Exercises in notes. In the notes, for the illustration of MD you have a diagram that has black filled in lattice sites and empty lattice sites. I still have trouble telling which is which in this case. I am inclined to think that the black are the overlayer, as they seem more hexagonal structure (fcc) to me, however I cannot think of concrete reasoning for this.
- **Q:** Think of the bcc(110) atoms as rectangles with an atom in the centre. The ratio of the sides of this rectangle is $1: \sqrt{2}$. The fcc(111) hexagonal arrangement also has a rectangle with an atom in the centre (lopping off the top and bottom atoms of the hexagon). But now the ratio of these sides of this rectangle are $1: \frac{2}{\sqrt{3}}$!! (twice the ratio of the height of an equilateral triangle to its base or twice the sin(60°) )

So there is a subtle difference that IS somewhat hard to spot. In slide 11 of lecture 7 I say that the substrate is bcc and overlayer is fcc; the diagram is from Zangwill chapter 16 (available on website). If in difficulty look for equal 60 degree angles in one that are not in the other and in the hexagonal arrangement there are equal distances between pairs of atoms.

**QUESTION 9: Asked ?**

**Quoting ?:**

- **Q:** In ...
- **A:**