

Modeling Surfaces

Objectives:

In this activity, you will

- 1) construct the supercell models for different surfaces
- 2) calculate the surface energies of different surface facets
- 3) write a written report of the results

Theory:

Surfaces are important in many industrial applications including catalysis, interfaces, membranes for gas separations, semiconductor fabrication, among others. In DFT calculations, surfaces can be created by cleavage along a particular plane in the bulk material. A vacuum space separates an infinite slab, which should be large enough so that the electron density of the material tails off to zero in the vacuum and the top of one slab has essentially no effect on the bottom of the next.

The directions in the lattice that define a particular plane are indicated by *Miller indices*. A plane of atoms is uniquely defined by the direction that is normal to the plane. In real space, Miller indices can be defined as inverse intercepts along the lattice vectors. The (hkl) notation denotes a plane that intercepts the three points \mathbf{a}_1/h , \mathbf{a}_2/k , and \mathbf{a}_3/l . A set of all planes equivalent to (hkl) by the symmetry of the lattice is denoted by $\{hkl\}$. In the context of crystal directions (not planes), the notation $[hkl]$ is used to denote a direction in the basis of the direct lattice vectors. Some common crystal planes for an fcc structure with the corresponding Miller indices are shown in Fig. 5.1.

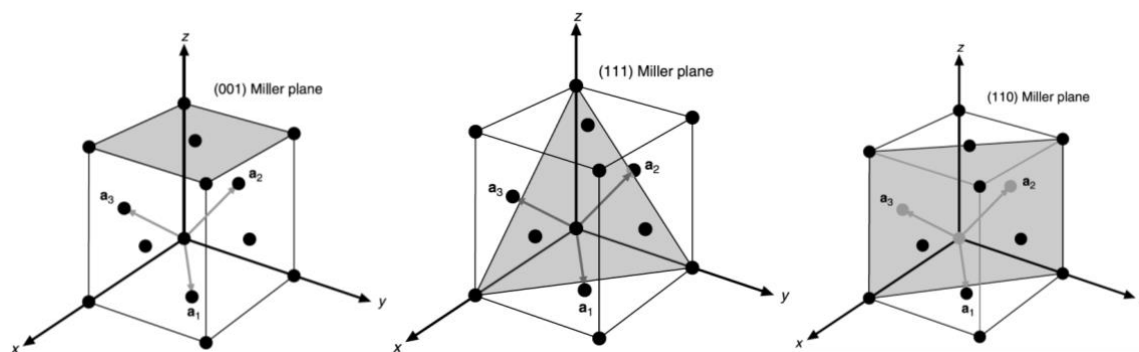


Figure 5.1: Some surface planes for an fcc metal. (Figure taken from K.W. Kolasinski, *Surface Science: Foundations of Catalysis and Nanoscience*, 2nd Ed., John Wiley & Sons, Ltd. 2008)

The simplest and flattest of the fundamental planes are the *low index planes*, which cut the crystal along directions with close-packed planes. For example, the low index planes in the fcc structure are (100), (110), and (111) surfaces. On the other hand, *high index planes* ($h, k, \text{ or } l > 1$) have open structures that can expose the sublayer atoms. Cutting the crystal at high index planes can lead to *vicinal surfaces*, where step-like discontinuities are introduced into the surface structure. A vicinal surface is composed of a series of terraces and steps, hence, they are also known as *stepped surfaces*. One example is the fcc (211) surface, which is composed of three-atom-wide terraces with (111) facet structure and one-atom step with (100) character.

Because stepped surfaces have both terraces and steps, they provide an interesting surface heterogeneity that directly affects the properties of the materials. The electrons of the atoms at the step edge site tend to smoothe out the discontinuity at the step in a process known as *Smoluchowski smoothing*. This has implications, for instance, in the diffusion of adsorbates over steps. Moreover, since the electronic properties of steps differs from that of terraces, the chemical reactivity is different as well. For instance, a study on the electronic states of Ru by Arevalo et al. showed that with respect to the bulk case, the d band of Ru is more forward-shifted (skewed) to the Fermi level for the case of the step-edge atom of the stepped surface compared to the terrace atom of the flat surface. This indicates an enhanced reactivity of the stepped surface compared to the low-index flat surface. [Arevalo, et al., *ACS Omega* 2 (2017) 1295-301]

The surface energy, σ , is the energy needed to cleave the bulk crystal, and can be computed in the following way:

$$\sigma = \frac{E_{\text{slab}} - nE_{\text{bulk}}}{2A}$$

where E_{slab} is the total energy of surface slab, n is the number of atoms in the surface slab, E_{bulk} is the bulk energy per atom, and A is the surface area. For a slab, there are two surfaces (top and bottom surfaces) that are of similar type; hence the number 2 in the denominator. Lower values of surface energy indicate a more stable surface (or more “bulk-like”).

Computational Model:

DFT calculations will be implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons will be described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations will be performed on a grid of $4 \times 4 \times 1$ Monkhorst-Pack k -points using Methfessel-Paxton smearing of $\sigma=0.2$ eV.

Method:

- 1) You will be assigned a particular metal with an fcc structure. Set up the position of the atoms as you have learned in the previous laboratory activities.
- 2) Use appropriate vacuum spacing (about 15 Å should be sufficient) and number of k points, following the structure of the supercell. Also, use the same thickness of slab for each case.
- 3) Identify the different sites on each surface (e.g., top, hollow, bridge, etc.).
- 4) Calculate the surface energies of the following surfaces:
 - a. (001)
 - b. (111)
 - c. (110)
 - d. (211)
- 5) Identify the most stable surface plane of the fcc metal assigned to you and compare your results with those reported in the literature.

Results and Guide Questions:

FCC Metal Assigned to you: _____

Figure 1: Top and Side views of the surface models for the different planes of an fcc metal and the corresponding surface sites

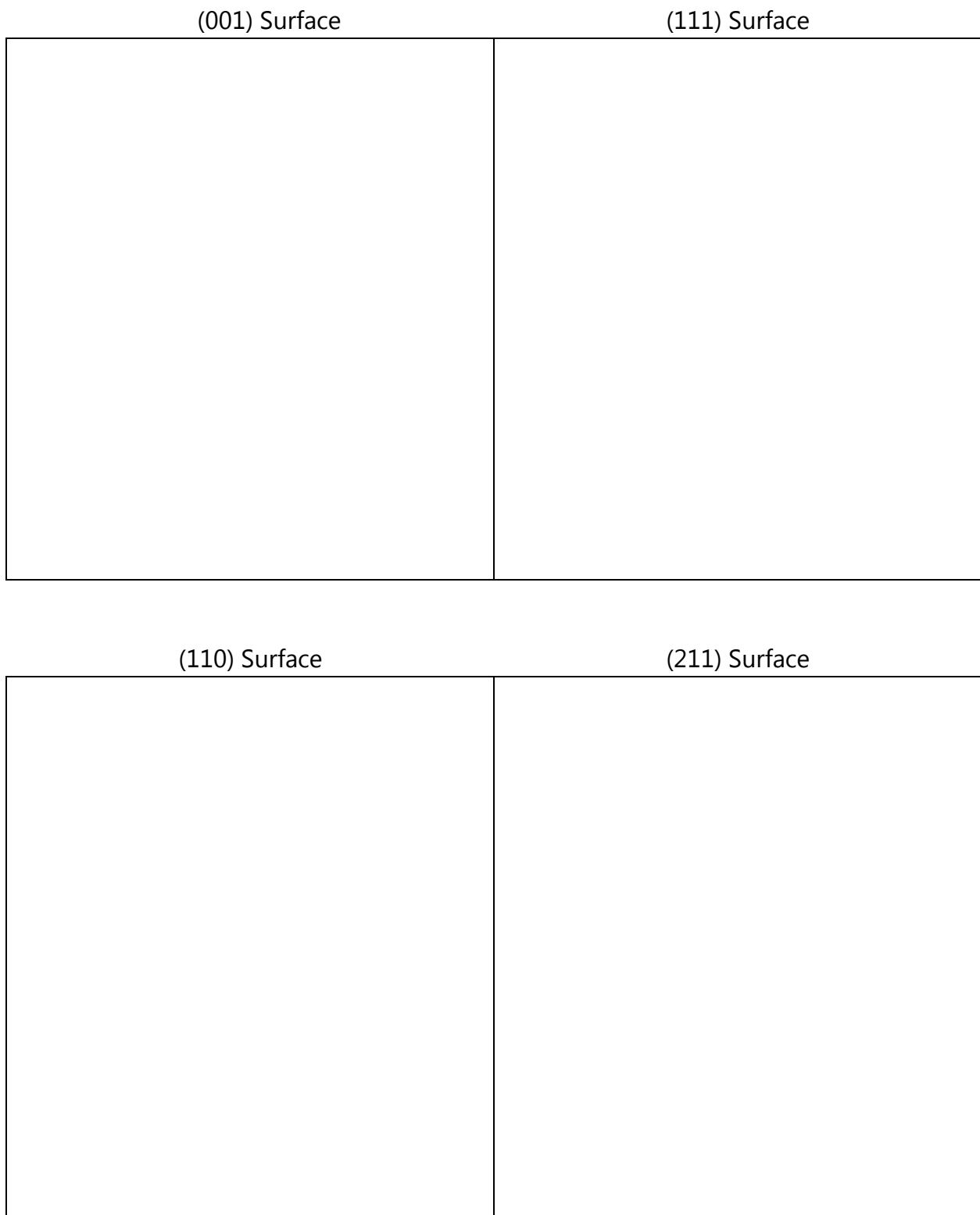


Table 1: Computation of the Surface Energy

E_{bulk} (eV): _____

Surface Facet	E_{slab} (eV)	n	A (m ²)	σ (eV/m ²)
(001)				
(111)				
(110)				
(211)				

1) Which of these surfaces is the most closed-packed? Compare its relative stability compared to other surfaces.

2) Which of these have “open” surfaces? Compare their relative stability compared to a more closed-packed surface.

3) Which of these surfaces is a stepped surface? Describe its stability compared to other surfaces.

4) Among these surfaces, which is the most stable? Compare your findings with those reported in the literature.

Computational Activity 5: Modeling Surfaces

Conclusion:
