Homework #4
The Tetrahedral Semiconductor Structures

Due 5pm Monday November 5
Turn in outside of Durand 110 or email to duerloo *at* stanford.edu

The diamond cubic, zincblende (sphalerite) and wurtzite structures are all closely related, each being made up of corner sharing tetrahedral units. Several important semiconductor elements (Si and Ge) and compounds (GaAs, InP, GaN, CdTe, etc.) adopt one of these structures. Each is derived from a simple crystal structure (FCC or HCP). The purpose of this homework is to examine their similarities and differences.

1. Perfect Crystals

The diamond cubic and zincblende structures are based on the FCC structure. The atomic positions in the conventional unit cell are as follows.

FCC Sites: (0,0,0), (1/2,1/2,0), (0,1/2,1/2),(1/2,0,1/2)
Tetrahedral Sites: (1/4,1/4,1/4),(3/4,3/4,1/4),(1/4,3/4,3/4),(3/4,1/4,3/4)

In the diamond structure all eight sites are occupied by the same atom. Note that with respect to the FCC sites, the tetrahedral sites are shifted by one fourth of the FCC cell's body diagonal (e.g., by 1/4 1/4 1/4), which is equivalent to saying that they are also arranged in an FCC array.

In compound materials adopting the zincblende structure, however, four atoms of one type occupy the FCC sites, while four of the other types occupy the tetrahedral sites. Wurtzite (hexagonal ZnS) is the hexagonal equivalent of zincblende:

Wurtzite HCP Sites: (0,0,0), (2/3,1/3,1/2)
Wurtzite Tetrahedral Sites: (2/3,1/3,1/8), (0,0,5/8)

(a) Draw the unit cells of the three structures (diamond, zincblende, wurtzite). For each, decide how many atoms there are per unit cell, and how many formula units there are per unit cell for the compound structures.

(b) For each structure, identify the closest atoms to a given atom and hence the configuration of the tetrahedral units. Calculate the atomic packing fraction of the diamond cubic structure (based on a hard sphere atom model).

(c) Given the following data, compare the density of silicon with that of aluminum (FCC) (e.g. g per cc)

atomic weights: Al = 26.96 u, Si = 28.09 u
cubic lattice parameter: Al = 0.404 nm , Si = 0.543 nm

Explain why the ratio of densities differs dramatically from the ratio of packing fractions for these structures. (FCC atomic packing fraction = 0.74)

(d) Draw to scale the (110) projections of the two types of ZnS structures (wurtzite and sphalerite), and hence establish the stacking sequence for each of the three structures. Give a structural description to account for the difference between cubic and hexagonal ZnS, i.e. how might one rapidly distinguish between these two structures by looking at the ordering of the bonds in a (110) projection?

(e) Recall that the primitive cell for the FCC structure is rhombohedral (i.e. $a = b = c$, $\alpha = \beta = \gamma \neq 90°$) with lattice vectors that point from the conventional cell corner to the adjacent face atoms. Sphalerite has a similar rhombohedral primitive cell with two atoms. Draw this primitive cell. Compute the lattice vector angles (i.e. $\alpha = \beta = \gamma = ?$) and lengths in terms of the cubic conventional cell edge length and specific the basis atoms for this cell. Remember that the basis atoms are expressed in terms of the lattice vectors, so they will be different than the cubic case.

(f) Another (non-primitive) sphalerite unit cell that contains four atoms exists. This cell is tetragonal (i.e. $a = b \neq c$, $\alpha = \beta = \gamma = 90°$). Draw this non-primitive cell. Give the lattice vector lengths in terms of the cubic conventional cell edge length and specify the basis atoms for this cell.

(g) A third (non-primitive) sphalerite unit cell contains six atoms. This cell is hexagonal (i.e. $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$). Draw this non-primitive cell. Give the lattice vector angles and lengths in terms of the cubic conventional cell edge length and specify the basis atoms for this cell. For inspiration, first determine the direction that the c axis must point; think about the c axis of the wurtzite structure.

2. Stacking Faults in Semiconductors

(a) Write the stacking sequence for an intrinsic stacking fault in zincblende noting that the tetrahedral coordination of both species must be maintained. What structure is created locally? Draw a (110) projection of this fault and label the layers with their associated stacking sequence letters. Orient your drawing so that the one of the <111> directions is vertical.

(b) Write the stacking sequence for a stacking fault in the wurtzite structure by assuming that the tetrahedral coordination of both species must be maintained. Draw a (110) projection of this fault and label the layers with their associated stacking sequence letters. Orient your drawing so that the [001] direction is vertical.

(c) Write the stacking sequence and draw the (110) projection atomic arrangements around a twin boundary in zincblende. Note that unlike the FCC structure, perfect mirror symmetry is not attained. Is perfect symmetry attained in the diamond cubic structure?

(d) Draw the atomic arrangement for an extrinsic stacking fault in zincblende. How can the intrinsic fault be distinguished from the extrinsic fault in terms of number of layers of locally

"twinned" crystal?

(e) There are two spacings of the atomic planes parallel to {111}, one being three times larger than the other. If an intrinsic stacking fault is created by movement of a partial dislocation in a {111} plane, on which of these two possible slip planes will it pass if we assume that tetrahedral coordination must be maintained? Dislocation motion in these structures is more complex than in FCC.

3. High Resolution Electron Micrographs (HREM)

HREM pictures of semiconductor materials and devices are normally taken in the [110] orientation (i.e. [110] is parallel to the imaging electron beam and the image is similar to the (110) plane projection drawings). In many micrographs, the closest atoms (eg. Ga and As) are not individually resolved, although this is now possible in the most advanced transmission electron microscopes.

The attached photographs show the interface between an epitaxially grown CdTe thin film (upper half of image) on a GaAs substrate (lower half of image). The bottom image is a zoomed version of the top image. Both have the sphalerite crystal structure. This image is courtesy of Alan Schwartzman.

(a) Draw the outline of the unit cell (110) projection in the upper and lower crystals. Identify two sets of non-parallel {111} type planes, and determine the stacking sequence in both sets. What are the Miller indices of the vertical direction in the images?

(b) By looking at the micrographs from an oblique angle, find the extra planes associated with the dislocation. Look across the boundary between the two crystals and try to connect {111} type planes on opposite sites to find the mismatch.