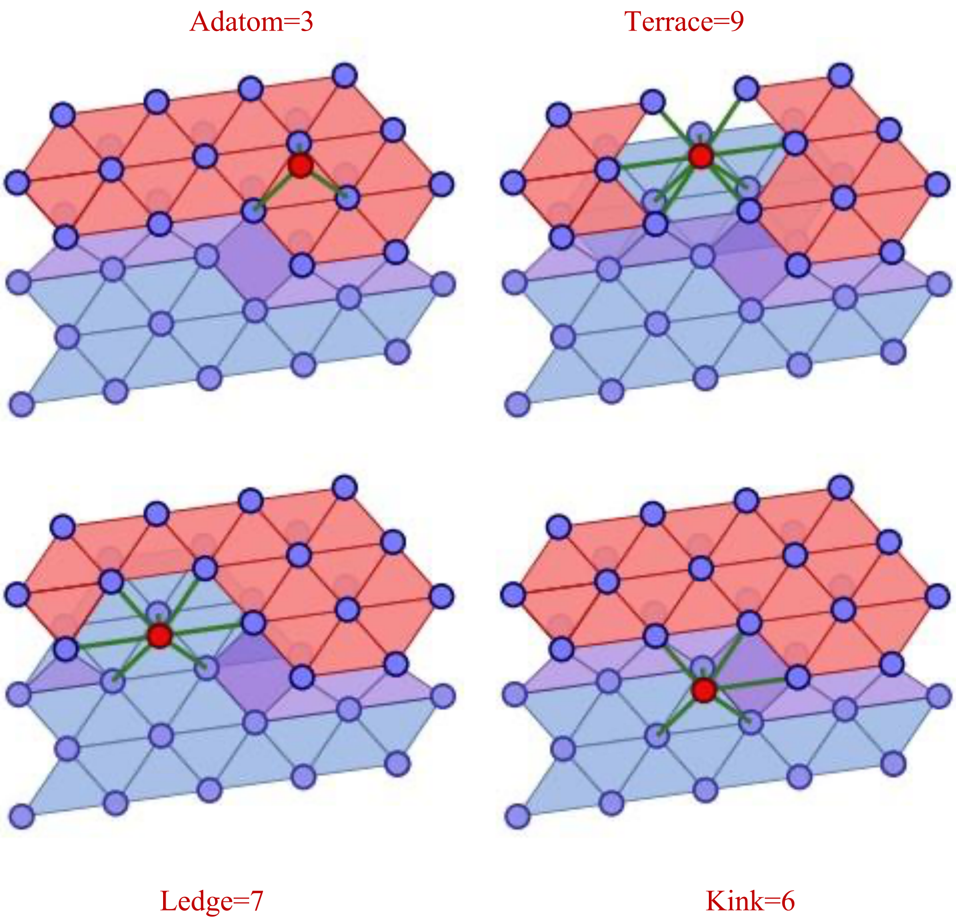
Surface and Interface 2024 Fall Semester Exercise 2 Solutions

1. Consider a surface with a step (ledge) and terraces. We have seen how to calculate the equilibrium concentration of vacancies (n_v) on a terrace. The argument was based purely on the calculation and minimization of the Gibbs free energy associated with the defect's formation. Do you expect that the energy required for the formation of a ledge vacancy is greater or smaller than that of a simple surface vacancy? Justify the answer.

   Solution:
   The energy required for the formation of a vacancy on a ledge is lower than the that necessary to create the same defect on a terrace. This is true on general grounds; you can convince yourself of this by counting the number of broken bonds. For the FCC (111) surface, for example, a vacancy on a terrace will break 9 bonds, while for a vacancy on a ledge the number of broken bonds is 7.



2. Consider a step with the edge along the ⟨100⟩, on the (100) surface of a simple cubic crystal, at zero temperature. At finite temperature the step edge fluctuates (this is called roughening transition) as a result of the formation of kinks. We can consider the edge line as made up of N segments of length equal to the lattice parameter ($L = Na$). On each of these segments we may find a positive kink (i.e. an atom that sticks from the step), a negative kink (a missing atom on the step) or no kink at all.

a) Assuming that the temperature is low enough so that only kinks of atomic size occur, show that the average distance λ_0 between kinks is

$$\lambda_0 = a\frac{1+2\zeta}{2\zeta} \qquad \text{with} \qquad \zeta = e^{\frac{-\epsilon_{kink}}{kT}}$$

Where α is the lattice parameter, ϵ is the formation energy of a kink and β is the Boltzman factor ($\frac{1}{kT}$)

Hints:

- *Write down the "constraints" on the number of positive and negative kinks per unit length of steps (you can denote them as p_- and p_+). Take into account that in a segment of the step, no kink p_0 is also possible!*
- *By minimizing the free energy F, one can prove the following relation:* $\frac{p_- p_+}{p_0^2} = \zeta^2$

b) Are you able to sketch a rough plot of $1/\lambda_0$ as a function of temperature with ϵ fixed? Does it make sense from a physical point of view?

Solution:

a) You can consider number density (p) of kinks;

$$ap_- + ap_+ + ap_0 = 1$$

$$a(p_- + p_+ + p_0) = 1$$

$$(p_- + p_+ + p_0) = 1/a$$

i.e. the total number of kinks per unit length must be equal to the linear density of atoms on the step. And

$$p_+ - p_- = 0$$

in order to conserve the average orientation of the step line. We can determine the values of n_-, n_+ *and* n_0 by solving the two above equations simultaneously with the relation coming from the minimization of the free energy. Thus, we need to solve the system:

$$\begin{cases} (p_- + p_+ + p_0) = 1/a \\ p_+ - p_- = 0 \\ \dfrac{p_- p_+}{{p_0}^2} = \zeta^2 \end{cases}$$

We obtain

$$p_0 = \frac{e^{\epsilon_{kink}\beta}}{\alpha(2+e^{\epsilon_{kink}\beta})} \text{ and}$$

$$p_+ = p_- = \frac{1}{a(2+e^{\epsilon_{kink}\beta})}$$

The average distance between two kinks can be defined as the reciprocal of the total number of kinks per unit length,

$$\lambda_0 = \frac{1}{p_+ + p_-}$$

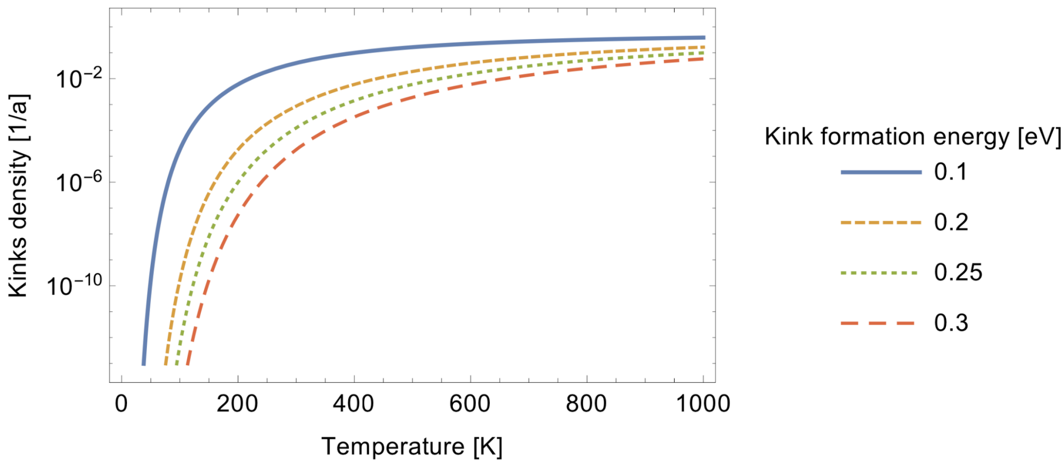
recalling that

$$p_\pm = \frac{N}{L} = \frac{1}{a}$$

We get the result

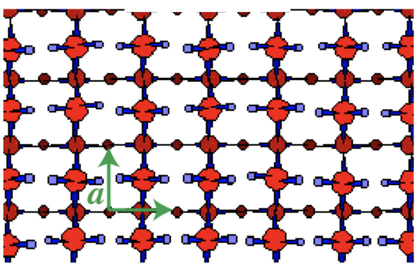
$$\lambda_0 = \frac{1}{\frac{2(\frac{1}{a})}{(2+e^{\epsilon_{kink}\beta})}} = a\frac{2+e^{\epsilon_{kink}\beta}}{2} = a\frac{1+2\zeta}{2\zeta}$$

b) The figure below is the plot of the function $1/\lambda_0$ (log scale), the average number of the kinks per unit length, with respect to the temperature. With an increase in temperature, the kink density increases exponentially, while with a decrease, it falls off. This can be interpreted as that the increase in thermal energy is modulating the creation of kinks. Saturation is also consistent since the number of kinks can't increase to infinity.

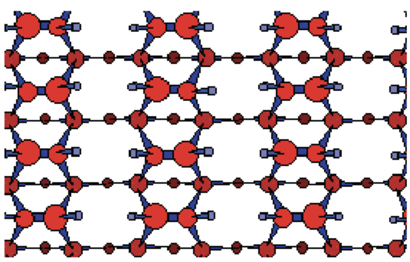


3. Figure A) is an illustration of unreconstructed silicon (100) surface. A silicon atom in the structure of a silicon crystal can form four bonds with the four nearest neighboring atoms. In the bulk of a silicon crystal, viewed from the (100) plane, two of these bonds reach to the level below and two reach to the next level above. In the figure A) three successive planes of silicon are represented with dots of different shades of red (each shade represent atoms on different levels). Cleaving a crystal along a (100) plane leaves the surface atoms with only two bonds intact and the other two dangling (blue dots in Fig. A). The surface atoms then swing toward neighboring atoms to form pairs, known as dimers. Figure B) shows the same Si (100) plane reconstructed to form rows of dimers along the surface.

A) Si (100)



B) Si (100) reconstruction



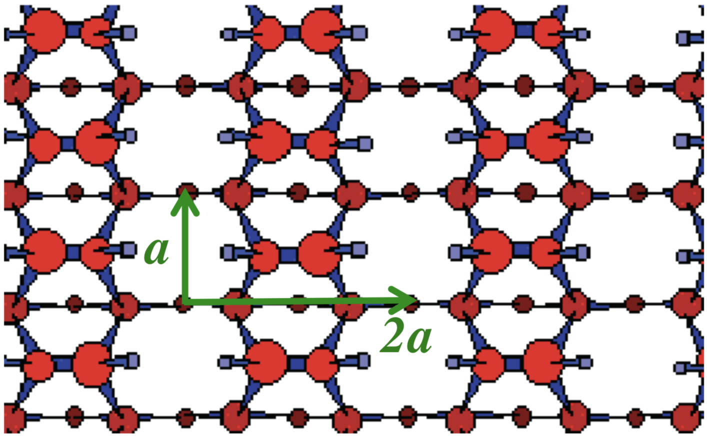
a) Determine the unit cell of the reconstructed Si(100) surface.

b) Using exclusively the broken bond model in the first nearest neighbor approximation determine the surface energies of the surface reconstructed and unreconstructed, as a function of ε(bond energy) and a (lattice parameter of the unconstructed surface)

c) What is the gain in energy due to the reconstruction with this approximation?

Solution:

a) A unit cell is the smallest building block of which repetition forms the crystal structure. The unit cells of Si(100) surface after reconstruction is indicated by the green arrows in Figure B). The reconstructed surface is: Si(100) 2x1



b) Before reconstruction: As stated in the question, there are two dangling bonds for each unit cell on the Si(100) surface. Therefore, $2\varepsilon \times \frac{1}{2}=\varepsilon$ is the energy for the unit cell associated to the creation of the surface (Note: dangling bonds are shared between two atoms, so corresponding energy for each atom is the half of the total bond energy. Also, the area of the unit cell is simply a^2. Therefore, the total surface energy for the unit cell can be described as:

$$\gamma_{100}(unreconstructed) = \frac{2\varepsilon \cdot \frac{1}{2}}{a^2} = \frac{\varepsilon}{a^2}$$

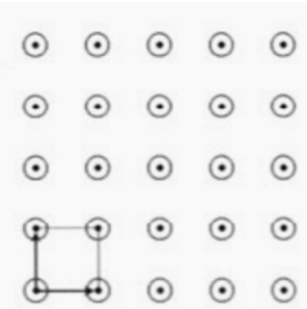
After reconstruction: Considering the new unit cell after reconstruction, two red atoms share two dangling bonds. In this case the area of the unit cell has changed after reconstruction:

$$\gamma_{100}(Si(100)2\times 1) = \frac{2\varepsilon \cdot \frac{1}{2}}{2a^2} = \frac{\varepsilon}{2a^2}$$

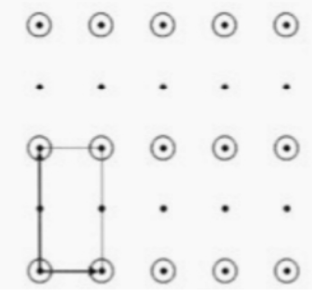
c) $\gamma_{100}(unreconstructed) - \gamma_{100}(Si(100)2\times 1) = \frac{\varepsilon}{a^2} - \frac{\varepsilon}{2a^2} = \frac{\varepsilon}{2a^2}$

4. For the following surface structures, determine for each the Wood's notation

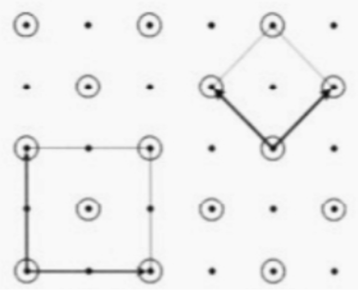
Solution:



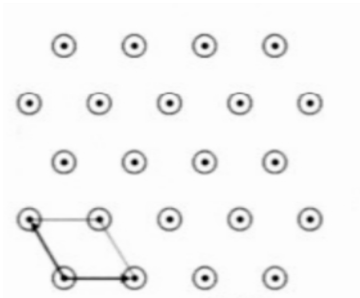
Unreconstructed
1x1



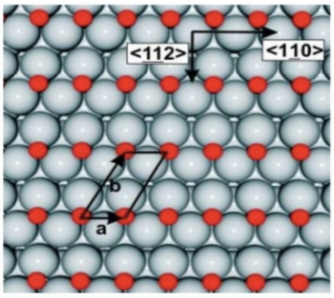
reconstructed
1x2



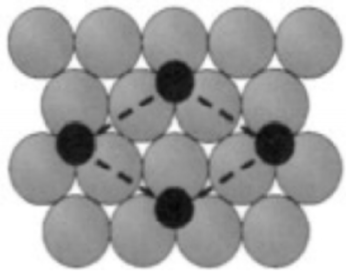
reconstructed
c(2x2) or $\sqrt{2} \times \sqrt{2}$ R45°



Unreconstructed
1x1

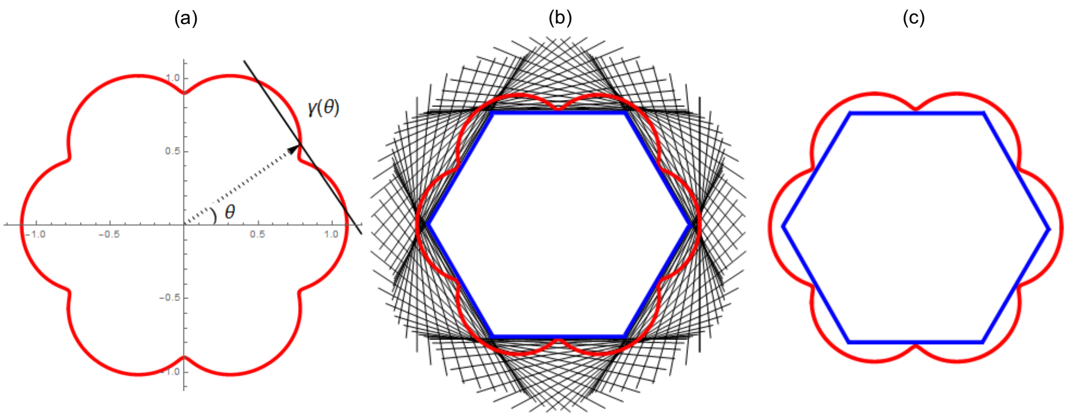


reconstructed
2x1

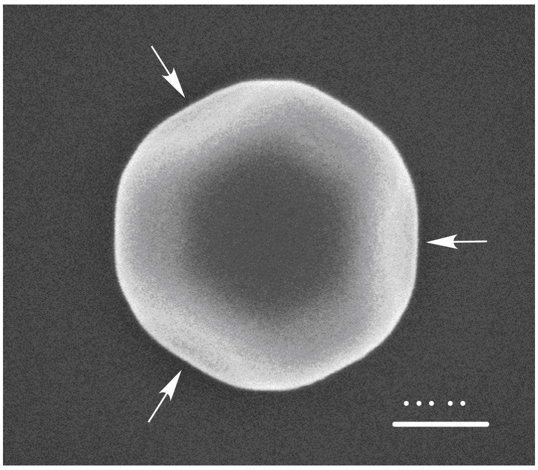


reconstructed
$\sqrt{3} \times \sqrt{3}$ R30°

5. The following figures is a 2D illustration of Wulff construction. As you learned from the lecture, the Wulff shape is the envelope shape enclosed by the tangent lines of surface energy vectors in the $\gamma - plot$ in polar coordination, which is the red shape below. The enclosed faceted blue shape, which is the equilibrium crystal shape for this specific $\gamma - plot$, depends largely on the cusps, lowest surface energy orientations, from the $\gamma - plot$.



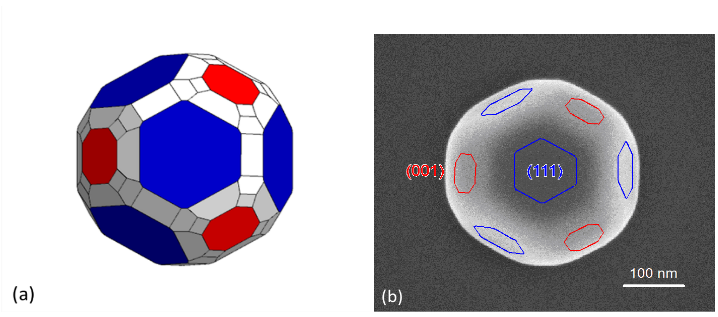
This is also true for 3D shapes, the facets indicate the lowest surface energy orientations. Below is a high resolution SEM micrograph of 3D equilibrium crystal shape (ECS) of gold supported on Yttria Stabilized Zirconia (YSZ), read more on publication: [10.1007/s10853-019-03436-5](https://doi.org/10.1007/s10853-019-03436-5). Determine what are the facet families you can see from this shape. Use the Wulffmaker Mathematica file and try to reproduce a 3D carton shape of this experimental ECS of gold. Write down the values of surface energies you insert and recall what you did in the first problem in exercise 1. Do these values apply to the result you got from the broken bond model?



Solution:

Judging from the three-fold symmetry and the fact that gold crystal is FCC, you should be able to tell that the top facet and the three side facets are from the {111} facet family. As for the three other facets adjacent to the side {111} facets, they are the {100} facets. You may also see smooth roughened surfaces connecting these two facet families, which includes the {110} family. Inserting the values below should give you a good shape that agrees with the SEM micrograph. With other higher order of facet planes, you can also get an ECS shape like below:

$\gamma_{\{100\}}/\gamma_{\{111\}}$	$\gamma_{\{110\}}/\gamma_{\{111\}}$
1.091	1.125



The The values agree with $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$