The University of Western Ontario

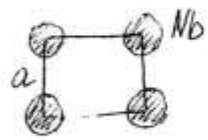
Name:_____
Student #:_____

P9826b Winter 2013

Midterm exam
February 25, 2013 – Solutions

Questions (Total - 30 points):

1. (*4 points*) (a) Niobium has *bcc* structure with the lattice parameter a=3.30Å. Draw a schematic representation of Nb(001) surface and calculate atomic density of the Nb (001) surface (number of Nb atoms per m^2).



$$\text{Area} = (3.3\times10^{-10}\,m)^2 = 10.89\times10^{-20}\,m^2$$

$$n_{Nb(001)} = \frac{1\ \text{atom}}{1.089\times10^{-19}\,m^2} = 9.18\times10^{18}\,\frac{\text{atoms}}{m^2}$$

(b) Niobium sample is oxidized by exposure to O_2 at 300°. The dissociative sticking coefficient of O_2 on Nb (001) is 0.05 at 300°C. Estimate the coverage of O atoms that results from exposing Nb surface to 10^{-5} Pa of O_2 for 1 min.

$T = 573\,K$ $\quad k_B = 1.38\times10^{-23}\,J/K$ $\quad Z_W = \dfrac{p}{(2\pi m k_B T)^{1/2}}$

$S_c = 0.05$ $\quad n_{Nb(001)} = 9.18\times10^{18}\,\dfrac{\text{atoms}}{m^2}$

$p = 10^{-5}\,Pa$

$t = 60\,s$

$m_{O_2} = 5.31\times10^{-26}\,kg$

$$Z_W = \frac{10^{-5}}{(2\pi\cdot5.31\times10^{-26}\times1.38\times10^{-23}\times573)^{1/2}} = \frac{10^{-5}}{5.14\times10^{-23}} = 1.95\times10^{17}\,\frac{\text{molecules}}{m^2\cdot s}$$

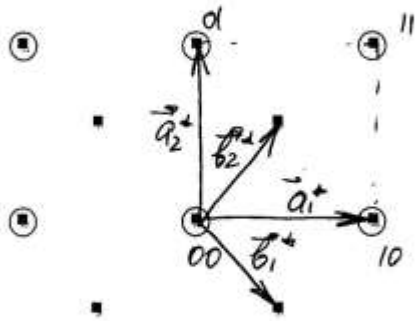
Coverage $\quad W_0 = \dfrac{Z_W\cdot2\cdot S_c\cdot t}{n_{Nb(001)}}$

$O_2 = 2O$

$$W_0 = \frac{1.95\times10^{17}\times2\times0.05\times60}{9.18\times10^{18}} = \frac{11.7}{91.8} = 0.127\,ML$$

(c) Following this oxygen exposure LEED pattern was observed from O/Nb(001) surface, and its schematic representation is shown on the figure below. Open circles correspond to the substrate peak positions, while squares are for the overlayer diffraction pattern.

Write a reciprocal space matrix for the overlayer pattern, real space matrix and name it using Wood's notation.



$$G^* = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \qquad \det G^* = \frac{1}{4} + \frac{1}{4} = \frac{1}{2}$$

$$G = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \qquad \det G = 1 + 1 = 2$$

$c(2\times2)$
or $p(\sqrt{2}\times\sqrt{2})R45°$

(d) Express oxygen coverage obtained in (c) as fractional coverage in monolayers, and as atoms/cm^2. Compare with your results in (b). How can you explain the difference?

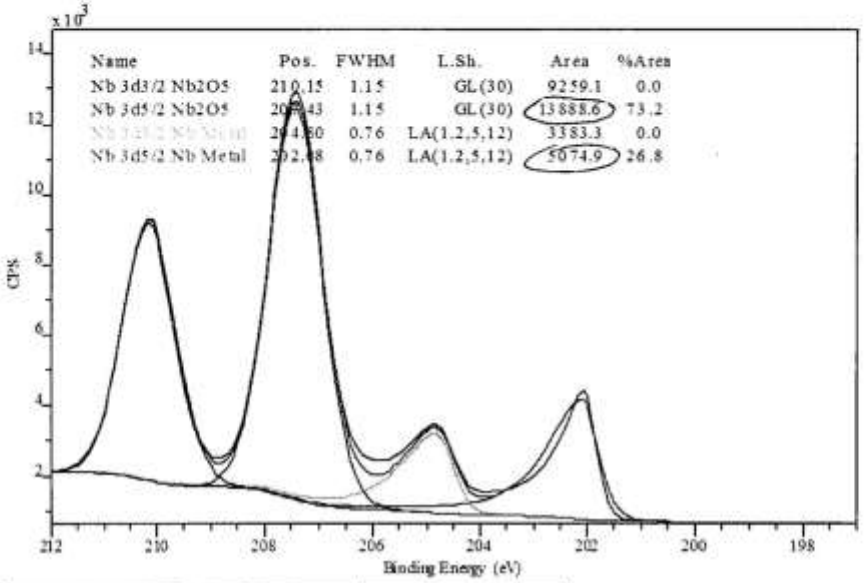
$$W^{O}_{c(2\times2)} = 0.5\,ML \qquad n_{O,c(2\times2)} = 4.59\times10^{18}\,\frac{atoms}{m^2} = 4.59\times10^{14}\,\frac{atoms}{cm^2}$$

Ideal $c(2\times2)$ O/Nb overlayer structure has coverage of 0.5 ML when all possible Nb sites are occupied by O atoms.

Even the fraction of the macroscopic surface is covered with oxygen, $c(2\times2)$ LEED pattern is observed

2. (4 *points*) Your lab partner has prepared Nb_2O_5 film by oxidation of metallic substrates, and wants to estimate oxide thickness. You propose to perform XPS to evaluate thickness of the oxide, and get the spectrum as illustrated below.

(a) Calculate Nb_2O_5 layer thickness using integrated areas of $3d_{5/2}$ peaks for Nb and Nb_2O_5 (refer to "Area" on the graph below), and properties of Nb and Nb_2O_5 in the table below.



IMFP Nb	27.25 Å
IMFP Nb_2O_5	24.61 A
Density Nb	8.57 g/cm3
Atomic Weight Nb	92.91 g/mol
Density Nb_2O_5	4.6 g/cm3
Atomic Weight Nb_2O_5	265.82 g/mol

$\sin\theta$

$$d(Nb_2O_5, Å) = IMFP_{ox} \times 1 \times \ln\left(\frac{n_M\, IMFP_M\, I_{ox}}{n_{ox}\, IMFP_{ox}\, I_M} + 1\right)$$

$$n_{Nb} = \frac{8.57}{92.91} = 0.092;\ n_{Nb_2O_5} = \frac{4.6}{265.82} = 0.017$$

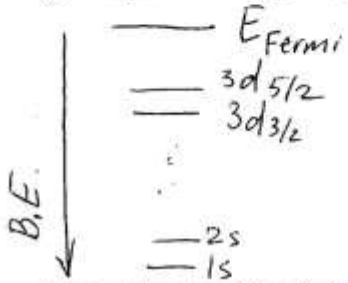
$$d(Nb_2O_5, Å) = 24.61 \times \ln\left(\frac{0.092 \times 27.25 \times 13888.6}{0.0173 \times 24.61 \times 5074.9} + 1\right) = 6.9\,nm = 69.8\,Å$$

(b) Explain to your lab partner what is "binding energy" and relatively to which energy level it is measured?

Binding energy of an electron is equal to the energy difference between the initial and final states of the atom, measured relatively to Fermi level

$E_B = h\nu - E_K$ (Einstein equation)

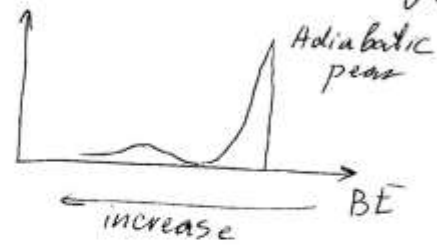
(c) Why is the binding energy of 3 $d_{3/2}$ peak higher than the one for 3 $d_{5/2}$ peak?



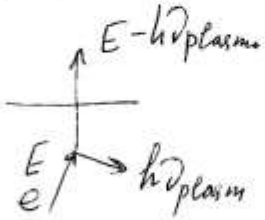
$3d_{5/2}$ has a higher angular momentum ($j = l + s$) compared to $3d_{3/2}$ and it is further away from nucleus but closer to Fermi level

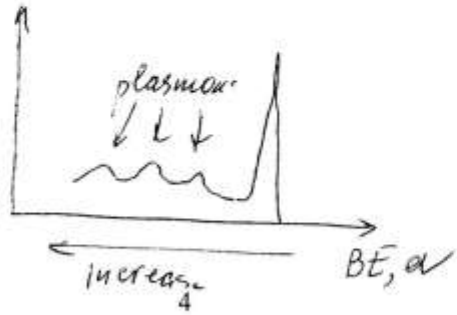
(d) Explain the origin of **shake-up** and **plasmon peaks** in XPS spectrum. Schematically draw their position (in binding energy coordinates) relatively to the main adiabatic peak.

Shake-up: the outgoing photoelectron can excite a valence $\bar{e}$ to unoccupied state, thus forming relatively stable electron-hole pair. Thus kinetic energy of such electron will be lower ⇒ B.E. higher.



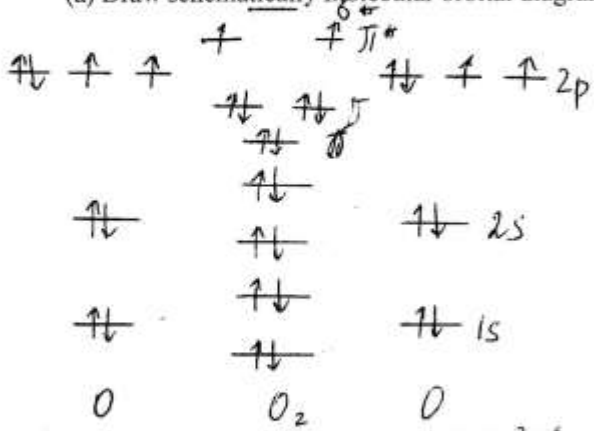
Plasmon





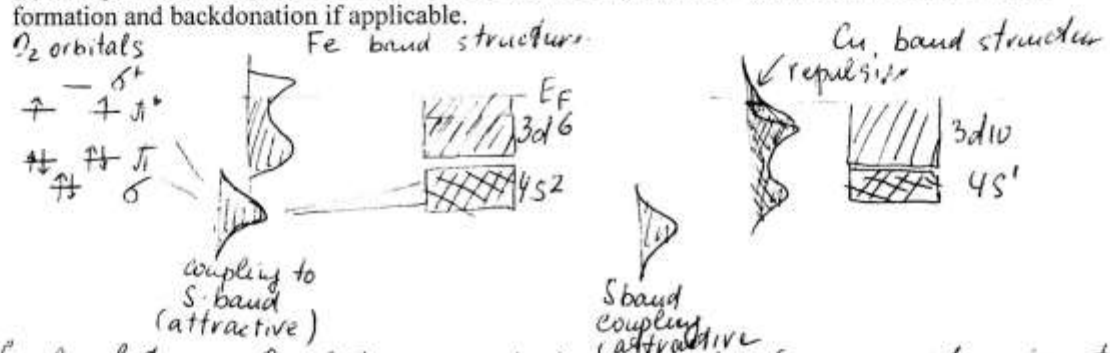
3. (*4 points*) Consider adsorption of O_2 molecule on transition metal surfaces.

(a) Draw schematically molecular orbital diagram for O_2 in the gas phase.



O $1s^2 2s^2 2p^4$

(b) Compare O_2 adsorption on Fe ([Ar]$4s^2 3d^6$) and Cu ([Ar]$4s^1 3d^{10}$) in terms of metal-O bond formation and backdonation if applicable.



① Coupling between O_2 electrons and 4s band is of weak chemisorption type (below E_{Ferm}, attractive, same for Fe & Cu)

② Coupling between O_2 and 3d band leads to the formation of two levels ("bonding" and "antibonding") ⇒ filling of antibonding state ⇒ position of "antibonding" state with respect to Fermi level ⇒ this state is filled for Cu but not for Fe. Therefore, both ① & ② for Fe result in attractive interaction and M-O bond is strong. Where as for Cu, antibonding state is below E_F and is filled (overall interaction is "marginal attractive). Additionally, Cu has filled 3d state. ⇒ Fe-O_2 bond is stronger Cu-O.

(c) What is important parameter (or parameters) influencing the strength of chemisorption interactions?

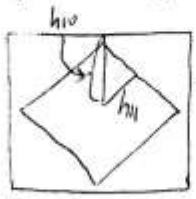
Chemisorption is a strong adsorption interaction in which orbital overlap leads to chemical bond formation. Strength of the chemisorption depends on the position of M-O (adsorbate) orbitals with respect to Fermi level.

5. (*10 points*)

Answer 5 of the following 10 questions (*2 points each*). Justify your answer, i.e., show computations, sketch figures, etc., needed to obtain the answer.

5.1 Consider a hypothetical 2D crystal having a simple square unit cell. Assume that there are deep cusps in the γ-plot in the (10) and (11) directions. Given that γ_{10} is 500ergs/cm and γ_{11} is 250ergs/cm, find the equilibrium crystal shape. Calculate the energy of the final equilibrium Crystal Shape (ECS).

$$\frac{\gamma_{10}}{\gamma_{11}} = \frac{500}{250} = \frac{2}{1} = \frac{h_{10}}{h_{11}}$$



← (11)-terminated crystal will be more energetically favourable

$$E_{11} = 4 \times 1cm \times 250 \frac{ergs}{cm} = 1000 ergs$$

5.2 The distance between atoms in a crystal are ~2 Å, so waves with approximately this wavelength are required to explore the crystal structure. Using de Broglie law (λ = h/p), calculate the energies of (a) neutrons (m=1.675×10^{-27}kg), (b) electrons (m=9.11×10^{-31}kg) and (c) X-rays required for the structural studies?

$$\lambda = \frac{h}{p} = \frac{h}{mV} = \frac{h}{\sqrt{2mE}} \qquad E = \frac{h^2}{2m\lambda^2} = \frac{p^2}{2m} \qquad h = 6.626 \times 10^{-34} J \cdot s$$

Waves with a comparable wavelength ($\lambda \sim 2Å$) are required to explore this structure. If the wavelength is much larger, structural details cannot be resolved, rather some average interaction occurs. If the wavelengths are much smaller, the beam is diffracted at extreme angles, making detection difficult

$$n's: E = \frac{(6.626 \times 10^{-34})^2}{2 \times 1.675 \times 10^{-27} \times 4 \times 10^{-20}} = 3.3 \times 10^{-22} J = 0.02 eV$$

$$e's: E = \frac{(6.626 \times 10^{-34})^2}{2 \times 0.911 \times 10^{-31} \times 4 \times 10^{-20}} = 6.03 \times 10^{-18} J = 37.5 eV$$

$$X\text{-rays}: E = pc = \frac{hc}{\lambda} \quad E = 9.4 \times 10^{-16} J = 6 \times 10^{3} eV$$

5.3 Explain how Xe and $CH_2{=}CH_2$ differ in their bonding to a metal surface. Rank their desorption temperatures.

Xe - physisorption, weak dispersion forces, low T_{desorp}
$CH_2 = CH_2$ - chemisorption (molecular or dissociative, depending on the substrate), higher T_{desorp}.

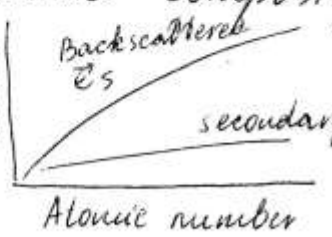
5.4 Your sample #1 consists of Fe_2O_3 nanoparticles on top of diamond-like carbon substrate. You also prepared a clean substrate (sample #2) for comparison. You accidentally dropped both samples on the way to Nanofab and they are now contaminated with the dust, and you do not know which sample is #1.

(a) What measurement use can do using SEM to distinguish two samples?

(b) Why do the backscattered electron micrographs, rather than secondary electron micrographs reveal the compositional contrast?

(a) EDX - to confirm what sample has Fe-containing particles
Dust particles have typically various minerals (e.g. $CaCO_3$, $MgSO_4$, $KAlSiO_8$, carbon-based).
You can use backscatted electron imaging to distinguish elements better. One expects to see narrow distribution of particles with high-Z (Fe) on light substrate, giving you a good contrast. Whereas in case of dust-covered sample, one expects to see a wide distribution of particle sizes and elemental compositions.

(b)



Backscattered electrons give you higher compositional contrast

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5.5 Calculate the diffusivity in m^2/s of carbon in HCP titanium at 700°C. Use $D_0 = 5.10 \times 10^{-4}\ m^2/s$; $E_a = 182$ kJ/mol; R = 8.314 J/(mol · K).

$$D_{C,Ti} = D_0 \times e^{\frac{-E_A}{RT}} = 5.10 \times 10^{-4} \frac{m^2}{s} \times e^{\frac{-182 \times 10^3}{8.314 \times 973}} =$$

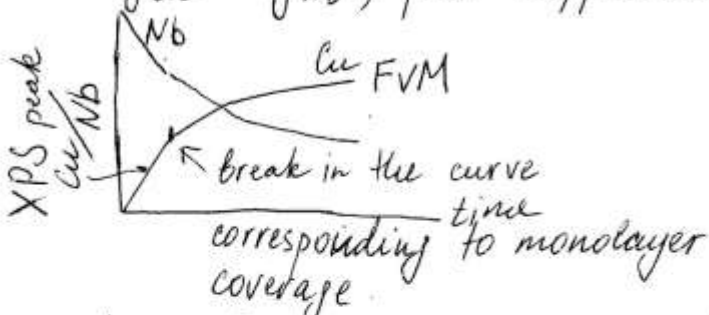
$$= 5.10 \times 10^{-4} \frac{m^2}{s}\, e^{-22.5} = 8.64 \times 10^{-14} \frac{m^2}{s}$$

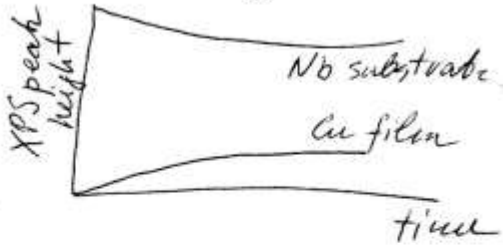
5.6 Surface energies of solid Cu and Nb are $\gamma_{Cu} = 1670$ ergs/cm^2 $\gamma_{Nb} = 2100$ ergs/cm^2. You deposited Cu on Nb substrate using slow deposition rate at elevated temperature. What growth mode do you expect? In your own words explain how XPS can be used to distinguish Frank-van der Merwe from Volmer-Weber growth in this case.

Slow deposition rate ⇒ thermodynamic parameters become important!

Elevated temperature ⇒ diffusion is fast

$\gamma_{Cu} < \gamma_{Nb}$, fast diffusion ⇒ FvM growth





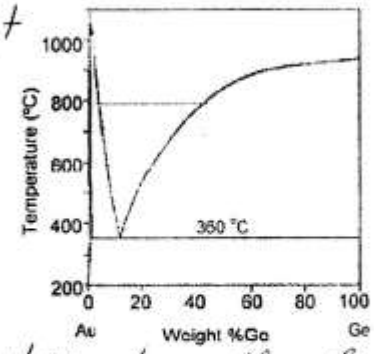
Layer-by-layer growth manifest itself by "segmented" curves, where you can see individual breaks corresponding to 1ML coverage.

Island growth leads to a very slow increase in film signal, and decrease in the substrate signal with time.

5.7 (a) What is the function of Au during the growth of Ge nanowires? (b) Name two general approaches to growth nanowires? (c) Using the phase diagram below describe 4 steps of Ge nanowire growth; (d) What parameters determine nanowire diameter? (e) Name (at least) three ways to terminate the growth process.

(a) Au nanoparticles act as a catalyst to aid the growth of the NW.

(b) Two general approaches: top-down & bottom-up. Alternative answer: CVD, VLS growth, lithography, electrochem. step decoration.



(c) 4 steps: (1) metal catalyst deposition, (2) forming eutectic; (3) nucleation of Ge phase when alloy become supersaturated, (4) growth

(d) diameter of catalyst droplet (e) → decreasing temp. below 360 C; → reducing Ge pressure; → contaminating catalyst surface.

5.8 The diffusivity of iron atoms in the *bcc* iron lattice is 4.5×10^{-23} m²/s at 400°C and 5.9×10^{-16} m²/s at 800°C. Calculate the activation energy in kJ/mol for this case in this temperature range. R = 8.314 J/(mol · K).

$$D = D_0 e^{-\frac{E_A}{RT}}$$

$$\frac{D_{800}}{D_{400}} = \frac{\cancel{D_0}}{\cancel{D_0}} \frac{e^{\frac{-E_A}{RT_1}}}{e^{\frac{-E_A}{RT_2}}} = e\left(-\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\frac{5.9\times10^{-16}}{4.5\times10^{-23}} = \exp\left(\frac{-E_A}{8.314}\left(\frac{1}{1073} - \frac{1}{673}\right)\right)$$

$$\ln(13111111.1) = 6.662\times10^{-5} E_A$$

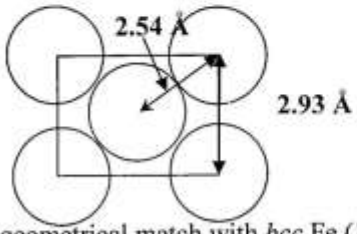
$$E_A = 246\times10^3 \text{ J/mol} = 246 \frac{\text{kJ}}{\text{mol}}$$

5.9 Discuss the advantages and disadvantages of using Low Energy Electron Microscope in comparison with Low Energy Electron Diffraction for determining the reconstructions on a single crystal metal surface.

Advantages: - dynamics of the reconstruction formation can be monitored in situ
- LEEM includes LEED! LEED pattern reveals the symmetry of the reconstructed surface (coverage)
Disadvantage: cost of the instrument

5.10 You are depositing *fcc* Ni (lattice constant d_{Ni}=3.52Å) onto the *bcc* Fe(110) surface (d_{Fe}-2.54 Å) What growth mode do you expect in the first monolayer, Nishyama-Wasserman or Kurdjimov-Sachs? Indicate why.

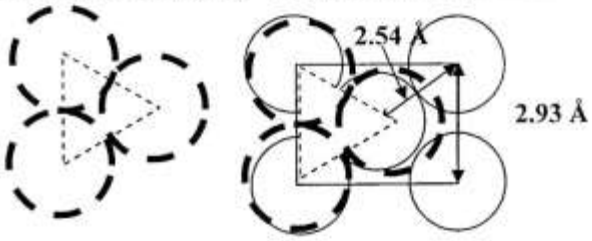
bcc Fe(110) surface



$2d = \sqrt{3}\,a$

Assuming that *fcc* Ni (111) has good geometrical match with *bcc* Fe (110), We can calculate geometrical parameter, *r*, for close-packed Ni-Ni distance (or d_{Ni}=2.7Å) and lattice parameter in *bcc* Fe (d_{Au}=2.93Å)

$$r = \frac{2.49}{2.54} = 0.98$$



From the structural phase diagram, and depending on the coupling strength within the film compared to interlayer coupling strength, one predicts either complete coherence or coherence in one direction and NW misfit in another