

Homework Set #2:

1a. Consider simple, body-centered, and face-centered cubic Bravais lattices. How many “nearest neighbor” lattice points are there for each lattice point in the three lattice types? How many lattice points are in each unit cell? (Note: It is conventional for a lattice point “shared” by more than one unit cell to be divided evenly between the unit cells.) Diamond cubic (Si, Ge) and zincblende (GaAs) lattices are face centered cubic. However, each atom is tetrahedrally bonded to four nearest neighbors. Explain how a diamond cubic or zincblende lattice can also be face centered cubic.

For a simple cubic lattice, it is clear that the nearest neighbor distance is just the lattice parameter, a . Therefore, for a simple cubic lattice there are six (6) nearest neighbors for any given lattice point.

For a body centered cubic (BCC) lattice, the nearest neighbor distance is half of the body diagonal distance, $a\sqrt{3}/2$. Therefore, for a BCC lattice there are eight (8) nearest neighbors for any given lattice point.

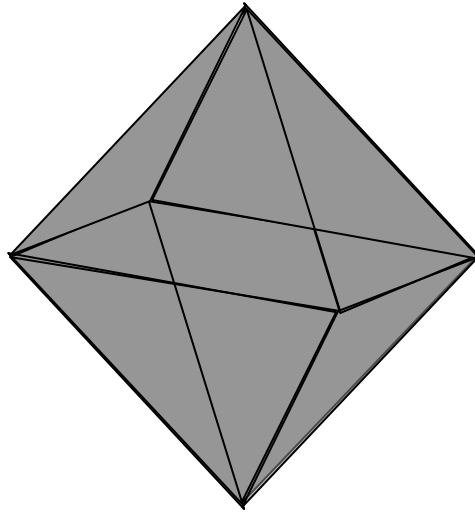
For a face centered cubic (FCC) lattice, the nearest neighbor distance is half of the face diagonal distance, $a\sqrt{2}/2$. Hence, there are three groups of four lattice points lying in three perpendicular face planes, that also lie at this distance from any given lattice point. Therefore, there are twelve (12) nearest neighbors for any given lattice point.

One can further observe that the FCC lattice is more densely packed since each unit cell contains an equivalent of four lattice points, compared to two for the BCC lattice, and one for a simple cubic lattice.

Both the diamond cubic and zincblende structures have an FCC Bravais lattice with each lattice point associated with two atoms, i.e., basis group, rather than just one as in the simple case. Alternatively, both the diamond cubic and the zincblende lattice can be regarded as two primitive interpenetrating FCC lattices offset by a displacement of $a/4, a/4, a/4$. (Of course, the lattice parameter, a , is the same for both primitive lattices.) This geometry requires each atom to be bonded to four other atoms in a tetrahedral coordination (bond angles $109^\circ 28'$). In the diamond cubic structure both atoms associated with a lattice point are the same, e.g., silicon. In the zincblende structure, they are different, e.g., gallium and arsenic.

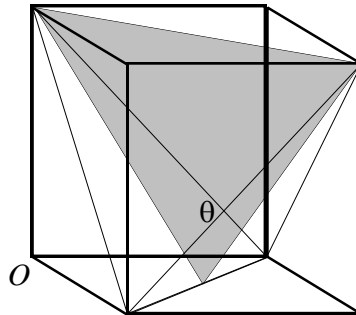
b. Consider the intersection of [111]-type planes within a cubic crystal. What type of solid figure does the intersection of [111]-type planes make? (Hint: The intersecting planes need not be restricted to a single unit cell.) What then, is the angle between adjacent [111] planes? Similarly, what is the angle between a [111] plane and a [100] plane. (Use elementary geometry to find the angles.)

If one considers a cubic unit cell, any face of the cell is a $[100]$ -type plane since the origin can be translated arbitrarily and the unit cell has rotational and inversion symmetry. Moreover, there are eight archetypical $[111]$ -type planes, viz., $\langle 111 \rangle$, $\langle 11\bar{1} \rangle$, $\langle \bar{1}11 \rangle$, $\langle 1\bar{1}1 \rangle$, $\langle \bar{1}\bar{1}1 \rangle$, $\langle 1\bar{1}\bar{1} \rangle$, $\langle \bar{1}\bar{1}\bar{1} \rangle$, and $\langle \bar{1}\bar{1}\bar{1} \rangle$ planes. In this case, a solid figure will be generated if one considers eight unit cells stacked to form a cube of dimension $2a$:



The geometry of the resulting figure is illustrated above. Clearly, the desired solid figure turns out to be an octahedron with all edges having a length of $a\sqrt{2}$, i.e., each edge is a face diagonal.

Alternatively, each unit cell also has four $[111]$ -type planes that intersect any three corners for which each pair can be connected by a diagonal running along a cell face, viz., $\langle 111 \rangle$, $\langle 11\bar{1} \rangle$, $\langle \bar{1}11 \rangle$, and $\langle 1\bar{1}1 \rangle$ planes. Therefore, if one inscribes these four $[111]$ -type planes within a single cell one can immediately construct the figure:



Accordingly, it is evident that within a cubic unit cell $[111]$ -type planes form a tetrahedron. Moreover, it is further clear that any face diagonal lies in a $[110]$ -type plane and is perpendicular to a second $[110]$ -type plane. Using this

observation, one can construct an isosceles triangle having a face diagonal as its base and having two equivalent sides that both simultaneously lie in [110] and [111]-type planes. Clearly, the sides of the triangle run from the precise center of one face to diagonal cell corners on the opposite face. This is indicated by the shaded region in the preceding figure. Naturally, the angle, θ , is the desired angle between adjacent [111]-type planes as well as, by definition, the vertex angle of the isosceles triangle. Obviously, the height, i.e., altitude, of the triangle is merely the lattice parameter, a . Furthermore, by definition, the altitude runs from the base to the vertex of the isosceles triangle and exactly bisects it into two identical right triangles. Consequently, each hypotenuse of the resulting two right triangles corresponds to one of the equivalent sides of the original isosceles triangle. It is now a simple matter to determine the hypotenuse length, L_{side} , by means of the Pythagorean Theorem:

$$L_{side} = \sqrt{\left[\frac{a\sqrt{2}}{2} \right]^2 + a^2} = a\sqrt{\frac{3}{2}}$$

Of course, it follows from the elementary definition of the cosine (as the ratio of the “adjacent side” to the hypotenuse of a right triangle) that:

$$\cos \theta/2 = \frac{a}{L_{side}} = \sqrt{\frac{2}{3}}$$

Therefore, θ , is given by the formula:

$$\theta = 2 \arccos \sqrt{\frac{2}{3}} \cong 70.52^\circ$$

In addition, the angle between [111] and [100]-type planes can easily be determined by consideration of the same figure. Clearly, the two right triangles obtained by bisection of the original isosceles triangle are, in addition to the right angle, characterized by the same two angles. One of these is, of course, $\theta/2$. The other one (denoted as φ) is precisely the angle between [111] and [100]-type planes. (Obviously, the two base angles of the original isosceles triangle are both equal to φ .) Since, φ is clearly the complement of $\theta/2$, one finds that φ is given by the trivial formula:

$$\varphi = \frac{\pi}{2} - \frac{\theta}{2} \cong 54.74^\circ$$

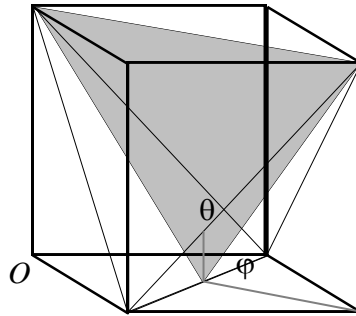
Alternatively, the same result follows from the elementary definition of the sine (as the ratio of the “opposite side” to the hypotenuse of a right triangle):

$$\sin \varphi = \frac{a}{L_{side}} = \sqrt{\frac{2}{3}}$$

Hence, one finds that:

$$\varphi = \arcsin \sqrt{\frac{2}{3}} \cong 54.74^\circ$$

The geometry is illustrated below:



2a. Assuming that rapid stirring conditions prevail, a CZ grown arsenic doped silicon crystal is required to have a resistivity of $2.0 \Omega \text{ cm}$ at a point exactly halfway between the top and bottom of the ingot. Further assuming an initial 100 kg charge of pure silicon and neglecting any silicon added to the melt by the seed, what is the amount of $0.01 \Omega \text{ cm}$ arsenic doped polysilicon that must be added to the melt to obtain the desired result? For this condition, what is the resistivity of the ingot one quarter and three quarters of the way between top and bottom? Assume no silicon is wasted during initial growth or the final “pull-out” of the ingot, that the arsenic distribution coefficient of 0.27, that all resistivities are measured at 300°K , and that electron mobility is $1350 \text{ cm}^2/\text{volt-sec}$.

Arsenic is, of course, an n-type extrinsic dopant. Thus, the concentration corresponding to a resistivity of $2.0 \Omega \text{ cm}$ can be determined simply from electron mobility:

$$N_{As} = n = \frac{1}{q\rho\mu_e}$$

$$N_{As} = \frac{1}{(1.602(10^{-19}) \text{ C})(2.0 \Omega \text{ cm})(1350 \text{ cm}^2/\text{volt sec})} \cong 2.312(10^{15}) \text{ cm}^{-3}$$

The dopant concentration as a function of growth is given by the formula:

$$C_s = KC_o \left(1 - \frac{W}{W_o}\right)^{K-1}$$

Since the melt is well-stirred, one uses the ideal value of the distribution coefficient, K , which for arsenic is 0.27. When the crystal is half grown W/W_o equals one half irrespective of the initial amount of silicon. Thus, one can solve for the initial concentration, C_o , as follows:

$$C_o = \frac{C_s}{K} \left(1 - \frac{W}{W_o}\right)^{1-K}$$

$$C_o = \frac{2.312(10^{15}) \text{ cm}^{-3}}{0.27} \left(\frac{1}{2}\right)^{0.73} \cong 5.5163(10^{15}) \text{ cm}^{-3}$$

The concentration of arsenic in the doping charge is:

$$N_{As} = \frac{1}{(1.602(10^{-19}) \text{ C})(0.01 \Omega \text{ cm})(1350 \text{ cm}^2/\text{volt sec})} \cong 4.624(10^{17}) \text{ cm}^{-3}$$

This is much more concentrated than is required. Therefore, if one notes that the volume of silicon is just the mass divided by the density, and then if w is defined as the mass of doped silicon to be added, it follows that:

$$(4.624(10^{17}) \text{ cm}^{-3}) \frac{w}{\rho} = \frac{(w+100 \text{ kg})}{\rho} 5.5163(10^{15}) \text{ cm}^{-3}$$

Of course, one assumes that the density of silicon is unchanged by doping. Clearly, density “cancels out” and, thus, it follows that:

$$w = \frac{5.5163(10^{17}) \text{ kg cm}^{-3}}{4.5028(10^{17}) \text{ cm}^{-3}} = 1.142 \text{ kg}$$

Hence, 1.142 kg of arsenic doped silicon must be added to the 100 kg of pure silicon to obtain the correct initial doping.

To calculate resistivity at one quarter and three quarters down the ingot, one combines the formula for resistivity with the CZ growth formula:

$$\rho = \frac{1}{qKC_o \left(1 - \frac{W}{W_o}\right)^{K-1} \mu_e}$$

Substituting numerical values gives:

$$qKC_o\mu_e = (1.602(10^{-19}) \text{ C})(0.27)(5.5163(10^{15}) \text{ cm}^{-3})(1350 \text{ cm}^2/\text{volt sec})$$

$$qKC_o\mu_e = 1.206 \Omega^{-1} \text{ cm}^{-1}$$

Therefore at one quarter down the ingot resistivity is: 2.689 Ω cm

and at three quarters down the ingot, resistivity is: 1.206 Ω cm

Naturally, the resistivity falls because the dopant concentration rises from top to bottom of the ingot.

b. If instead of rapid stirring, programmed growth conditions are imposed such that effective boundary layer thickness, δ , is 0.5 cm during growth of the crystal and dopant diffusivity in the melt, D , is $8(10^{-4}) \text{ cm}^2/\text{sec}$, what freezing rate is necessary to achieve an effective segregation coefficient of 0.99? Would this seem a reasonable pull rate for a practical CZ process?

The effective distribution coefficient is related to the thermodynamic distribution coefficient by the formula:

$$K_e = \frac{K}{K + (1 - K)e^{-R\delta/D}}$$

Inverting this expression one finds that:

$$\left(\frac{1 - K_e}{K_e}\right)\left(\frac{K}{1 - K}\right) = e^{-R\delta/D}$$

From this, one constructs an expression for the freezing rate as follows:

$$R = \frac{D}{\delta} \ln\left(\left(\frac{1 - K}{K}\right)\left(\frac{K_e}{1 - K_e}\right)\right)$$

Substituting numerical quantities gives:

$$R = \frac{(8(10^{-4}) \text{ cm}^2/\text{s})}{0.5 \text{ cm}} \ln\left(\left(\frac{1 - 0.27}{0.27}\right)\left(\frac{0.99}{1 - 0.99}\right)\right) = 8.944(10^{-3}) \text{ cm/s}$$

This rate implies that 32.1 cm of ingot are grown per hour. Thus a 2 meter ingot would require 6.2 hours for growth. In practice, this is probably too fast for good control of temperature and heat fluxes; however, it is not unreasonably fast.

Accordingly, one can trade-off pull rate and rotation to optimize crystal quality. Practical values result in growth times on the order of a day or a day and a half.

3. The lattice parameter of crystalline silicon is known with very high precision to have a value of 0.357102064 nm. Assuming that energies of formation of a single vacancy and a single self-interstitial (ΔE_v and ΔE_i) are 2.3 and 1.1 eV, respectively (values taken from Handbook of Photovoltaic Science and Engineering by Antonio Luque and Steven Hegedus), estimate equilibrium concentrations of vacancies and self-interstitials within a pure silicon crystal at 27°C and 1327°C. Also, estimate the equilibrium constant at these two temperatures. (Boltzmann's constant = $8.61735(10^{-5})$ eV/°K; Avogadro's number = $6.023(10^{23})$ mole⁻¹)

As mentioned in the notes, N can be considered as atomic number density rather than an absolute number of atoms. Accordingly, one can easily determine the atomic number density in a silicon crystal by recalling that each unit cell of a perfect crystal "contains" eight silicon atoms, hence:

$$N = \frac{8 \text{ atoms}}{(0.3571(10^{-7}) \text{ cm})^3} = 4.994(10^{22}) \text{ atoms/cm}^3$$

Although vacancy and self-interstitial "concentrations" can be ideally constructed by considering "reactions" in which a defected crystal is formed from a perfect crystal by moving atoms from the interior to the surface or vice-versa, in reality within a bulk crystal they can be regarded as satisfying a mass action equilibrium of the usual form:

$$K_{eq} = [V][I]$$

Here, $[V]$ and $[I]$ are defined as vacancy and self-interstitial concentrations, respectively. Accordingly, an expression for the equilibrium constant can be constructed as follows:

$$K_{eq} = \frac{5}{8} N^2 \exp\left(-\frac{\Delta E_v + \Delta E_i}{kT}\right)$$

Upon substitution of the previous value for N , one finds that as a function of temperature, the equilibrium constant has the form:

$$K_{eq} = (1.55873(10^{45}) \text{ cm}^{-6}) \exp\left(-\frac{39455.3^\circ\text{K}}{T}\right)$$

Thus:

at 27°C(300°K), the equilibrium constant is $1.18959(10^{-12}) \text{ cm}^{-6}$

at 1327°C(1600°K), the equilibrium constant is $3.04273(10^{34}) \text{ cm}^{-6}$

In analogy to mobile carriers, one expects that vacancy and self-interstitial concentrations strictly generated thermally must be equal; hence:

at 27°C(300°K), [V] equals [I] equals $1.0906(10^{-6}) \text{ cm}^{-3}$

at 1327°C(1600°K), [V] equals [I] equals $1.7443(10^{17}) \text{ cm}^{-3}$

Clearly, at 300°K equilibrium concentrations of vacancies and self-interstitials are ridiculously low. Nevertheless,, significant concentrations of point defects may exist at room temperature because they can be formed by athermal processes such as damage or stress and, once formed, can be expected to recombine very slowly. In contrast, at 1600°K equilibrium concentrations are much larger and, moreover, significant in comparison to atomic density. Indeed, a typical published value for the melting point of silicon is 1685°K and, of course, in the neighborhood of this temperature one expects vacancy and self-interstitial concentrations to approach the atomic concentration since melting completely disrupts the crystal lattice.

In addition, it should be mentioned that vacancies and interstitials have a fundamental role in impurity diffusion in silicon. These processes are generally carried out at temperatures in the range of 1100-1300°K. Accordingly, although not large, vacancy and interstitial concentrations can be expected to be significant.

4. Ignore temporarily the effect of lattice strain on the free energy of an oxygen precipitate in a silicon crystal. At 1100°C, the energy of formation of SiO_2 is 900 kJ/mole and the free energy of formation is 644 kJ/mole. Suppose that the surface energy of an Si/ SiO_2 interface is 25000 erg/sq. cm. What is the size of a critical nucleus (*i.e.*, what is the minimum radius of a stable oxygen precipitate?) What is the effect of the omitted strain term on the critical nucleus size? Assuming that strain energy is simply proportional to the volume of the precipitate, what is the critical value of strain energy per unit volume above which oxygen precipitates cannot be formed? (Note the unit conversions: $1 \text{ J} = 1 \times (10^7) \text{ ergs}$)

By definition, the free energy of formation of SiO_2 is given by:

$$\Delta A_{\text{SiO}_2} = \Delta E_{\text{SiO}_2} - T\Delta S_{\text{SiO}_2}$$

Therefore, the free energy of formation of a precipitate containing $N \text{ SiO}_2$ “molecules” is:

$$\Delta A = N\Delta E_{\text{SiO}_2} - NT\Delta S_{\text{SiO}_2} + A\sigma + gV$$

Here, A is the surface area and V is the volume of a single precipitate. For the moment, one takes g equal to zero. It follows that N is given by the formula:

$$N = \rho V \left(\frac{N_o}{M_{\text{SiO}_2}} \right)$$

where N_o is Avogadro's number, M_{SiO_2} is the formula weight of SiO_2 , and ρ is mass density of SiO_2 . Thus,

$$\Delta A = \rho V \left(\frac{N_o}{M_{\text{SiO}_2}} \right) (\Delta E_{\text{SiO}_2} - T \Delta S_{\text{SiO}_2}) + A \sigma + gV$$

$$\Delta A = \rho V \left(\frac{N_o}{M_{\text{SiO}_2}} \right) \Delta A_{\text{SiO}_2} + A \sigma + gV$$

Now, as is usual, one considers the precipitate to be spherical. The volume of a sphere of radius, r , is $4\pi r^3/3$, and the surface area is $4\pi r^2$, thus,

$$\frac{\Delta A}{4\pi} = \frac{r^3}{3} \left(\frac{\rho N_o}{M_{\text{SiO}_2}} \Delta A_{\text{SiO}_2} + g \right) + r^2 \sigma$$

The critical nucleus size is determined by the maximum of the free energy as a function of radius. Thus, one determines the criticality condition as follows:

$$0 = \frac{1}{4\pi} \frac{\partial}{\partial r} \Delta A = r_{\text{crit}}^2 \left(\frac{\rho N_o}{M_{\text{SiO}_2}} \Delta A_{\text{SiO}_2} + g \right) + 2r_{\text{crit}} \sigma$$

$$0 = r_{\text{crit}} \left(\frac{\rho N_o}{M_{\text{SiO}_2}} \Delta A_{\text{SiO}_2} + g \right) + 2\sigma$$

$$r_{\text{crit}} = \frac{-2\sigma}{\left(\frac{\rho N_o}{M_{\text{SiO}_2}} \Delta A_{\text{SiO}_2} + g \right)}$$

One can now substitute the numerical quantities into this expression. At this point it is clear that the heat of formation is not needed since the free energy of formation is given explicitly. First, however, convert free energy to cgs units:

$$\Delta A_{\text{SiO}_2} = \frac{(-644 \text{ kJ/mole})(1000 \text{ J/kJ})(10^7 \text{ erg/J})}{6.023(10^{23}) \text{ mole}^{-1}}$$

$$\Delta A_{\text{SiO}_2} = -1.069(10^{-11}) \text{ erg}$$

Clearly, the free energy of formation must be formally negative since SiO_2 forms spontaneously. Thus, if strain energy is ignored, the critical radius is given by the expression:

$$r_{\text{crit}} = \frac{-2(25000 \text{ erg/cm}^2)}{\left(\frac{(2.27 \text{ g/cm}^3)(6.023(10^{23}) \text{ mole}^{-1})(-1.069(10^{-11}) \text{ erg})}{60.1 \text{ g/mole}} \right)} = 2.056 \text{ nm}$$

If one considers the functional behavior of the various components of the free energy, it is clear that for r equal to zero, the surface term invariably dominates so that an SiO_2 precipitate is unstable, *i.e.*, the free energy increases with increasing radius. At the critical radius, the free energy of formation term begins to dominate which causes the SiO_2 precipitate to become stable, *i.e.*, the free energy decreases with increasing radius. Accordingly, precipitate growth is thermodynamically favored. The result obtained above indicates that the critical radius is fairly small and that only a small cluster of SiO_4 tetrahedra would be sufficient to nucleate stable precipitates at this temperature. Therefore, if this result is valid, then oxygen precipitates can be expected to be prevalent in a silicon crystal even at a high temperature such as 1100°C . It is well-known that this is not the case. Why is this result wrong?

Obviously, the effect of strain energy has not been included. Addition of a positive strain energy term serves to make the critical radius larger since it offsets the negative free energy of formation. Clearly, the strain energy must make a significant contribution to the overall free energy of an SiO_2 precipitate. Indeed, if g were to exactly balance the free energy of formation, the denominator of the preceding formula would vanish implying that critical radius becomes infinite and indicating that SiO_2 precipitates never become stable. Of course, if g dominates, the calculated radius becomes negative which is an unphysical result and also indicates that precipitates are exceedingly unstable.

Consequently, it is clear from preceding observations that oxygen precipitates can never be stable if the strain energy entirely compensates the free energy of formation. This will occur for the condition:

$$g \geq -\frac{\rho N_o}{M_{\text{SiO}_2}} \Delta A_{\text{SiO}_2}$$

$$g \geq \frac{(2.27 \text{ g/cm}^3)(6.023(10^{23}) \text{ mole}^{-1})(1.069(10^{-11}) \text{ erg})}{60.1 \text{ g/mole}} = 2.434(10^{11}) \text{ erg/cm}^3$$

5. Consider an ingot of crystalline silicon uniformly contaminated with antimony (Sb) which has a distribution equilibrium coefficient, K , of 0.020. (Assume, K and K_e are the same.) What is the lowest concentration of Sb that can be obtained by a single pass zone refining process? Where in the crystal does this occur? What is the Sb concentration at a point halfway along the ingot?

The initial unrefined antimony concentration, although uniform, was not specified numerically, but it can be represented as a variable, C_o . The equation relating concentration in the solid to the initial concentration for a single pass zone refining process was given in the notes and is as follows:

$$C_s(x) = C_o \left(1 - (1 - K)e^{-Kx/L} \right)$$

Obviously, the lowest concentration occurs at the very beginning of refining and is merely the product of K and C_o . Hence, for the present case this is just $0.02 \times C_o$. Concomitantly, at a point halfway along the ingot, x/L is 0.5. Therefore, upon substitution into the preceding formula, one finds that:

$$C_s(0.5) = C_o (1 - (1 - 0.02)e^{-0.02 \times 0.5}) = (0.0297511 \dots) C_o$$

Clearly, the concentration is almost 50% larger halfway along the ingot. Even so, it is still quite small compared to C_o , thus, for contaminants with small distribution coefficients, zone refining is quite effective.