The University of Western Ontario
Department of Physics and Astronomy

P9826b Winter 2013

January 28, 2013

Homework Assignment #1 (due on February 6, 2013)

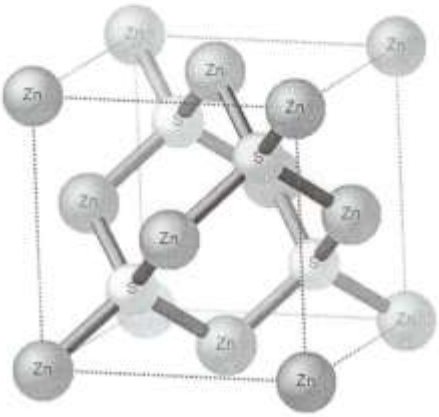
Problems:

1. (4 points) Find the crystallographic structure of one of the materials studied in your research project. If this material is known to have several crystallographic forms, list all of them and select the one with the highest symmetry group. For instance, if you study corrosion of Ni alloys, consider Ni crystal structure. If you project has no connection with crystalline solids, take zincblende crystal structure as shown in the figure below.

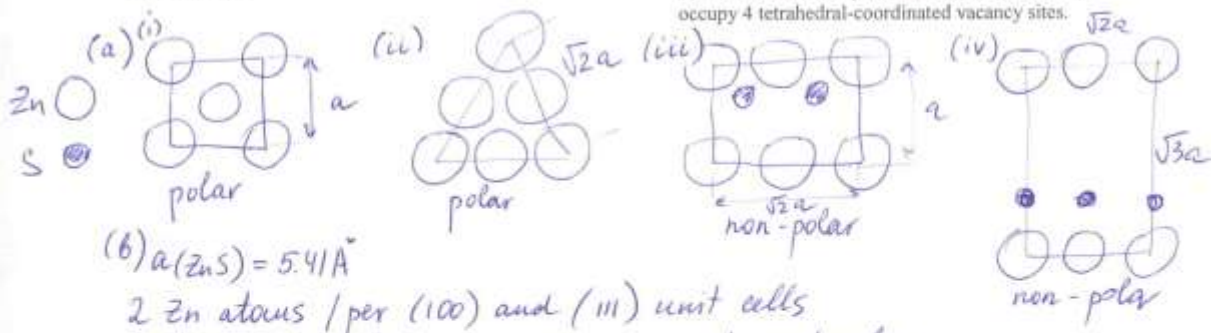
(a) Consider the following surfaces: (*i*) (100); (*ii*) (111); (*iii*) (110); (*iv*) (211). Sketch out the ideal surface structure of each. If applicable, identify the ones with the polar termination.

(b) *Order of magnitude estimates of γ.* Estimate how many bonds does one need to break to form (100) and (111) surfaces of this material. Which surface has lower surface energy: (100) or (111)?

(c) Compare your predictions for surface energies with the values from the literature (list your references).



ZnS structure is similar to diamond structure. It has Zn cations at the *fcc* lattice sites and S anions occupy 4 tetrahedral-coordinated vacancy sites.



(b) $a(ZnS) = 5.41\,\text{Å}$

2 Zn atoms / per (100) and (111) unit cells

4 broken bonds / per (001) and (111) unit cells

$\text{Area}(001) = (5.41)^2\,\text{Å}^2 = 2.93\times10^{-13}\,\text{cm}^2$

$\text{Area}(111) = \frac{1}{2}\sqrt{2}\sqrt{\frac{3}{2}}(5.41)^2\,\text{Å}^2 = 2.53\times10^{-13}\,\text{cm}^2$

$(001) \Rightarrow 1.36\times10^{13}\ \frac{\text{bonds}}{\text{cm}^2}$; $(111) \Rightarrow 1.58\times10^{13}\ \frac{\text{bonds}}{\text{cm}^2}$

Use $E_{coh} = 3.16\,\text{eV} \Rightarrow \gamma_{100} < \gamma_{111}$ (c) Table 2 in Am. Mineralogist, 83 (1998) p. 141.

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2. (4 points) Consider that in the pictures (including next page) you are looking down at a surface. The larger circles represent the substrate atom positions and dark dots represent the overlayer atom positions. Overlayer unit cells are shown. For each structure:

(a) Draw the substrate unit cell and vectors, and the primitive overlayer unit cell and unit cell vectors.

(b) Calculate the ideal coverage (in monolayers) of the overlayer.

(c) If the primitive overlayer surface unit cell can be named with Wood's notation, do so. If it cannot, try to identify a nonprimitive cell which can be so named.

(d) Give the matrix notation for the primitive overlayer unit cell.

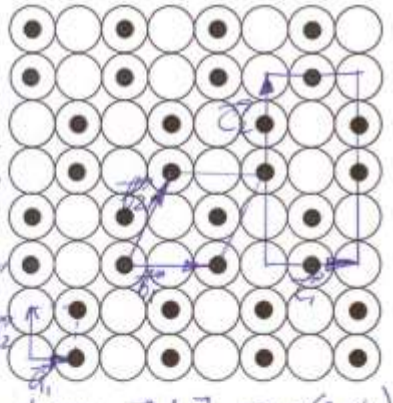
(e) Classify the surface overlayer as simple, coincident or incoherent.

For each real space surface structure provided:

(f) Construct reciprocal unit cells for the substrate and the overlayer (show both the magnitude and the directions of the vectors).

(g) Sketch LEED patterns for each case, using different symbols distinguish the peak positions for the substrate and the overlayer (Hint: don't forget about possible domains!).

(a)



(a)

(b) $W = \frac{1}{2}$ ML

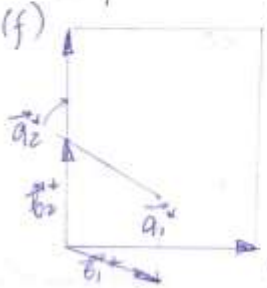
(c) If $\vec{b}_1$ & $\vec{b}_2$ describe our primitive cell, it cannot be named

If we choose $\vec{c}_1$ & $\vec{c}_2$ => $p(2\times4)$

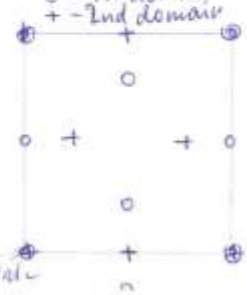
(d) $G = \begin{pmatrix} 2 & 0 \\ 1 & 2 \end{pmatrix}$ $|G| = 4$ $G^* = \begin{pmatrix} \frac{1}{2} & -\frac{1}{4} \\ 0 & \frac{1}{2} \end{pmatrix}$

(e) simple

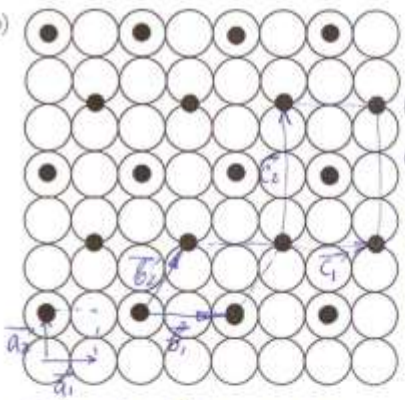
(f)



(g)



(b)



(b) $W = \frac{1}{3}$ ML

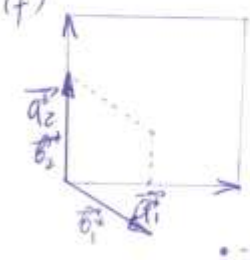
(c) For $\vec{b}_1$ & $\vec{b}_2$ no Wood's notation

For $\vec{c}_1$ & $\vec{c}_2$ (Not primitive) $C(2\times3)$

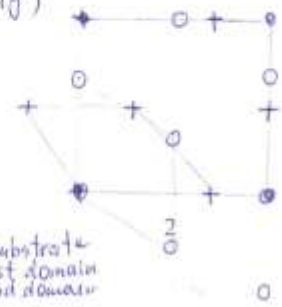
(d) $G = \begin{pmatrix} 2 & 0 \\ 1 & \frac{3}{2} \end{pmatrix}$ $\det G = 3$ $G^* = \begin{pmatrix} \frac{1}{2} & -\frac{1}{3} \\ 0 & \frac{2}{3} \end{pmatrix}$

(e) coinc.

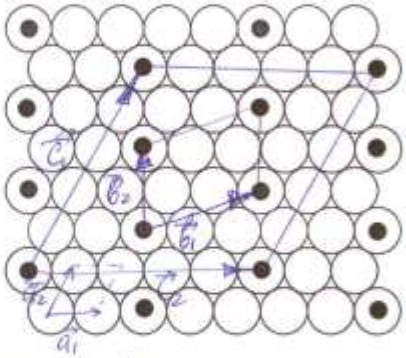
(f)



(g)



(c)



(b) $W = \frac{1}{5} ML$

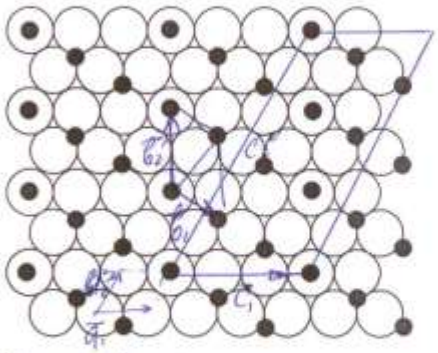
(c) If $\vec{b}_1$ & $\vec{b}_2$ ⇒ no name
if $\vec{c}_1$ & $\vec{c}_2$ $p(5\times5)$

(d) $G = \begin{pmatrix} 2 & 1 \\ -1 & 2 \end{pmatrix}$ $|G| = 5$

$G^* = \begin{pmatrix} \frac{2}{5} & \frac{1}{5} \\ -\frac{1}{5} & \frac{2}{5} \end{pmatrix}$

(e) simple.

(d)



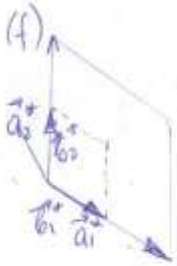
(b) $W = \frac{1}{2} ML$

(c) If $\vec{b}_1$ & $\vec{b}_2$ ⇒ no name
If $\vec{c}_1$ & $\vec{c}_2$ $p(3\times6)$

(d) $G = \begin{pmatrix} \frac{3}{2} & -\frac{1}{2} \\ -1 & 2 \end{pmatrix}$ $|G| = \frac{5}{2}$

(e) coinc.

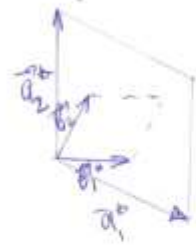
(f)



(g)

o - 1st
+ - 2nd
× - 3rd

(f)



3. (2 points) According to Hertz-Knudsen equation, the flux of molecules hitting unit area of a surface in unit time is

$$Z_w = \frac{p}{(2\pi m k_B T)^{1/2}}$$

where p is pressure, m molecular mass, k_B Bolzmann constant and T temperature. The dissociative sticking coefficient of H_2 on Si (001) is 1×10^{-10} at room temperature. There are 6.8×10^{18} Si atom per m^2 on the Si (100) surface. Estimate the coverage of H atoms that results from exposing a Si (100) surface to 1×10^{-5} Pa of H_2 for 30 min. Justify the use of a constant sticking coefficient.

$p = 10^{-5}$ Pa $\quad S_c = 1\times10^{-10}$

$T = 298$K $\quad n_{Si} = 6.8\times10^{18}$ Si/m^2

$t = 1800$s

$m_{H_2} = 3.36\times10^{-27}$ kg

$k_B = 1.38\times10^{-23}$ J/K

$$Z_w = \frac{10^{-5}\text{ Pa}}{\sqrt{2\pi\, 3.36\cdot10^{-27}\cdot 298\cdot 1.38\cdot10^{-23}}} = 1.07\times10^{18}\ \frac{\text{molec}}{m^2\cdot s}$$

each H_2 will make 2H atoms after dissociation, we should multiply $Z_w \times 2$

$$\text{Coverage } W = \frac{Z_w\times 2\times S_c\cdot t}{n_{Si}} = \frac{1.07\cdot10^{18}\cdot 2\cdot10^{-10}\cdot 1800}{6.8\times10^{18}} =$$

$= 5.68\times10^{-8}$ ML

We can assume that sticking coef. is constant, becaus the coverage is very small, there will be always empty Si sites for the new H_2 molecules to absorb.

5. (2 points) Consider the oxidation of steel plate in a gas atmosphere at T=927°C. Calculate the time necessary to increase the oxygen content to 0.36 wt% at 0.4 mm below the surface of the plate. Assume the oxygen content at the surface to be 2.0 wt % and that the nominal oxygen content of the steel gear before oxidation is 0.18 wt%. Diffusion coefficient of oxygen in γ iron ay 927°C is $1.28 \times 10^{-11} m^2/s$.

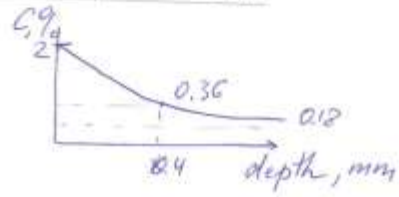
Use the value of the error function from the table below for a solution. (*Hint:* refer to the second Fick's law of diffusion to solve it).

z	erf z	z	erf z	z	erf z	z	erf z
0	0	0.40	0.4284	0.85	0.7707	1.6	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.7	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.8	0.9891
0.10	0.1125	0.55	0.5633	1.0	0.8427	1.9	0.9928
0.15	0.1680	0.60	0.6039	1.1	0.8802	2.0	0.9953
0.20	0.2227	0.65	0.6420	1.2	0.9103	2.2	0.9981
0.25	0.2763	0.70	0.6778	1.3	0.9340	2.4	0.9993
0.30	0.3286	0.75	0.7112	1.4	0.9523	2.6	0.9998
0.35	0.3794	0.80	0.7421	1.5	0.9661	2.8	0.9999

$C_s = 2.0\%$ $\quad x = 4\times10^{-4} m$

$C_o = 0.18\%$ $\quad D_{927} = 1.28\times10^{-11} \frac{m}{s}$

$C_x = 0.36\%$



Using Fick's second law

$$\frac{C_s - C_x}{C_s - C_o} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{2-0.36}{2-0.18} = \frac{1.64}{1.82} = 0.9011 = erf\left(\frac{4\times10^{-4}}{2\sqrt{1.28\times10^{-11}\,t}}\right) = erf\left(\frac{55.90}{\sqrt{t}}\right) = erf\, Z$$

z	erf z
1.1	0.8802
x_1	0.9011
1.2	0.9103

$$\frac{0.9011-0.8802}{0.9103-0.8802} = \frac{x_1 - 1.1}{1.2-1.1}$$

$$\frac{0.0209}{0.0301} = \frac{x_1 - 1.1}{0.1} \qquad x_1 = 1.17$$

$$Z = \frac{55.90}{\sqrt{t}} = 1.17 \qquad t = 2282.7s = 38.0\,min$$