03. Surface of Crystals

It might come as a big surprise initially that we need to worry about the surface of crystals. First you, well the physicist do, dispose of the crystal surface when calculating the properties of a bulk crystal. That's justified as we are dealing with a small fraction of the total material.

It would be instructive to calculate the surface of a cube of material that has Avogadro number of atoms and compare it with the surface: bulk ratio of a 15 nm particle made up of the same atoms. (Bulk: roughly 1 in 10^7 atoms, Nano: 12% atoms)

Its no longer justified to ignore the surface in case of nanomaterials (that includes thin films) where it contributes a good big fraction to the total number of atoms. Another thing which could be intriguing is that different surfaces of the nanocrystals behave differently. We will worry about this later.

Other than ease of calculation, there is no reason to assume that the surface atoms adopt the same crystal structure as the bulk of the crystal. This can be figured out easily by seeing that the surface atoms do not have a complete coordination sphere and therefore have unsatisfied valencies or dangling bonds. Figure 3.1 shows three kinds of dangling bonds in a wurtzite nanoparticle. The yellow atoms have three dangling bonds, the reds have two whereas the blue shaded atoms have only a single dangling bond.

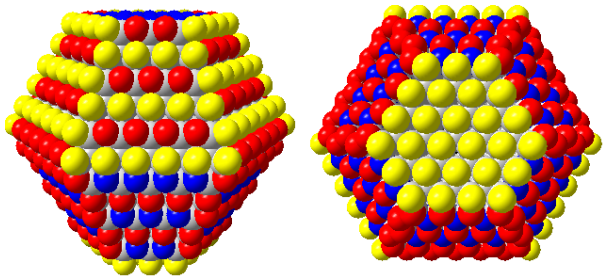


Figure 3.1: Different faces of 4.2 nm wurtzite nanocrystal.

This deficiency of chemical bonding is described by the surface energy – the work that must be done in order to cleave the crystal thereby creating the dangling surface bonds. Surface reconstitution is known to occur in a number of materials in order to reduce the surface energy. For example, on the (111) surface of silicon atoms, which is a hexagonal surface, two Si atoms come closer within the bonding distance to get rid of the dangling bonds. The top surface layer contracts by about 25% while the layers below expand to the tune of 1-5% to compensate for this contraction.

The surface energy is defined as the work that needs to be done to cleave a crystal along a certain plane thereby exposing two faces or facets. To calculate the energy we need to account for the number of bonds that will be broken in the process. If an atom type, each with n_i dangling bonds of energy $2\epsilon_i$ (that should take care of the two dangling bonds created on both the new surfaces), has density ρ_i, then the surface energy density, γ (i.e. surface energy per unit area) will be given by

$$\gamma = \Sigma \rho_i n_i \epsilon_i$$

Lets run through a few calculations. These are the most common facets one would encounter dealing with nanomaterials.

FCC surfaces

The FCC unit cell is shown in Figure 3.2; atoms are at the corners and the face centers. Lets calculate the radius of these atoms. Place the atoms so that they touch the nearest neighbors. The (100) face is shown in Figure 3.2b. For an edge length a, the diameter of the atom equals $\sqrt{2}/2\ a$ or $0.707a$.

Also, one should calculate the size of an octahedral hole (lying in the center of the unit cell, the six face centers form the hole) and that of a tetrahedral hole (take one corner atom and the three nearest face centers). $d_{Oh} = 0.293a, d_{Td} = 0.159a$

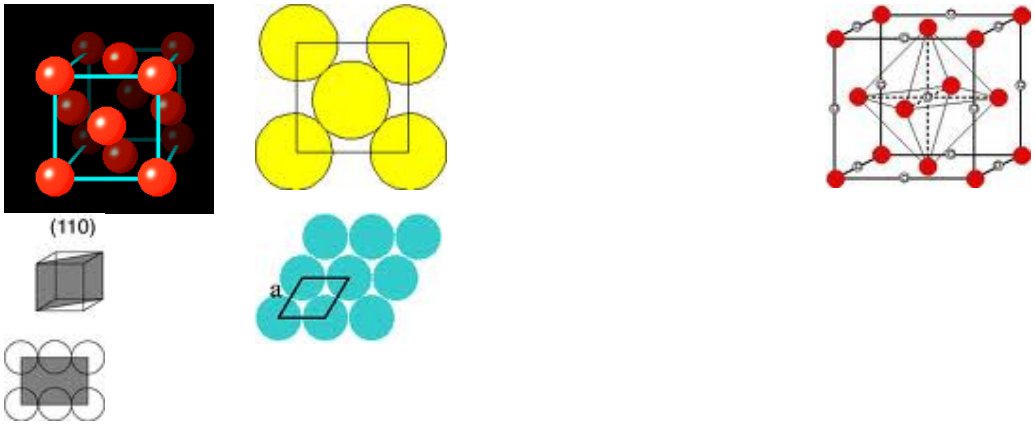


Figure 3.2: The face-centred cubic unit cell. (a) FCC unit cell, (b) (100) plane showing the packing of large atoms. The small atoms (not shown here) occupy the octahedral holes – the empty spaces between the large spheres along the unit cell edges, (c) the tetrahedral holes, (d) the NaCl structure.

Lets start with the easy one. Cut the FCC crystal to expose the (100) face. The (100) face contains a total of 2 atoms (1 face-centered atom + 4 quarter atoms on the corners). The central atom has four nearest neighbors below, four in the plane and therefore has four dangling bonds pointing out of the plane. Since the corner atoms contribute a fourth, we need to count only a quarter of the dangling bonds per atom, i.e. 1 per atom. That makes a total of 8 dangling bonds in an area a^2. The surface energy density, γ_{FCC} is therefore $8\epsilon/a^2$.

Next, we move onto the (110) plane. The plane can be easily constructed by taking one edge and its diametrically opposite edge. The area comes out to be $\sqrt{2}a^2$. This gives us 2 atoms on the plane – four 1/4th atoms and two 1/2 atoms (at the face center positions). Each atom is bonded to two surface atoms and five atoms below it and therefore has five dangling bonds. The surface energy density comes out to be $\gamma = 5\sqrt{2}\epsilon/a^2$.

A little more courage brings us to the (111) plane. Easier to visualize this plane in the ABC kind of staking we saw in lecture 2. The area of the rhombus (single atom unit cell) shown in Figure 3.2f is

$\sqrt{3}a^2/4$. Each atom, as we have seen in lecture 2, is bonded to 3 atoms below the plane and six in the plane, giving rise to three dangling bonds. The surface energy density is $\gamma = 4\sqrt{3}\epsilon/a^2$.

Table 3.1: The density of atoms on the surface, number of dangling bonds and the surface energy, γ, for different facets of the FCC and diamond structures.

Structure (plane)	Density of atoms	Dangling bonds/atom	γ
FCC (100)	$2/a^2$	4	$8\epsilon/a^2$
FCC (110)	$\sqrt{2}/a^2$	5	$5\sqrt{2}\epsilon/a^2$
FCC (111)	$4/a^2$	3	$5\sqrt{2}\epsilon/a^2$
Diamond (100)	$2/a^2$	2	$4\epsilon/a^2$
Diamond (110)	$2\sqrt{2}/a^2$	1	$2\sqrt{2}\epsilon/a^2$
Diamond (111)	$4/a^2$	1	$4\epsilon/\sqrt{3}a^2$

a = lattice constant, ϵ = surface energy per dangling chemical bond


Calculating the surface energy of zinc blende and diamond structures would be a good exercise. The answers for the diamond structure are given in Table 3.1.