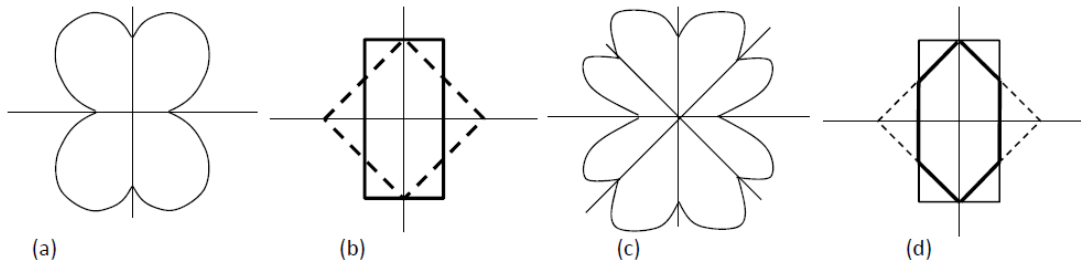


Surface/Interface Science P627/Chem 541 Fall 2010  
 Problem Set 1  
 Solutions

1)  $\gamma_{10} = 200 \text{ erg/cm}^2$  ;  $\gamma_{01} = 400 \text{ erg/cm}^2$  so the  $\gamma(\theta)$  plot schematically looks like figure (a):



With this energy plot, Wulff construction has sides perp to the [10] and [01] directions with the length of the [10] twice that of the [01] sides, as in the rectangle in Fig. (b). Let  $l$  = length of [01] side, then perimeter is  $6l$ . The area is  $(2l)(l) = 2l^2 = 1$  for unit area sample. Therefore,  $l = 1/\sqrt{2}$ . From this, we see that the total edge energy of a sample of unit area is

$$E = \frac{4}{\sqrt{2}}(200) + \frac{2}{\sqrt{2}}(400) = \sqrt{2}(800) = 1131 \text{ erg}$$

(b) If we now consider the addition of cusps in the  $\gamma(\theta)$  plot in the [11] directions, the  $\gamma(\theta)$  plot looks like the Fig. (c). This allows for the possible stabilization of [11] planes in addition to the [10] and [01] planes. As indicated by the Wulff construction, if  $\gamma_{11} \leq (1/\sqrt{2})(400)$  erg then the higher energy [01] edges are eliminated in favor of the longer, but lower surface energy, [11] planes as indicated by the heavy shape in Fig. (d).

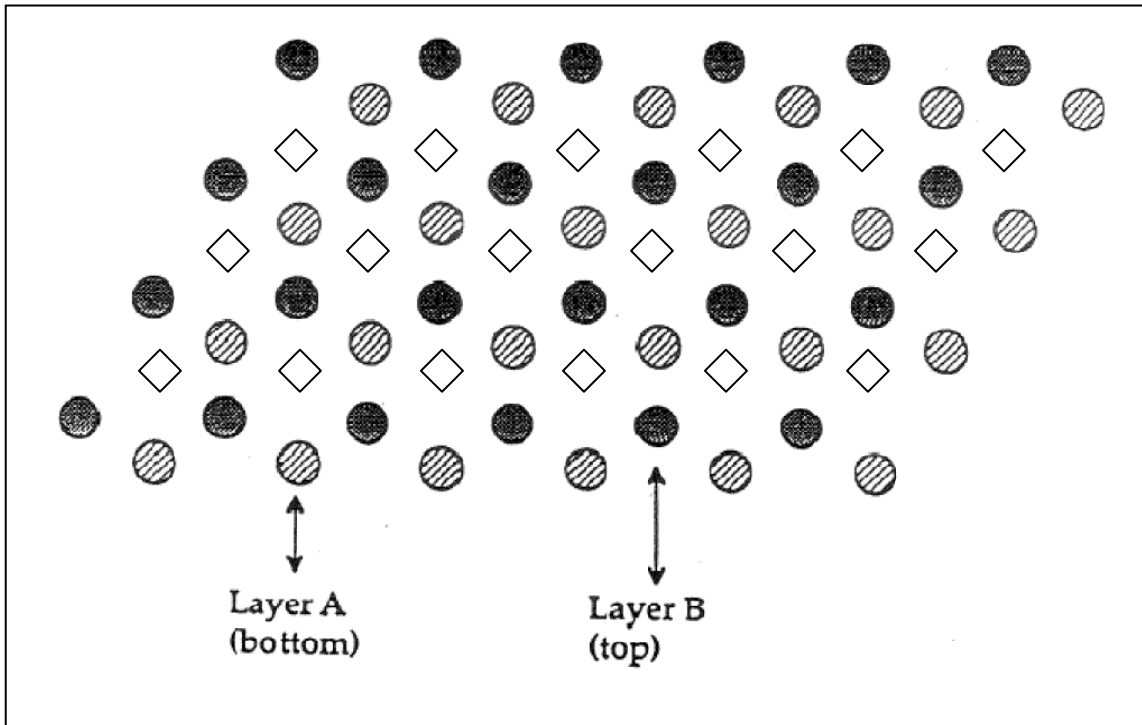
Here now, if  $l$  = length of [10] side, then each of the [11] sides has length  $l/\sqrt{2}$  and the area is  $A = l^2 + \left(\frac{l}{\sqrt{2}}\right)^2 = \frac{3}{2}l^2 = 1 \Rightarrow l = \sqrt{\frac{2}{3}}$ . From this, the total edge energy for a unit area sample is

$$E = 2\sqrt{\frac{2}{3}}(200) + \frac{4}{\sqrt{2}}\sqrt{\frac{2}{3}}\frac{(400)}{\sqrt{2}} = (1+2)\sqrt{\frac{2}{3}}(400) = 980 \text{ erg}$$

(c) finally, if  $\gamma_{11} \leq 200/\sqrt{2}$  erg then all sides will be [11] as in the dashed lines in Fig. (b). Then  $A = l^2$  and  $l = 1$ . In this case,

$$E = 4\frac{(200)}{\sqrt{2}} = 566 \text{ erg} .$$

2)



(a) In the fcc(111) direction, layers have *abcabc...* stacking while for hcp(0001) the stacking is *ababab...*. Therefore, for fcc(111) the next layer atoms would lie in the position of the diamond shapes in the above diagram. For hcp, the next layer of atoms would lie in the same position as the layer A atoms.

(b) Cu has an fcc equilibrium crystal structure. Therefore, the next layer of atoms would most likely form a minimum energy configuration by ordering in the x positions in the diagram above.

3) (i) (a) see fig. (b)  $\frac{1}{2}$  ML (c)  $(\sqrt{2} \times \sqrt{2})R45^\circ$  (d)  $\begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix}$  (e) simple (f) No

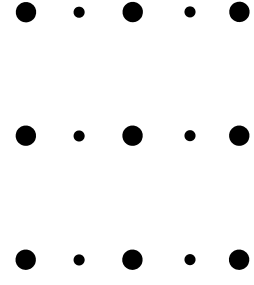
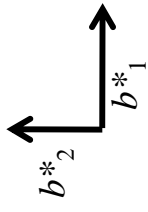
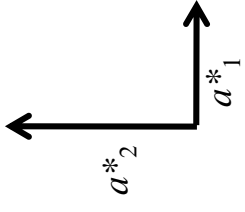
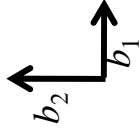
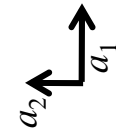
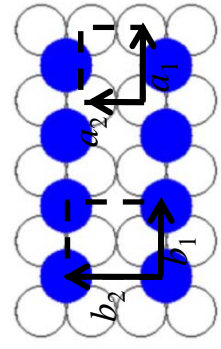
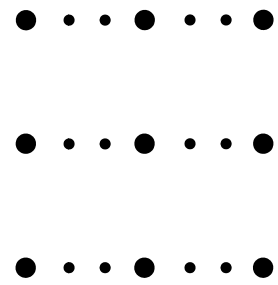
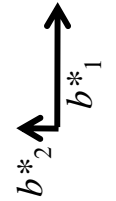
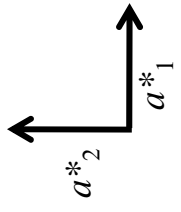
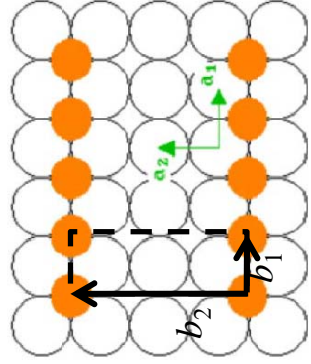
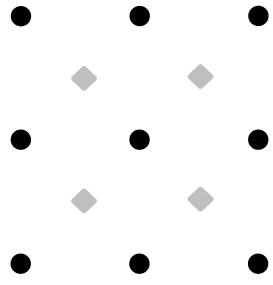
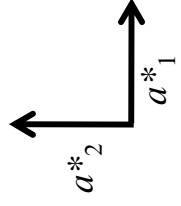
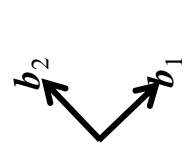
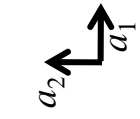
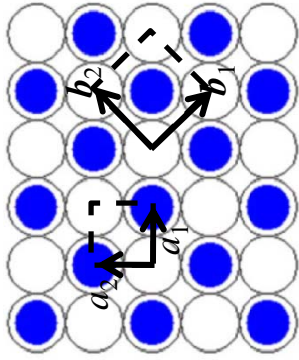
(ii) (a) see fig. (b)  $\frac{1}{3}$  ML (c)  $(1 \times 3)$  (d)  $\begin{bmatrix} 1 & 0 \\ 0 & 3 \end{bmatrix}$  (e) simple (f) yes

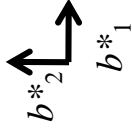
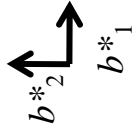
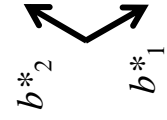
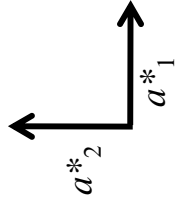
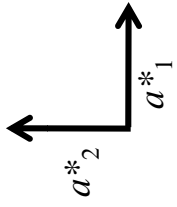
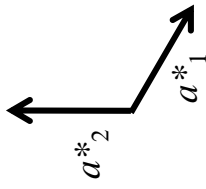
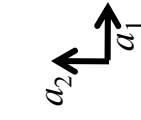
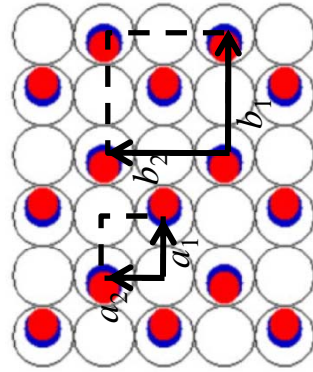
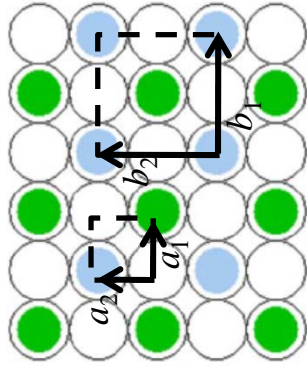
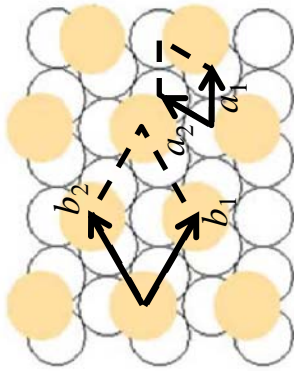
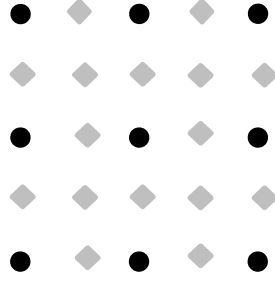
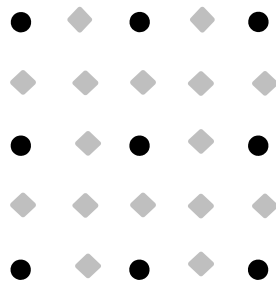
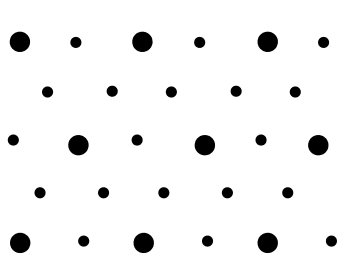
(iii) (a) see fig. (b)  $\frac{1}{2}$  ML (c)  $(1 \times 2)$  (d)  $\begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix}$  (e) simple (f) No

(iv) (a) see fig. (b)  $\frac{1}{3}$  ML (c)  $(\sqrt{3} \times \sqrt{3})R30^\circ$  (d)  $\begin{bmatrix} 2 & -1 \\ 1 & 1 \end{bmatrix}$  (e) simple (f) yes

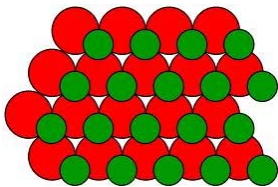
(v) (a) see fig. (b)  $\frac{1}{2}$  ML (c)  $(2 \times 2)$  (d)  $\begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$  (e) simple (f) No

(vi) (a) see fig. (b)  $\frac{1}{2}$  ML (c)  $(2 \times 2)$  (d)  $\begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$  (e) simple (f) No





- 4) Lattice vectors, reciprocal lattice vectors, and LEED patterns are sketched for all structures on the attached sheets.
- 5) (a) While GaAs and NaCl have different crystal structures (zincblende and rocksalt, respectively), the (111) surface of both consists of a hexagonal array of one of the atoms of the binary compound. The second layer is also a hexagonal array, but of the other element. So, the geometry of the first two layers are structurally identical, as shown in the figure.



(b) While NaCl is an ionic solid, GaAs is covalently bonded. As a result, the NaCl(111) surface is highly unstable and tends to massively reconstruct to neutralize. In contrast, dangling covalent bonds in the GaAs surface tend to pair to form two-electron bonds, lowering the surface energy with much less structural modification.

- 6) Faceting of the (001) surface in favor of (105)-like facets would increase the surface area, therefore this increase must be more than compensated for by the decrease in the surface free energy.

The angle between the [001] and [105] surface normals is given by

$$\hat{n}_{001} \cdot \hat{n}_{105} = |\hat{n}_{001}| |\hat{n}_{105}| \cos \theta \Rightarrow \cos \theta = \frac{\hat{n}_{001} \cdot \hat{n}_{105}}{|\hat{n}_{001}| |\hat{n}_{105}|}$$

Where  $\hat{n}_{001} \cdot \hat{n}_{105} = 5$ ;  $|\hat{n}_{001}| |\hat{n}_{105}| = (1)(\sqrt{1+25}) = \sqrt{26}$  so  $\cos \theta = \frac{5}{\sqrt{26}} = 0.98 \Rightarrow \theta = 11.3^\circ$

In order for faceting to be favorable, we need:  $\frac{\gamma_{105}}{\cos \theta} < \gamma_{001}$  or  $\gamma_{105} < (0.98)\gamma_{001}$

7) The Kelvin equation is:

$$\frac{P_r}{P_o} = e^{\left(\frac{K\gamma}{r}\right)} = e^{\left(\frac{2\bar{V}\gamma}{RT r}\right)}$$

$$\gamma_{Au} = 1410 \text{ erg/cm}^2; \quad T = 1300\text{K}; \quad V_{Au} = 10 \text{ cm}^3/\text{mol}$$

$$\gamma_{H_2O} = 72.75 \text{ erg/cm}^2 \quad T = 300\text{K}; \quad V_{H_2O} = 18 \text{ cm}^3/\text{mol} \quad R = 8.31 \times 10^7 \text{ erg/K-mol}$$

$$\frac{P_r}{P_o} = 2 \Rightarrow \frac{2\bar{V}\gamma}{RT r} = \ln 2 \Rightarrow r = \frac{2\bar{V}\gamma}{RT \ln 2}$$

$$r_{Au} = \frac{2(10 \text{ cm}^3/\text{mol})(1410 \text{ erg/cm}^2)}{(8.31 \times 10^7 \text{ erg/K - mol})(1300\text{K}) \ln 2} = 3.77 \times 10^{-7} \text{ cm} = 3.77 \text{ nm}$$

$$r_{H_2O} = \frac{2(18 \text{ cm}^3/\text{mol})(72.75 \text{ erg/cm}^3)}{(8.31 \times 10^7 \text{ erg/K} \cdot \text{mol})(300\text{K}) \ln 2} = 1.67 \times 10^{-7} \text{ cm} = 1.67 \text{ nm}$$

b) 125 atoms  $\rightarrow 5 \times 5 \times 5 \rightarrow$  # of surface atoms is  $5^3 - 3^3 = 98$  atoms  $\rightarrow 78\%$

1000 atoms  $\rightarrow 10 \times 10 \times 10 \rightarrow$  # surf atoms =  $10^3 - 8^3 = 1000 - 512 = 488 \rightarrow 49\%$

8) For all three surfaces,  $r = 1.36 \times 10^{-8}$  cm.

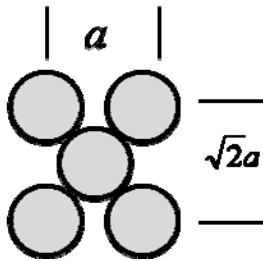
(a) Pd(111) is fcc(111)  $\rightarrow$  closed packed. So there is one atom per rhombus of side  $2r$  [see figure for problem 3(iv)].

$$\text{Area of rhombus is } (2r)(2r \sin 60^\circ) = (4)(0.866)(1.36 \times 10^{-8} \text{ cm})^2 \Rightarrow 1.56 \times 10^{15} \text{ atoms/cm}^2$$

(b) Pd(110) is fcc(110) so area per atom [see fig. for problem 3(iii)] is

$$(2r)(\sqrt{2}2r) = (4)(\sqrt{2})(1.36 \times 10^{-8} \text{ cm})^2 = 1.05 \times 10^{-15} \text{ cm}^2 \Rightarrow 9.56 \times 10^{14} \text{ atoms/cm}^2$$

(c) W(110) in the diagram, the body diagonal is  $\sqrt{3}a = 4r \Rightarrow a = \frac{4r}{\sqrt{3}}$  where  $a$  is the cubic



parameter. So the area of the rectangle is:

$$\sqrt{2}a^2 = \left(\sqrt{2}\right)\left(\frac{4}{\sqrt{3}}\right)^2 (1.36 \times 10^{-8} \text{ cm})^2 = 1.39 \times 10^{-15} \text{ cm}^2 \text{ for}$$

two atoms. Therefore, per atom we have  $6.97 \times 10^{-16} \text{ cm}^2 \Rightarrow 1.43 \times 10^{15} \text{ atoms/cm}^2$ .

(d) W(111) each atom contained in a rhombus whose side is a face diagonal, so

$$(\sqrt{2}a)(\sqrt{2}a \sin 60^\circ) = (\sqrt{2}a)^2 (\sin 60^\circ) = \left(\frac{4\sqrt{2}}{\sqrt{3}}\right)^2 (0.866)(1.36 \times 10^{-8} \text{ cm})^2$$

$$= 1.7 \times 10^{-15} \text{ cm}^2 \Rightarrow 5.85 \times 10^{14} \text{ atoms/cm}^2$$