SEMICONDUCTOR PHYSICS

Electron Momentum: $\mathrm{p} = m^*\mathrm{v} = \hbar\mathbf{k} = \frac{h}{\lambda}$ Planck: $E = h\nu = \hbar\omega$

Kinetic: $E = \frac{1}{2}m^*\mathrm{v}^2 = \frac{1}{2}\frac{\mathrm{p}^2}{m^*} = \frac{\hbar^2}{2m^*}\mathbf{k}^2$ (3-4) Effective mass: $m^* = \frac{\hbar^2}{d^2E/d\mathbf{k}^2}$ (3-3)

Total electron energy $= P.E. + K.E. = E_c + E(\mathbf{k})$

Fermi-Dirac e^- distribution: $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \cong e^{(E_F-E)/kT}$ for $E \gg E_F$ (3-10)

Equilibrium: $n_0 = \int_{E_c}^{\infty} f(E)N(E)dE = N_c f(E_c) = N_c e^{-(E_c-E_F)/kT}$ (3-15)

$N_c = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$ $N_v = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$ (3-16), (3-20)

$p_0 = N_v[1 - f(E_v)] = N_v e^{-(E_F-E_v)/kT}$ (3-19)

$n_i = N_c e^{-(E_c-E_i)/kT}$, $p_i = N_v e^{-(E_i-E_v)/kT}$ (3-21)

$n_i = \sqrt{N_c N_v}\, e^{-E_g/2kT} = 2\left(\frac{2\pi kT}{h^2}\right)^{3/2}(m_n^* m_p^*)^{3/4}e^{-E_g/2kT}$ (3-23), (3-26)

Equilibrium: $\begin{matrix} n_0 = n_i e^{(E_F-E_i)/kT} \\ p_0 = n_i e^{(E_i-E_F)/kT} \end{matrix}$ (3-25) $n_0 p_0 = n_i^2$ (3-24)

Steady state: $\begin{matrix} n = N_c e^{-(E_c-F_n)/kT} = n_i e^{(F_n-E_i)/kT} \\ p = N_v e^{-(F_p-E_v)/kT} = n_i e^{(E_i-F_p)/kT} \end{matrix}$ (4-15) $np = n_i^2 e^{(F_n-F_p)/kT}$ (5-38)

$\mathcal{E}(x) = -\frac{d\mathcal{V}(x)}{dx} = \frac{1}{q}\frac{dE_i}{dx}$ (4-26)

Poisson: $\frac{d\mathcal{E}(x)}{dx} = -\frac{d^2\mathcal{V}(x)}{dx^2} = \frac{\rho(x)}{\epsilon} = \frac{q}{\epsilon}(p - n + N_d^+ - N_a^-)$ (5-14)

$\mu \equiv \frac{q\bar{t}}{m^*}$ (3-40a) Drift: $\mathrm{v}_d \cong \frac{\mu\mathcal{E}}{1 + \mu\mathcal{E}/\mathrm{v}_s}\begin{cases} = \mu\mathcal{E} \text{ (low fields, ohmic)} \\ = \mathrm{v}_s \text{ (high fields, saturated vel.)} \end{cases}$ (Fig. 6-9)

Drift current density: I_x

Conduction Current:
$$\begin{matrix} J_n(x) = q\mu_n n(x)\mathcal{E}(x) + qD_n\frac{dn(x)}{dx} \\ \text{drift} \qquad\qquad \text{diffusion} \quad (4\text{–}23) \\ J_p(x) = q\mu_p p(x)\mathcal{E}(x) - qD_p\frac{dp(x)}{dx} \end{matrix}$$

$J_{\text{total}} = J_{\text{conduction}} + J_{\text{displacement}} = J_n + J_p + C\frac{dV}{dt}$

Continuity: $\frac{\partial p(x,t)}{\partial t} = \frac{\partial\delta p}{\partial t} = -\frac{1}{q}\frac{\partial J_p}{\partial x} - \frac{\delta p}{\tau_p}$ $\frac{\partial\delta n}{\partial t} = \frac{1}{q}\frac{\partial J_n}{\partial x} - \frac{\delta n}{\tau_n}$ (4-31)

For steady state diffusion: $\frac{d^2\delta n}{dx^2} = \frac{\delta n}{D_n\tau_n} \equiv \frac{\delta n}{L_n^2}$ $\frac{d^2\delta p}{dx^2} = \frac{\delta p}{L_p^2}$ (4-34)

Diffusion length: $L \equiv \sqrt{D\tau}$ Einstein relation: $\frac{D}{\mu} = \frac{kT}{q}$ (4-29)

p-n JUNCTIONS

Equilibrium: $V_0 = \frac{kT}{q}\ln\frac{p_p}{p_n} = \frac{\mathrm{kT}}{\mathrm{q}}\ln\frac{N_a}{n_i^2/N_d} = \frac{\mathrm{kT}}{\mathrm{q}}\ln\frac{N_aN_d}{n_i^2}$ (5-8)

$\frac{p_p}{p_n} = \frac{n_n}{n_p} = e^{qV_0/kT}$ (5-10) $W = \left[\frac{2\epsilon(V_0 - V)}{q}\left(\frac{N_a + N_d}{N_aN_d}\right)\right]^{1/2}$ (5-57)

One-sided abrupt p^+-n: $x_{n0} = \frac{WN_a}{N_a + N_d} \simeq W$ (5-23) $V_0 = \frac{qN_dW^2}{2\epsilon}$

$\Delta p_n = p(x_{n0}) - p_n = p_n(e^{qV/kT} - 1)$ (5-29)

$\delta p(x_n) = \Delta p_n e^{-x_n/L_p} = p_n(e^{qV/kT} - 1)e^{-x_n/L_p}$ (5-31b)

Ideal diode: $I = qA\left(\frac{D_p}{L_p}p_n + \frac{D_n}{L_n}n_p\right)(e^{qV/kT} - 1) = I_0(e^{qV/kT} - 1)$ (5-36)

Non-ideal: $\begin{matrix} I = I_0'(e^{qV/\mathbf{n}kT} - 1) \\ (\mathbf{n} = 1 \text{ to } 2) \end{matrix}$ (5-74)

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CONTENTS

Chapter 1

Crystal Properties and Growth of Semiconductors

OBJECTIVES

1. Describe what a semiconductor is
2. Perform simple calculations about crystals
3. Understand what is involved in bulk Czochralski and thin-film epitaxial crystal growth
4. Learn about crystal defects

In studying solid state electronic devices we are interested primarily in the electrical behavior of solids. However, we shall see in later chapters that the transport of charge through a metal or a semiconductor depends not only on the properties of the electron but also on the arrangement of atoms in the solid. In the first chapter we shall discuss some of the physical properties of semiconductors compared with other solids, the atomic arrangements of various materials, and some methods of growing semiconductor crystals. Topics such as crystal structure and crystal growth technology are often the subjects of books rather than introductory chapters; thus we shall consider only a few of the more important and fundamental ideas that form the basis for understanding electronic properties of semiconductors and device fabrication.

1.1 SEMICONDUCTOR MATERIALS

Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators. It is significant that the conductivity of these materials can be varied over orders of magnitude by changes in temperature, optical excitation, and impurity content. This variability of electrical properties makes the semiconductor materials natural choices for electronic device investigations.

Semiconductor materials are found in column IV and neighboring columns of the periodic table (Table 1–1). The column IV semiconductors, silicon and germanium, are called *elemental* semiconductors because they are composed of single species of atoms. In addition to the elemental materials, compounds of column III and column V atoms, as well as certain combinations from II and VI, and from IV, make up the *compound* semiconductors.

As Table 1–1 indicates, there are numerous semiconductor materials. As we shall see, the wide variety of electronic and optical properties of these semiconductors provides the device engineer with great flexibility in the design of electronic and optoelectronic functions. The elemental semiconductor Ge was widely used in the early days of semiconductor development for transistors and diodes. Silicon is now used for the majority of rectifiers, transistors, and integrated circuits. However, the compounds are widely used in high-speed devices and devices requiring the emission or absorption of light. The two-element (*binary*) III–V compounds such as GaN, GaP, and GaAs are common in light-emitting diodes (LEDs). As discussed in Section 1.2.4, three-element (*ternary*) compounds such as GaAsP and four-element (*quaternary*) compounds such as InGaAsP can be grown to provide added flexibility in choosing materials properties.

Fluorescent materials such as those used in television screens usually are II–VI compound semiconductors such as ZnS. Light detectors are commonly made with InSb, CdSe, or other compounds such as PbTe and HgCdTe. Si and Ge are also widely used as infrared and nuclear radiation detectors. An important microwave device, the Gunn diode, is usually made of GaAs or InP. Semiconductor lasers are made using GaAs, AlGaAs, and other ternary and quaternary compounds.

One of the most important characteristics of a semiconductor, which distinguishes it from metals and insulators, is its *energy band gap*. This property, which we will discuss in detail in Chapter 3, determines among other things the wavelengths of light that can be absorbed or emitted by the semiconductor. For example, the band gap of GaAs is about 1.43 electron volts (eV), which corresponds to light wavelengths in the near infrared. In contrast, GaP has a band gap of about 2.3 eV, corresponding to wavelengths in the green portion of the spectrum.[1] The band gap E_g for various semiconductor materials is listed along with other properties in Appendix III. As a result of the wide variety of semiconductor band gaps, light-emitting diodes and lasers can be constructed with wavelengths over a broad range of the infrared and visible portions of the spectrum.

Table 1–1. Common semiconductor materials: (a) the portion of the periodic table where semiconductors occur; (b) elemental and compound semiconductors.

(a)	II	III	IV	V	VI
		B	C	N	
		Al	Si	P	S
	Zn	Ga	Ge	As	Se
	Cd	In		Sb	Te

(b)	Elemental	IV compounds	Binary III–V compounds	Binary II–VI compounds
	Si	SiC	AlP	ZnS
	Ge	SiGe	AlAs	ZnSe
			AlSb	ZnTe
			GaN	CdS
			GaP	CdSe
			GaAs	CdTe
			GaSb	
			InP	
			InAs	
			InSb	

The electronic and optical properties of semiconductor materials are strongly affected by impurities, which may be added in precisely controlled amounts. Such impurities are used to vary the conductivities of semiconductors over wide ranges and even to alter the nature of the conduction processes from conduction by negative charge carriers to positive charge carriers. For example, an impurity concentration of one part per million can change a sample of Si from a poor conductor to a good conductor of electric current. This process of controlled addition of impurities, called *doping*, will be discussed in detail in subsequent chapters.

To investigate these useful properties of semiconductors, it is necessary to understand the atomic arrangements in the materials. Obviously, if slight alterations in purity of the original material can produce such dramatic changes in electrical properties, then the nature and specific arrangement of atoms in each semiconductor must be of critical importance. Therefore, we begin our study of semiconductors with a brief introduction to crystal structure.

1.2 CRYSTAL LATTICES

In this section we discuss the arrangements of atoms in various solids. We shall distinguish between single crystals and other forms of materials and then investigate the periodicity of crystal lattices. Certain important crystallographic terms will be defined and illustrated in reference to crystals having a basic cubic structure. These definitions will allow us to refer to certain planes and directions within a lattice. Finally, we shall investigate the diamond lattice; this structure, with some variations, is typical of most of the semiconductor materials used in electronic devices.

1.2.1 Periodic Structures

A crystalline solid is distinguished by the fact that the atoms making up the crystal are arranged in a periodic fashion. That is, there is some basic arrangement of atoms that is repeated throughout the entire solid. Thus the crystal appears exactly the same at one point as it does at a series of other equivalent points, once the basic periodicity is discovered. However, not all solids are crystals (Fig. 1–1); some have no periodic structure at all (*amorphous* solids), and others are composed of many small regions of single-crystal material (*polycrystalline* solids). The high-resolution micrograph shown in Fig. 6–33 illustrates the periodic array of atoms in the single-crystal silicon of a transistor channel compared with the amorphous SiO_2 (glass) of the oxide layer.

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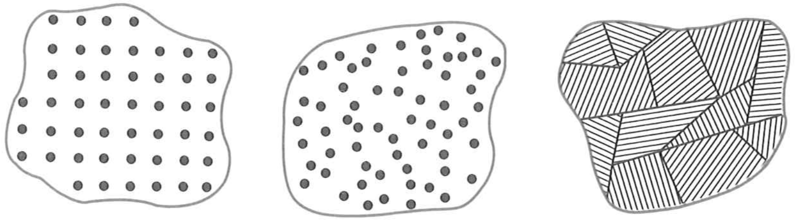
[1] The conversion between the energy E of a photon of light (eV) and its wavelength $\lambda(\mu m)$ is $\lambda = 1.24/E$. For GaAs, $\lambda = 1.24/1.43 = 0.87\ \mu m$.



(a) Crystalline (b) Amorphous (c) Polycrystalline

Figure 1–1
Three types of solids, classified according to atomic arrangement: (a) crystalline and (b) amorphous materials are illustrated by microscopic views of the atoms, whereas (c) polycrystalline structure is illustrated by a more macroscopic view of adjacent single-crystalline regions, such as (a).

The periodicity in a crystal is defined in terms of a symmetric array of points in space called the *lattice*. We can add atoms at each lattice point in an arrangement called a *basis*, which can be one atom or a group of atoms having the same spatial arrangement, to get a *crystal*. In every case, the lattice contains a volume or *cell* that represents the entire lattice and is regularly repeated throughout the crystal. As an example of such a lattice, Fig. 1–2 shows a two-dimensional arrangement of atoms called a rhombic lattice, with a *primitive* cell ODEF, which is the smallest such cell. Notice that we can define vectors **a** and **b** such that if the primitive cell is translated by integral multiples of these vectors, a new primitive cell identical to the original is found (e.g., O′D′E′F′). These vectors, **a** and **b** (and **c** if the lattice is three dimensional), are called the *primitive vectors* for the lattice. Points within the lattice are indistinguishable if the vector between the points is

$$\mathbf{r} = p\mathbf{a} + q\mathbf{b} + s\mathbf{c} \qquad (1\text{–}1)$$

where p, q, and s are integers. A primitive cell has lattice points *only* at the corners of the cell. It is not unique, but the convention is to choose the smallest primitive vectors. Note that, in a primitive cell, the lattice points at the corners are shared with adjacent cells; thus, the *effective* number of lattice points belonging to the primitive cell is always unity. Since there are many different ways of placing atoms in a volume, the distances and orientation between atoms can take many forms, but it is the *symmetry* that determines the lattice, not the magnitudes of the distances between the lattice points.

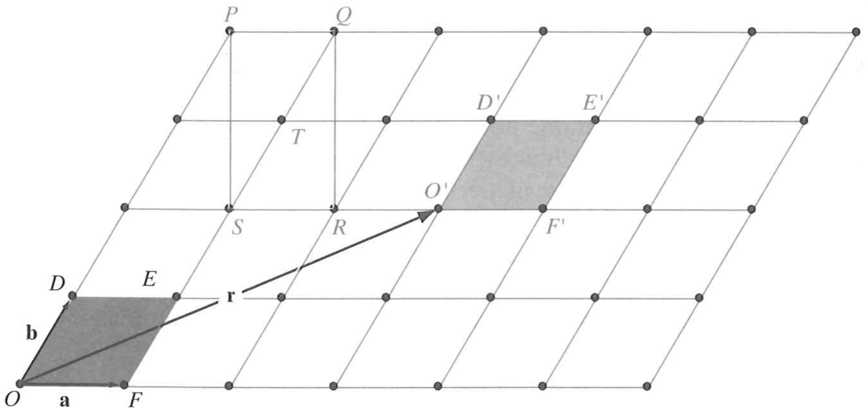


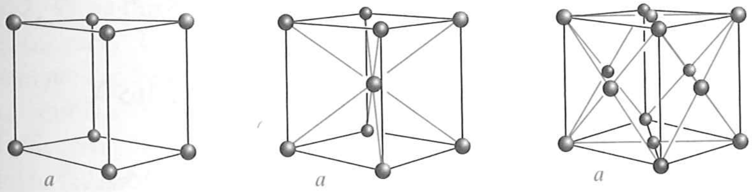
Figure 1–2
A two-dimensional lattice showing translation of a unit cell by $\mathbf{r} = 3\mathbf{a} + 2\mathbf{b}$.

In many lattices, however, the primitive cell is not the most convenient to work with. For example, in Fig. 1–2, we see that the rhombic arrangement of the lattice points is such that it can also be considered to be rectangular (PQRS) with a lattice point in the center at T (a so-called *centered rectangular* lattice). [Note that this is not true of all rhombic lattices!] Clearly, it is simpler to deal with a rectangle rather than a rhombus. So, in this case we can choose to work with a larger rectangular *unit* cell, PQRS, rather than the smallest primitive cell, ODEF. A unit cell allows lattice points not only at the corners, but also at the face center (and body center in 3-D) if necessary. It is sometimes used instead of the primitive cell if it can represent the symmetry of the lattice better (in this example "centered rectangular" 2-D lattice). It replicates the lattice by integer translations of *basis* vectors.

The importance of the unit cell lies in the fact that we can analyze the crystal as a whole by investigating a representative volume. For example, from the unit cell we can find the distances between nearest atoms and next nearest atoms for calculation of the forces holding the lattice together; we can look at the fraction of the unit cell volume filled by atoms and relate the density of the solid to the atomic arrangement. But even more important for our interest in electronic devices, the properties of the periodic crystal lattice determine the allowed energies of electrons that participate in the conduction process. Thus the lattice determines not only the mechanical properties of the crystal but also its electrical properties.

1.2.2 Cubic Lattices

The simplest three-dimensional lattice is one in which the unit cell is a cubic volume, such as the three cells shown in Fig. 1–3. The *simple cubic* structure (abbreviated *sc*) has an atom located at each corner of the unit cell. The *body-centered cubic* (*bcc*) lattice has an additional atom at the center of the cube, and the *face-centered cubic* (*fcc*) unit cell has atoms at the eight corners and centered on the six faces. All three structures have different primitive cells, but the same cubic unit cell. We will generally work with unit cells.



Simple cubic Body-centered cubic Face-centered cubic

Figure 1–3
Unit cells for three types of cubic lattice structures.

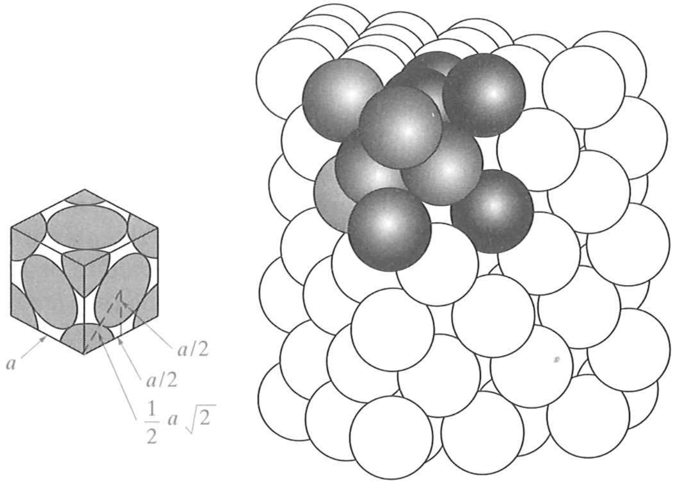


Figure 1–4
Packing of hard spheres in an fcc lattice.

As atoms are packed into the lattice in any of these arrangements, the distances between neighboring atoms will be determined by a balance between the forces that attract them together and other forces that hold them apart. We shall discuss the nature of these forces for particular solids in Section 3.1.1. For now, we can calculate the maximum fraction of the lattice volume that can be filled with atoms by approximating the atoms as hard spheres. For example, Fig. 1–4 illustrates the packing of spheres in a face-centered cubic cell of side a, such that the nearest neighbors touch. The dimension a for a cubic unit cell is called the *lattice constant*. For the fcc lattice the nearest neighbor distance is one-half the diagonal of a face, or $\frac{1}{2}(a\sqrt{2})$. Therefore, for the atom centered on the face to just touch the atoms at each corner of the face, the radius of the sphere must be one-half the nearest neighbor distance, or $\frac{1}{4}(a\sqrt{2})$.

EXAMPLE 1–1 For a bcc lattice of identical atoms with a lattice constant of 5 Å, calculate the maximum packing fraction and the radius of the atoms treated as hard spheres with the nearest neighbors touching.

SOLUTION Each corner atom in a cubic unit cell is shared with seven neighboring cells; thus, each unit cell contains one-eighth of a sphere at each of the eight corners for a total of one atom. The bcc cell contains one atom in the center of the cube. Thus, we have

$$\text{Nearest atoms are at a separation } \frac{1}{2} \times \sqrt{5^2 + 5^2 + 5^2} = 4.330\ \text{Å}$$

$$\text{Radius of each atom } = \frac{1}{2} \times 4.330\ \text{Å} = 2.165\ \text{Å}$$

$$\text{Volume of each atom } = \frac{4}{3}\pi(2.165)^3 = 42.5\ \text{Å}^3$$

$$\text{Number of atoms per cube } = 1 + 8 \times \frac{1}{8} = 2$$

$$\text{Packing fraction } = \frac{42.5 \times 2}{(5)^3} = 68\%$$

Therefore, if the atoms in a bcc lattice are packed as densely as possible, with no distance between the outer edges of nearest neighbors, 68% of the volume is filled. This is a relatively high percentage compared with some other lattice structures (Prob. 1.14).

1.2.3 Planes and Directions

In discussing crystals it is very helpful to be able to refer to planes and directions within the lattice. The notation system generally adopted uses a set of three integers to describe the position of a plane or the direction of a vector within the lattice. We first set up an xyz coordinate system with the origin at any lattice point (it does not matter which one because they are all equivalent!), and the axes are lined up with the edges of the cubic unit cell. The three integers describing a particular plane are found in the following way:

1. Find the intercepts of the plane with the crystal axes and express these intercepts as integral multiples of the basis vectors (the plane can be moved in and out from the origin, retaining its orientation, until such an integral intercept is discovered on each axis).
2. Take the reciprocals of the three integers found in step 1 and reduce these to the smallest set of integers h, k, and l, which have the same relationship to each other as the three reciprocals.
3. Label the plane (hkl).

EXAMPLE 1–2 The plane illustrated in Fig. 1–5 has intercepts at $2\mathbf{a}$, $4\mathbf{b}$, and $1\mathbf{c}$ along the three crystal axes. Taking the reciprocals of these intercepts, we get $\frac{1}{2}$, $\frac{1}{4}$, and 1. These three fractions have the same relationship to each other as the integers 2, 1, and 4 (obtained by multiplying each fraction by 4). Thus the plane can be referred to as a (214) plane. The only exception is if the intercept is a fraction of the lattice constant a. In that case, we do not reduce it to the lowest set of integers. For example, in Fig. 1–3, planes parallel to the cube faces, but going through the body center atoms in the bcc lattice, would be (200) and not (100).

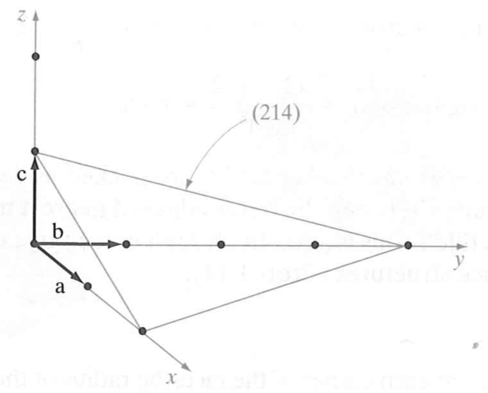


Figure 1–5
A (214) crystal plane.

The three integers h, k, and l are called the *Miller indices*; these three numbers define a set of parallel planes in the lattice. One advantage of taking the reciprocals of the intercepts is avoidance of infinities in the notation. One intercept is infinity for a plane parallel to an axis; however, the reciprocal of such an intercept is taken as zero. If a plane contains one of the axes, it is parallel to that axis and has a zero reciprocal intercept. If a plane passes through the origin, it can be translated to a parallel position for calculation of the Miller indices. If an intercept occurs on the negative branch of an axis, the minus sign is placed above the Miller index for convenience, such as $(h\bar{k}l)$.

From a crystallographic point of view, many planes in a lattice are equivalent; that is, a plane with given Miller indices can be shifted about in the lattice simply by choice of the position and orientation of the unit cell. The indices of such equivalent planes are enclosed in braces { } instead of parentheses. For example, in the cubic lattice of Fig. 1-6 all the cube faces are crystallographically equivalent in that the unit cell can be rotated in various directions and still appear the same. The six equivalent faces are collectively designated as {100}.

A direction in a lattice is expressed as a set of three integers with the same relationship as the components of a vector in that direction. The three vector components are expressed in multiples of the basis vectors, and the three integers are reduced to their smallest values while retaining the relationship among them. For example, the body diagonal in the cubic lattice (Fig. 1-7a) is composed of the components 1**a**, 1**b**, and 1**c**; therefore, this diagonal is the [111] direction. (Brackets are used for direction indices.) As in the case of planes, many directions in a lattice are equivalent, depending only on the arbitrary choice of orientation for the axes. Such equivalent direction indices are placed in angular brackets ⟨ ⟩. For example, the crystal axes in the cubic lattice [100], [010], and [001] are all equivalent and are called ⟨100⟩ directions (Fig. 1-7b).

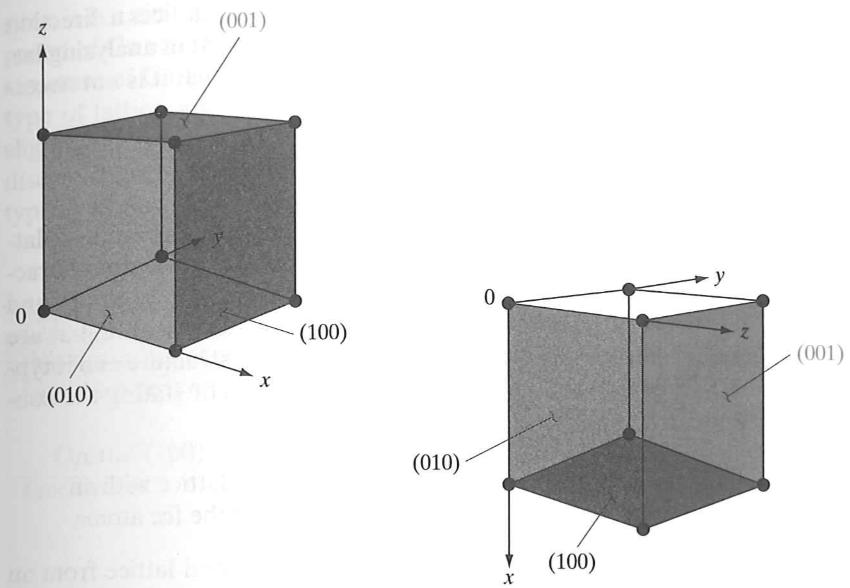
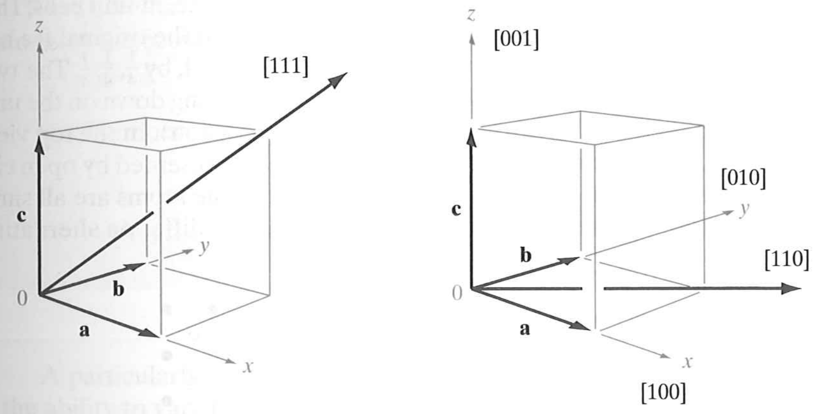


Figure 1–6
Equivalence of the cube faces ({100} planes) by rotation of the unit cell within the cubic lattice.



(a) (b)

Figure 1–7
Crystal directions in the cubic lattice.

Two useful relationships in terms of Miller indices describe the distance between planes and angles between directions. The distance d between two adjacent planes labeled (hkl) is given in terms of the lattice constant, a, as

$$d = a/(h^2 + k^2 + l^2)^{1/2} \tag{1–2a}$$

The angle θ between two different Miller index directions is given by

$$\text{Cos}\ \theta = \{h_1h_2 + k_1k_2 + l_1l_2\}/\{(h_1^2 + k_1^2 + l_1^2)^{1/2}(h_2^2 + k_2^2 + l_2^2)^{1/2}\} \tag{1–2b}$$

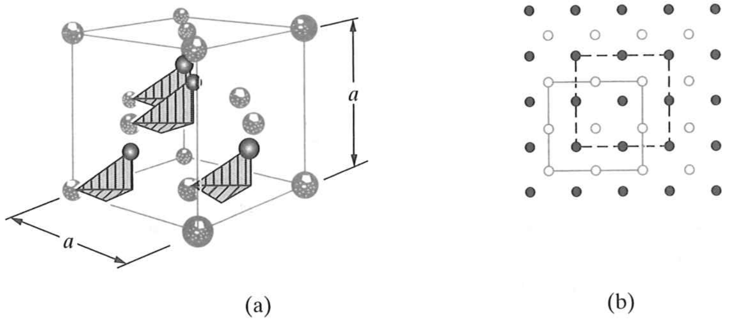
Comparing Figs. 1-6 and 1-7, we notice that in cubic lattices a direction $[hkl]$ is perpendicular to the plane (hkl). This is convenient in analyzing lattices with cubic unit cells, but it should be remembered that it is not necessarily true in noncubic systems.

1.2.4 The Diamond Lattice

The basic crystal structure for many important semiconductors is the fcc lattice with a basis of two atoms, giving rise to the *diamond* structure, characteristic of Si, Ge, and C in the diamond form. In many compound semiconductors, atoms are arranged in a basic diamond structure, but are different on alternating sites. This is called a *zinc blende* structure and is typical of the III–V compounds. One of the simplest ways of stating the construction of the diamond structure is the following:

> The diamond structure can be thought of as an fcc lattice with an extra atom placed at $\mathbf{a}/4 + \mathbf{b}/4 + \mathbf{c}/4$ from each of the fcc atoms.

Figure 1-8a illustrates the construction of a diamond lattice from an fcc unit cell. We notice that when the vectors are drawn with components one-fourth of the cube edge in each direction, only four additional points within the same unit cell are reached. Vectors drawn from any of the other fcc atoms simply determine corresponding points in adjacent unit cells. This method of constructing the diamond lattice implies that the original fcc has associated with it a second interpenetrating fcc displaced, by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. The two interpenetrating fcc *sublattices* can be visualized by looking down on the unit cell of Fig. 1-8a from the top (or along any ⟨100⟩ direction). In the top view of Fig. 1-8b, atoms belonging to the original fcc are represented by open circles, and the interpenetrating sublattice is shaded. If the atoms are all similar, we call this structure a diamond lattice; if the atoms differ on alternating sites, it is a zinc blende structure. For example, if one fcc sublattice is composed of Ga atoms and the interpenetrating sublattice is As, the zinc blende structure of GaAs results. Most of the compound semiconductors have this type of lattice, although some of the II–VI compounds are arranged in a slightly different structure called the *wurtzite* lattice. We shall restrict our discussion here to the diamond and zinc blende structures, since they are typical of most of the commonly used semiconductors.



(a) (b)

Figure 1–8
Diamond lattice structure: (a) a unit cell of the diamond lattice constructed by placing atoms $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from each atom in an fcc; (b) top view (along any ⟨100⟩ direction) of an extended diamond lattice. The colored circles indicate one fcc sublattice and the black circles indicate the interpenetrating fcc.

EXAMPLE 1–3

Calculate the volume density of Si atoms (number of atoms/cm^3), given that the lattice constant of Si is 5.43 Å. Calculate the areal density of atoms (number/cm^2) on the (100) plane.

SOLUTION

On the (100) plane, we have four atoms on corners and one on the face center.

$$\text{(100) plane: } \frac{4 \times \frac{1}{4} + 1}{(5.43 \times 10^{-8})(5.43 \times 10^{-8})} = 6.8 \times 10^{14}\text{ cm}^{-2}$$

For Si, we have 8 corner lattice points, 6 face centered points, and 2 atoms in the basis

$$\text{Number of atoms per cube} = \left(8 \times \frac{1}{8} + \frac{1}{2} \times 6\right) \times 2 = 8$$

$$\text{Volume density} = \frac{8}{(5.43 \times 10^{-8})^3} = 5.00 \times 10^{22}\text{ cm}^{-3}$$

A particularly interesting and useful feature of the III–V compounds is the ability to vary the mixture of elements on each of the two interpenetrating fcc sublattices of the zinc blende crystal. For example, in the ternary compound AlGaAs, it is possible to vary the composition of the ternary alloy by choosing the fraction of Al or Ga atoms on the column III sublattice. It is common to represent the composition by assigning subscripts to the various elements. For example, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ refers to a ternary alloy in which the column III sublattice in the zinc blende structure contains a fraction x of Al atoms and $1-x$ of Ga atoms. The composition $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ has 30 percent Al and 70 percent Ga on the column III sites, with the interpenetrating column V sublattice occupied entirely by As atoms. It is extremely useful to be able to grow ternary alloy crystals such as this with a given composition. For the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ example we can grow crystals over the entire composition range

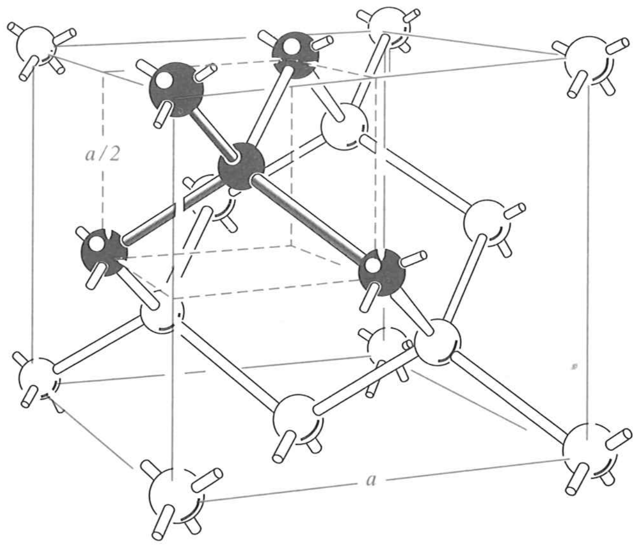


Figure 1–9 Diamond lattice unit cell, showing the four nearest neighbor structure. (From *Electrons and Holes in Semiconductors* by W. Shockley, © 1950 by Litton Educational Publishing Co., Inc.; by permission of Van Nostrand Reinhold Co., Inc.)

from $x = 0$ to $x = 1$, thus varying the electronic and optical properties of the material from that of GaAs ($x = 0$) to that of AlAs ($x = 1$). To vary the properties even further, it is possible to grow four-element (quaternary) compounds such as $In_xGa_{1-x}As_yP_{1-y}$ having a very wide range of properties.

It is important from an electronic point of view to notice that each atom in the diamond and zinc blende structures is surrounded by four nearest neighbors (Fig. 1–9). The importance of this relationship of each atom to its neighbors will become evident in Section 3.1.1 when we discuss the bonding forces which hold the lattice together.

The fact that atoms in a crystal are arranged in certain planes is important to many of the mechanical, metallurgical, and chemical properties of the material. For example, crystals often can be cleaved along certain atomic planes, resulting in exceptionally planar surfaces. This is a familiar result in cleaved diamonds for jewelry; the facets of a diamond reveal clearly the triangular, hexagonal, and rectangular symmetries of intersecting planes in various crystallographic directions. Semiconductors with diamond and zinc blende lattices have similar cleavage planes. Chemical reactions, such as etching of the crystal, often take place preferentially along certain directions. These properties serve as interesting illustrations of crystal symmetry, but in addition, each plays an important role in fabrication processes for many semiconductor devices.

1.3 BULK CRYSTAL GROWTH

The progress of solid state device technology since the invention of the transistor in 1948 has depended not only on the development of device concepts but also on the improvement of materials. For example, the fact that integrated circuits can be made today is the result of a considerable breakthrough in the growth of pure, single-crystal Si in the early and mid-1950s. The requirements on the growing of device-grade semiconductor crystals are more stringent than those for any other materials. Not only must semiconductors be available in large single crystals, but also the purity must be controlled within extremely close limits. For example, Si crystals now being used in devices are grown with concentrations of most impurities of less than one part in ten billion. Such purities require careful handling and treatment of the material at each step of the manufacturing process.

1.3.1 Starting Materials

The raw feedstock for Si crystal is silicon dioxide (SiO_2). We react SiO_2 with C in the form of coke in an arc furnace at very high temperatures (~1800°C) to reduce SiO_2 according to the following reaction:

$$SiO_2 + 2C \rightarrow Si + 2CO \qquad (1\text{-}3)$$

This forms metallurgical grade Si (MGS) which has impurities such as Fe, Al and heavy metals at levels of several hundred to several thousand parts per million (ppm). Refer back to Example 1-3 to see that 1 ppm of Si corresponds to an impurity level of $5 \times 10^{16} cm^{-3}$. While MGS is clean enough for metallurgical applications such as using Si to make stainless steel, it is not pure enough for electronic applications; it is also not single crystal.

The MGS is refined further to yield semiconductor-grade or electronic-grade Si (EGS), in which the levels of impurities are reduced to parts per billion or ppb (1 ppb=$5 \times 10^{13} cm^{-3}$). This involves reacting the MGS with dry HCl according to the following reaction to form trichlorosilane, $SiHCl_3$, which is a liquid with a boiling point of 32°C.

$$Si + 3HCl \rightarrow SiHCl_3 + H_2 \qquad (1\text{-}4)$$

Along with $SiHCl_3$, chlorides of impurities such as $FeCl_3$ are formed which fortunately have boiling points that are different from that of $SiHCl_3$. This allows a technique called fractional distillation to be used, in which we heat up the mixture of $SiHCl_3$ and the impurity chlorides, and condense the vapors in different distillation towers held at appropriate temperatures. We can thereby separate pure $SiHCl_3$ from the impurities. $SiHCl_3$ is then converted to highly pure EGS by reaction with H_2,

$$2SiHCl_3 + 2H_2 \rightarrow 2Si + 6HCl \qquad (1\text{-}5)$$

1.3.2 Growth of Single-Crystal Ingots

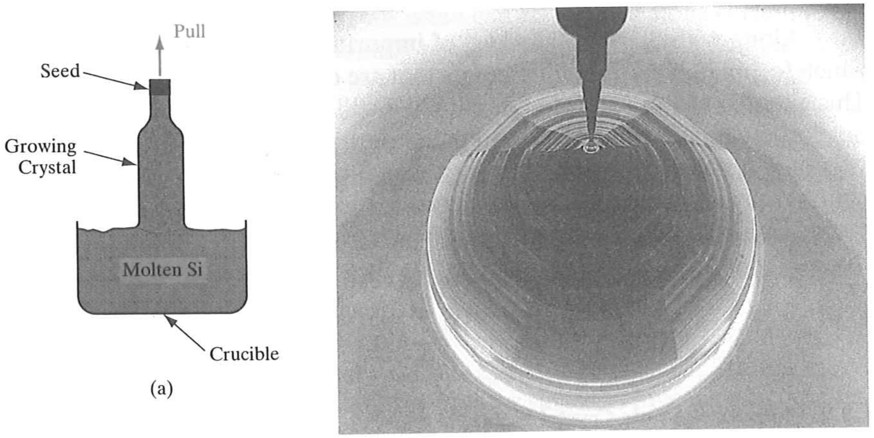
Next, we have to convert the high purity but still polycrystalline EGS to single-crystal Si ingots or boules. This is generally done today by a process commonly called the *Czochralski* method. In order to grow single-crystal material, it is necessary to have a seed crystal which can provide a template for growth. We melt the EGS in a quartz-lined graphite crucible by resistively heating it to the melting point of Si (1412°C).

A seed crystal is lowered into the molten material and then is raised slowly, allowing the crystal to grow onto the seed (Fig. 1–10). Generally, the crystal is rotated slowly as it grows to provide a slight stirring of the melt and to average out any temperature variations that would cause inhomogeneous solidification. This technique is widely used in growing Si, Ge, and some of the compound semiconductors.

In pulling compounds such as GaAs from the melt, it is necessary to prevent volatile elements (e.g., As) from vaporizing. In one method a layer of B_2O_3, which is dense and viscous when molten, floats on the surface of the molten GaAs to prevent As evaporation. This growth method is called *liquid-encapsulated Czochralski* (*LEC*) growth.

In Czochralski crystal growth, the shape of the ingot is determined by a combination of the tendency of the cross section to assume a polygonal shape due to the crystal structure and the influence of surface tension, which encourages a circular cross section. The crystal facets are noticeable in the initial growth near the seed crystal in Fig. 1–10b. However, the cross section of the large ingot in Fig. 1–11 is almost circular.

In the fabrication of Si integrated circuits (Chapter 9) it is economical to use very large Si wafers, so that many IC chips can be made simultaneously. As a result, considerable research and development have gone into methods for growing very large Si crystals. For example, Fig. 1–11 illustrates a 12-inch-diameter Si ingot, 1.0 m long, weighing 140 kg.



(a)

(b)

Figure 1–10
Pulling of a Si crystal from the melt (Czochralski method): (a) schematic diagram of the crystal growth process; (b) an 8-in. diameter, ⟨100⟩ oriented Si crystal being pulled from the melt. (Photograph courtesy of MEMC Electronics Intl.)

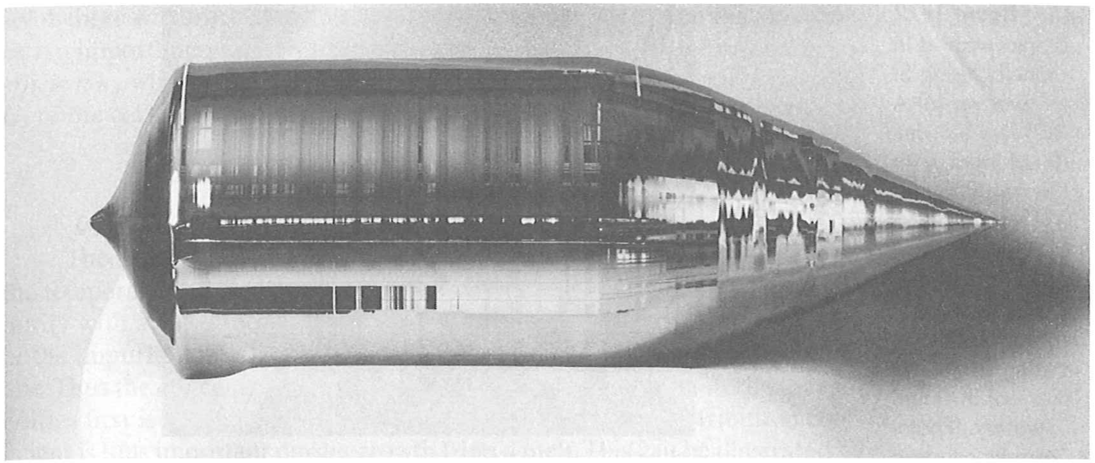


Figure 1–11
Silicon crystal grown by the Czochralski method. This large single-crystal ingot provides 300 mm (12-in.) diameter wafers when sliced using a saw. The ingot is about 1.0 m long (including the tapered regions), and weighs about 140 kg. (Photograph courtesy of MEMC Electronics Intl.)

1.3.3 Wafers

After the single-crystal ingot is grown, it is then mechanically processed to manufacture wafers. The first step involves mechanically grinding the more-or-less cylindrical ingot into a perfect cylinder with a precisely controlled diameter. This is important because in a modern integrated circuit fabrication facility many processing tools and wafer handling robots require tight tolerances on the size of the wafers. Using X-ray crystallography, crystal planes in the ingot are identified. For reasons discussed in Section 6.4.3, most Si ingots are grown along the ⟨100⟩ direction (Fig. 1–10). For such ingots, a small notch is ground on one side of the cylinder to delineate a {110} face of the crystal. This is useful because for ⟨100⟩ Si wafers, the {110} cleavage planes are orthogonal to each other. This notch then allows the individual integrated circuit chips to be made oriented along {110} planes so that when the chips are sawed apart, there is less chance of spurious cleavage of the crystal, which could cause good chips to be lost.

Next, the Si cylinder is sawed into individual wafers about 775 μm thick, by using a diamond-tipped inner-hole blade saw, or a wire saw (Fig. 1–12a). The resulting wafers are mechanically lapped and ground on both sides to achieve a flat surface, and to remove the mechanical damage due to sawing. Such damage would have a detrimental effect on devices. The flatness of the wafer is critical from the point of view of "depth of focus" or how sharp an image can be focussed on the wafer surface during photolithography, as discussed in Chapter 5. The Si wafers are then rounded or "chamfered" along the edges to minimize the likelihood of chipping the wafers during processing.

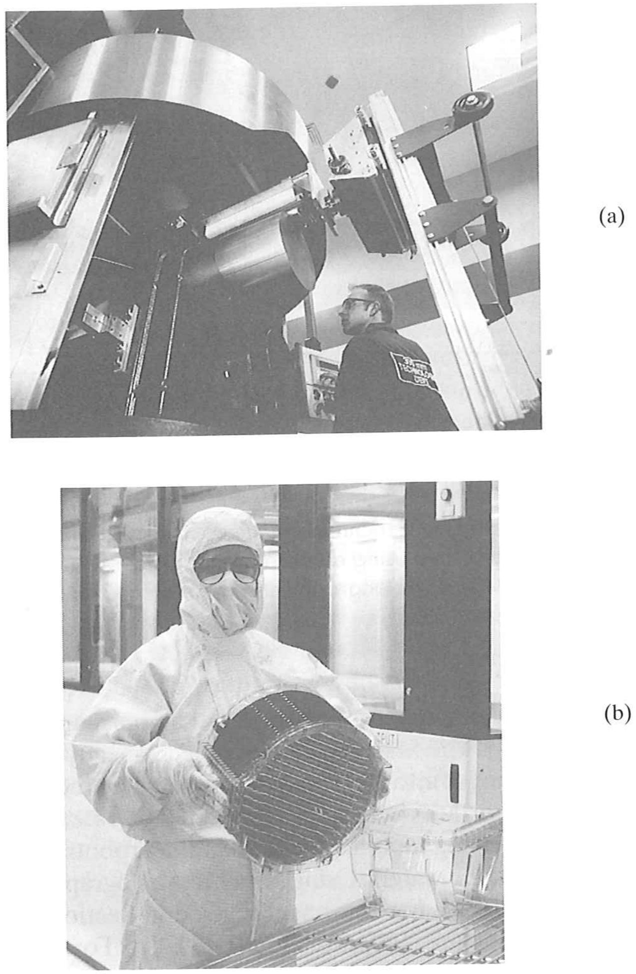


Figure 1–12 Steps involved in manufacturing Si wafers: (a) A 300 mm Si cylindrical ingot, with a notch on one side, being loaded into a wire saw to produce Si wafers; (b) a technician holding a cassette of 300 mm wafers. (Photographs courtesy of MEMC Electronics Intl.)

Finally, the wafers undergo chemical-mechanical polishing using a slurry of very fine SiO_2 particles in a basic NaOH solution to give the front surface of the wafer a mirror-like finish. The wafers are now ready for integrated circuit fabrication (Fig. 1–12b). The economic value added in this process is impressive. From sand (SiO_2) costing pennies, we can obtain Si wafers costing a few hundred dollars, on which we can make hundreds of microprocessors, for example, each costing several hundred dollars.

1.3.4 Doping

As previously mentioned, there are some impurities in the molten EGS. We may also add intentional impurities or dopants to the Si melt to change its electronic properties. At the solidifying interface between the melt and the

solid, there will be a certain distribution of impurities between the two phases. An important quantity that identifies this property is the *distribution coefficient* k_d, which is the ratio of the concentration of the impurity in the solid C_S to the concentration in the liquid C_L at equilibrium:

$$k_d = \frac{C_S}{C_L} \qquad (1\text{–}6)$$

The distribution coefficient is a function of the material, the impurity, the temperature of the solid–liquid interface, and the growth rate. For an impurity with a distribution coefficient of one-half, the relative concentration of the impurity in the molten liquid to that in the refreezing solid is two to one. Thus the concentration of impurities in that portion of material that solidifies first is one-half the original concentration C_0. The distribution coefficient is thus important during growth from a melt. This can be illustrated by an example involving Czochralski growth:

EXAMPLE 1–4

A Si crystal is to be grown by the Czochralski method, and it is desired that the ingot contain 10^{16} phosphorus atoms/cm^3.

(a) What concentration of phosphorus atoms should the melt contain to give this impurity concentration in the crystal during the initial growth? For P in Si, $k_d = 0.35$.

(b) If the initial load of Si in the crucible is 5 kg, how many grams of phosphorus should be added? The atomic weight of phosphorus is 31.

SOLUTION

(a) Assume that $C_S = k_d C_L$ throughout the growth. Thus the initial concentration of P in the melt should be

$$\frac{10^{16}}{0.35} = 2.86 \times 10^{16}\,\text{cm}^{-3}$$

(b) The P concentration is so small that the volume of melt can be calculated from the weight of Si. From Appendix III the density of Si is 2.33 g/cm^3. In this example we will neglect the difference in density between solid and molten Si.

$$\frac{5000 \text{ g of Si}}{2.33 \text{ g/cm}^3} = 2146 \text{ cm}^3 \text{ of Si}$$

$$2.86 \times 10^{16}\,\text{cm}^{-3} \times 2146\,\text{cm}^3 = 6.14 \times 10^{19} \text{ P atoms}$$

$$\frac{6.14 \times 10^{19} \text{ atoms} \times 31 \text{ g/mole}}{6.02 \times 10^{23} \text{ atoms/mole}} = 3.16 \times 10^{-3} \text{ g of P}$$

Since the P concentration in the growing crystal is only about one-third of that in the melt, Si is used up more rapidly than P in the growth. Thus the melt becomes richer in P as the growth proceeds, and the crystal is doped more heavily in the latter stages of growth. This assumes that k_d is not varied; a more uniformly doped ingot can be grown by varying the pull rate (and therefore k_d) appropriately. Modern Czochralski growth systems use computer controls to vary the temperature, pull rate, and other parameters to achieve fairly uniformly doped ingots.

1.4 EPITAXIAL GROWTH

One of the most important and versatile methods of crystal growth for device applications is the growth of a thin crystal layer on a wafer of a compatible crystal. The substrate crystal may be a wafer of the same material as the grown layer or a different material with a similar lattice structure. In this process the substrate serves as the seed crystal onto which the new crystalline material grows. The growing crystal layer maintains the crystal structure and orientation of the substrate. The technique of growing an oriented single-crystal layer on a substrate wafer is called *epitaxial growth*, or *epitaxy*. As we shall see in this section, epitaxial growth can be performed at temperatures considerably below the melting point of the substrate crystal. A variety of methods are used to provide the appropriate atoms to the surface of the growing layer. These methods include *chemical vapor deposition* (*CVD*),[2] growth from a melt (*liquid-phase epitaxy, LPE*), and evaporation of the elements in a vacuum (*molecular beam epitaxy, MBE*). With this wide range of epitaxial growth techniques, it is possible to grow a variety of crystals for device applications, having properties specifically designed for the electronic or optoelectronic device being made.

1.4.1 Lattice-Matching in Epitaxial Growth

When Si epitaxial layers are grown on Si substrates, there is a natural matching of the crystal lattice, and high-quality single-crystal layers result. On the other hand, it is often desirable to obtain epitaxial layers that differ somewhat from the substrate, which is known as *heteroepitaxy*. This can be accomplished easily if the lattice structure and lattice constant a match for the two materials. For example, GaAs and AlAs both have the zinc blende structure, with a lattice constant of about 5.65 Å. As a result, epitaxial layers of the ternary alloy AlGaAs can be grown on GaAs substrates with little lattice mismatch. Similarly, GaAs can be grown on Ge substrates (see Appendix III).

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[2] The generic term *chemical vapor deposition* includes the deposition of layers that may be polycrystalline or amorphous. When a CVD process results in a single-crystal epitaxial layer, a more specific term is *vapor-phase epitaxy* (*VPE*).

Since AlAs and GaAs have similar lattice constants, it is also true that the ternary alloy AlGaAs has essentially the same lattice constant over the entire range of compositions from AlAs to GaAs. As a result, one can choose the composition x of the ternary compound $Al_xGa_{1-x}As$ to fit the particular device requirement, and grow this composition on a GaAs wafer. The resulting epitaxial layer will be lattice-matched to the GaAs substrate.

Figure 1–13 illustrates the energy band gap E_g as a function of lattice constant a for several III–V ternary compounds as they are varied over their composition ranges. For example, as the ternary compound InGaAs is varied by choice of composition on the column III sublattice from InAs to GaAs, the band gap changes from 0.36 to 1.43 eV while the lattice constant of the crystal varies from 6.06 Å for InAs to 5.65 Å for GaAs. Clearly, we cannot grow this ternary compound over the entire composition range on a particular binary substrate, which has a fixed lattice constant. As Fig. 1–13 illustrates, however, it is possible to grow a specific composition of InGaAs on an InP substrate. The vertical (invariant lattice constant) line from InP to the InGaAs curve shows that a midrange ternary composition (actually, $In_{0.53}Ga_{0.47}As$) can be grown lattice-matched to an InP substrate. Similarly, a ternary InGaP alloy with about 50 percent Ga and 50 percent In on the column III sublattice can be grown lattice-matched to a GaAs substrate. To achieve a broader range of alloy compositions, grown lattice-matched on particular substrates, it is helpful to use quaternary alloys such as InGaAsP. The variation of compositions on both the column III and column V sublattices provides additional flexibility in choosing a particular band gap while providing lattice-matching to convenient binary substrates such as GaAs or InP.

In the case of GaAsP, the lattice constant is intermediate between that of GaAs and GaP, depending upon the composition. For example, GaAsP crystals used in red LEDs have 40 percent phosphorus and 60 percent arsenic on the column V sublattice. Since such a crystal cannot be grown directly on either a GaAs or a GaP substrate, it is necessary to gradually change the lattice constant as the crystal is grown. Using a GaAs or Ge wafer as a substrate, the growth is begun at a composition near GaAs. A region ~25 μm thick is grown while gradually introducing phosphorus until the desired As/P ratio is achieved. The desired epitaxial layer (e.g., 100 μm thick) is then grown on this graded layer. By this method epitaxial growth always occurs on a crystal of similar lattice constant. Although some crystal dislocations occur due to lattice strain in the graded region, such crystals are of high quality and can be used in LEDs.

In addition to the widespread use of lattice-matched epitaxial layers, the advanced epitaxial growth techniques described in the following sections allow the growth of very thin (~100 Å) layers of lattice-mismatched crystals. If the mismatch is only a few percent and the layer is thin, the epitaxial layer grows with a lattice constant in compliance with that of the seed crystal (Fig. 1–14). The resulting layer is in compression or tension along the surface plane as its lattice constant adapts to the seed crystal (Fig. 1–14). Such a layer is called

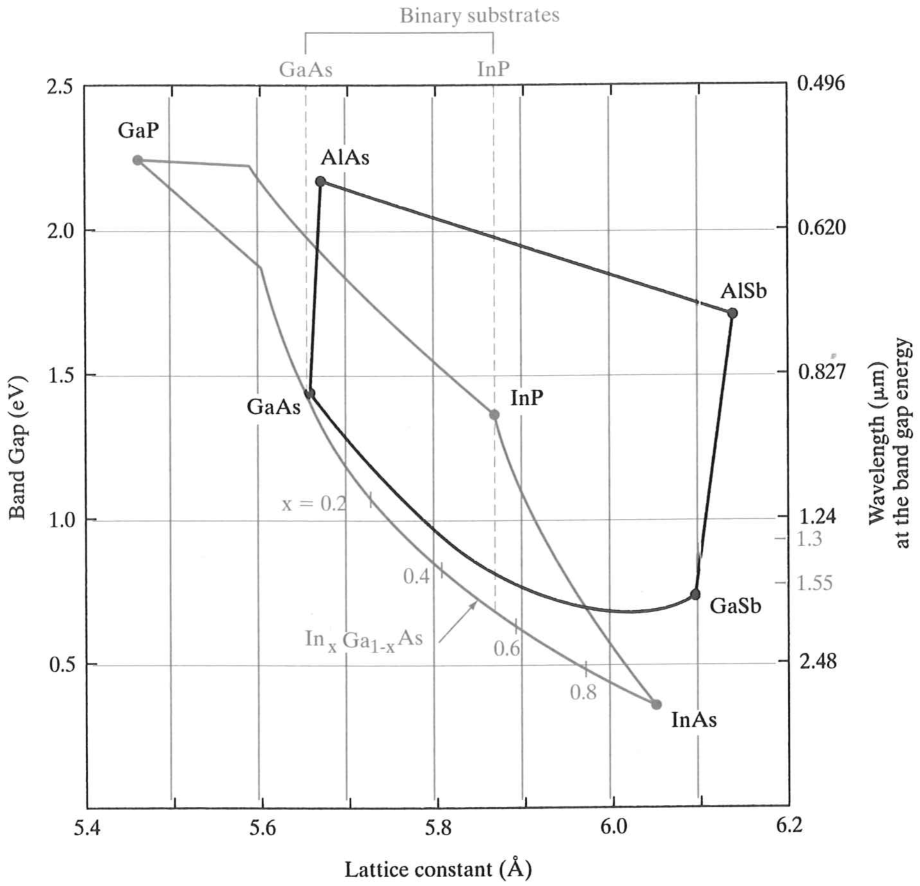


Figure 1–13
Relationship between band gap and lattice constant for alloys in the InGaAsP and AlGaAsSb systems. The dashed vertical lines show the lattice constants for the commercially available binary substrates GaAs and InP. For the marked example of $In_xGa_{1-x}As$, the ternary composition $x = 0.53$ can be grown lattice-matched on InP, since the lattice constants are the same. For quaternary alloys, the compositions on both the III and V sublattices can be varied to grow lattice-matched epitaxial layers along the dashed vertical lines between curves. For example, $In_xGa_{1-x}As_yP_{1-y}$ can be grown on InP substrates, with resulting band gaps ranging from 0.75 eV to 1.35 eV. In using this figure, assume the lattice constant a of a ternary alloy varies linearly with the composition x.

pseudomorphic because it is not lattice-matched to the substrate without strain. However, if the epitaxial layer exceeds a critical layer thickness, t_c, which depends on the lattice mismatch, the strain energy leads to formation of defects called *misfit dislocations.* Using thin alternating layers of slightly mismatched crystal layers, it is possible to grow a *strained-layer superlattice* (*SLS*) in which alternate layers are in tension and compression. The overall SLS lattice constant is an average of that of the two bulk materials.

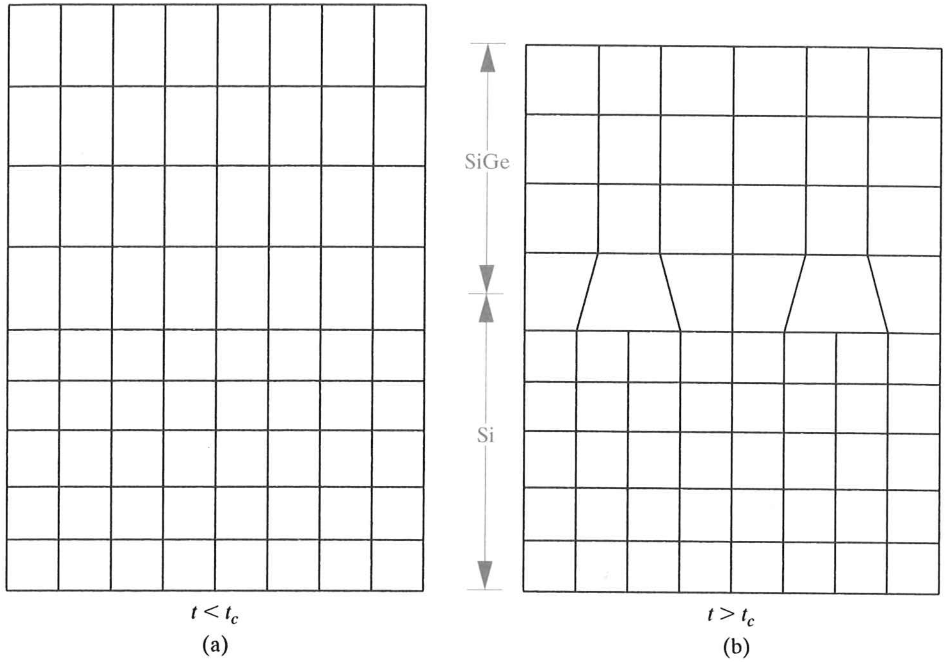


Figure 1–14
Heteroepitaxy and misfit dislocations. For example, in heteroepitaxy of a SiGe layer on Si, the lattice mismatch between SiGe and Si leads to compressive strain in the SiGe layer. The amount of strain depends on the mole fraction of Ge. (a) For layer thicknesses less than the critical layer thickness, t_c, pseudomorphic growth occurs. (b) However, above t_c, misfit dislocations form at the interface which may reduce the usefulness of the layers in device applications.

1.4.2 Vapor-Phase Epitaxy

The advantages of low temperature and high purity epitaxial growth can be achieved by crystallization from the vapor phase. Crystalline layers can be grown onto a seed or substrate from a chemical vapor of the semiconductor material or from mixtures of chemical vapors containing the semiconductor. *Vapor-phase epitaxy* (*VPE*) is a particularly important source of semiconductor material for use in devices. Some compounds such as GaAs can be grown with better purity and crystal perfection by vapor epitaxy than by other methods. Furthermore, these techniques offer great flexibility in the actual fabrication of devices. When an epitaxial layer is grown on a substrate, it is relatively simple to obtain a sharp demarcation between the type of impurity doping in the substrate and in the grown layer. The advantages of this freedom to vary the impurity will be discussed in subsequent chapters. We point out here, however, that Si integrated-circuit devices (Chapter 9) are usually built in layers grown by VPE on Si wafers.

Epitaxial layers are generally grown on Si substrates by the controlled deposition of Si atoms onto the surface from a chemical vapor containing Si. In one method, a gas of silicon tetrachloride reacts with hydrogen gas to give Si and anhydrous HCl:

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl \tag{1-7}$$

If this reaction occurs at the surface of a heated crystal, the Si atoms released in the reaction can be deposited as an epitaxial layer. The HCl remains gaseous at the reaction temperature and does not disturb the growing crystal. As indicated, this reaction is reversible. This is very important because it implies that by adjusting the process parameters, the reaction in Eq. (1-7) can be driven to the left (providing etching of the Si rather than deposition). This etching can be used for preparing an atomically clean surface on which epitaxy can occur.

This vapor epitaxy technique requires a chamber into which the gases can be introduced and a method for heating the Si wafers. Since the chemical reactions take place in this chamber, it is called a *reaction chamber* or, more simply, a *reactor*. Hydrogen gas is passed through a heated vessel in which $SiCl_4$ is evaporated; then the two gases are introduced into the reactor over the substrate crystal, along with other gases containing the desired doping impurities. The Si slice is placed on a graphite susceptor or some other material that can be heated to the reaction temperature with an rf heating coil or tungsten halogen lamps. This method can be adapted to grow epitaxial layers of closely controlled impurity concentration on many Si slices simultaneously (Fig. 1-15).

The reaction temperature for the hydrogen reduction of $SiCl_4$ is approximately 1150-1250°C. Other reactions may be employed at somewhat lower temperatures, including the use of dichlorosilane (SiH_2Cl_2) at 1000-1100°C, or

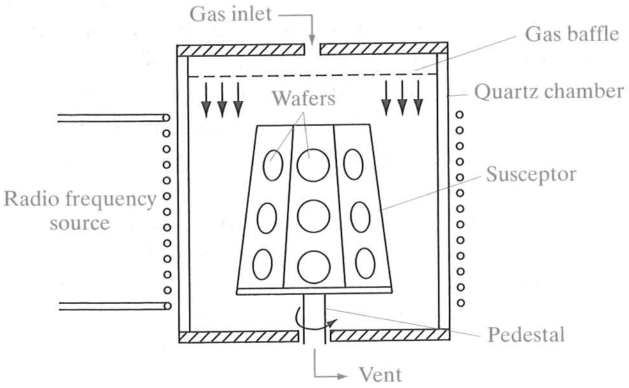


Figure 1–15 A barrel-type reactor for Si VPE. These are atmospheric pressure systems. The Si wafers are held in slots cut on the sides of a SiC-coated graphite susceptor that flares out near the base to promote gas flow patterns conducive to uniform epitaxy.

the pyrolysis of silane (SiH_4) at 500°C–1000°C. Pyrolysis involves the breaking up of the silane at the reaction temperature:

$$SiH_4 \rightarrow Si + 2H_2 \tag{1-8}$$

There are several advantages of the lower reaction temperature processes, including the fact that they reduce migration of impurities from the substrate to the growing epitaxial layer.

In some applications it is useful to grow thin Si layers on insulating substrates. For example, vapor-phase epitaxial techniques can be used to grow $\sim 1 \mu m$ Si films on sapphire and other insulators. This application of VPE is discussed in Section 9.3.2.

Vapor-phase epitaxial growth is also important in the III–V compounds, such as GaAs, GaP, and the ternary alloy GaAsP, which is widely used in the fabrication of LEDs. Substrates are held at about 800°C on a rotating wafer holder while phosphine, arsine, and gallium chloride gases are mixed and passed over the samples. The GaCl is obtained by reacting anhydrous HCl with molten Ga within the reactor. Variation of the crystal composition for GaAsP can be controlled by altering the mixture of arsine and phosphine gases.

Another useful method for epitaxial growth of compound semiconductors is called *metal-organic vapor-phase epitaxy* (*MOVPE*), or *organometallic vapor-phase epitaxy* (*OMVPE*). For example, the organometallic compound trimethylgallium can be reacted with arsine to form GaAs and methane:

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4 \tag{1-9}$$

This reaction takes place at about 700°C, and epitaxial growth of high-quality GaAs layers can be obtained. Other compound semiconductors can also be grown by this method. For example, trimethylaluminum can be added to the gas mixture to grow AlGaAs. This growth method is widely used in the fabrication of a variety of devices, including solar cells and lasers. The convenient variability of the gas mixture allows the growth of multiple thin layers similar to those discussed below for molecular beam epitaxy.

1.4.3 Molecular Beam Epitaxy

One of the most versatile techniques for growing epitaxial layers is called *molecular beam epitaxy* (*MBE*). In this method the substrate is held in a high vacuum while molecular or atomic beams of the constituents impinge upon its surface (Fig. 1-16a). For example, in the growth of AlGaAs layers on GaAs substrates, the Al, Ga, and As components, along with dopants, are heated in separate cylindrical cells. Collimated beams of these constituents escape into the vacuum and are directed onto the surface of the substrate. The rates at which these atomic beams strike the surface can be closely controlled, and growth of very high quality crystals results. The sample is held at a relatively low temperature (about 600°C for GaAs) in this growth procedure. Abrupt

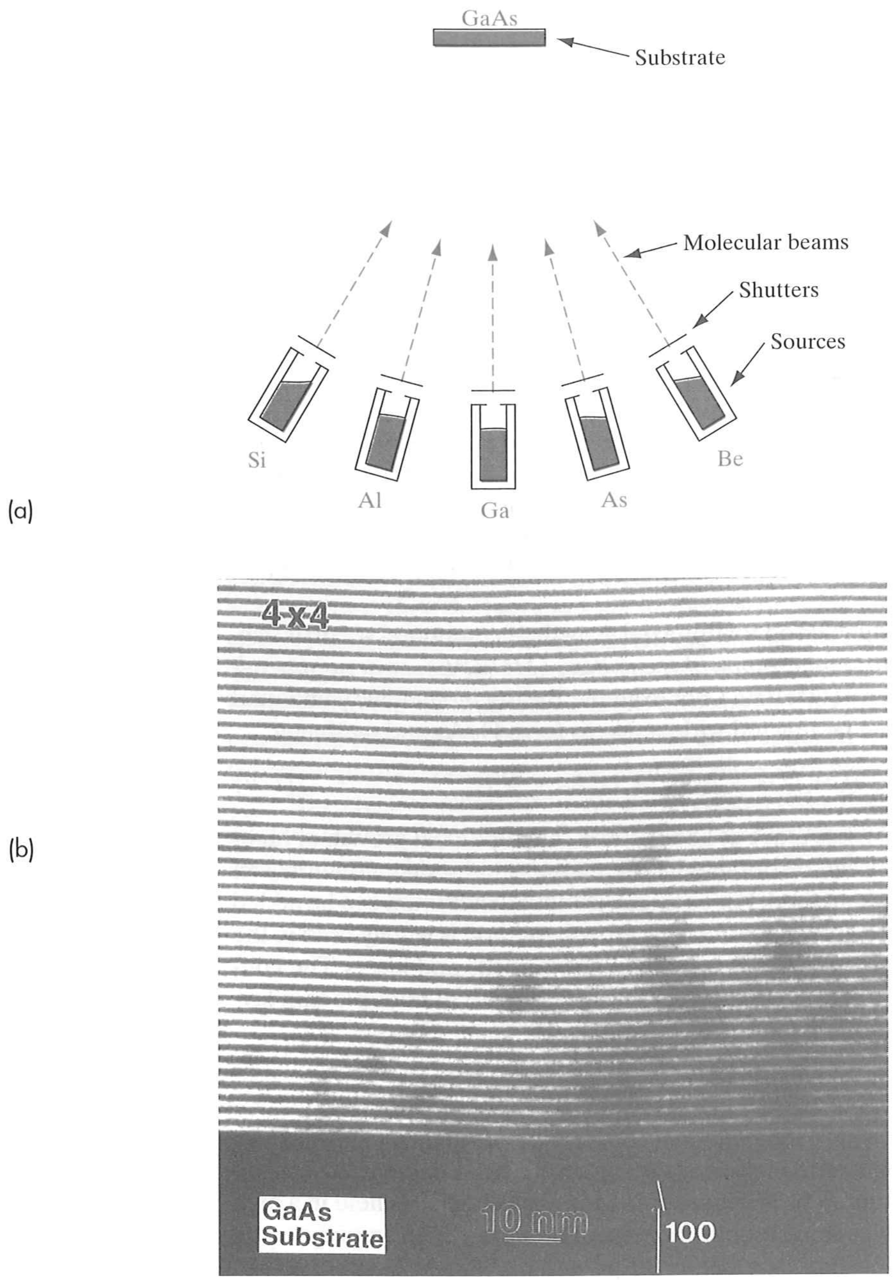


Figure 1–16
Crystal growth by molecular beam epitaxy (MBE): (a) evaporation cells inside a high-vacuum chamber directing beams of Al, Ga, As, and dopants onto a GaAs substrate; (b) scanning electron micrograph of the cross section of an MBE-grown crystal having alternating layers of GaAs (dark lines) and AlGaAs (light lines). Each layer is four monolayers ($4 \times a/2 = 11.3$ Å) thick. (Photograph courtesy of Bell Laboratories.)

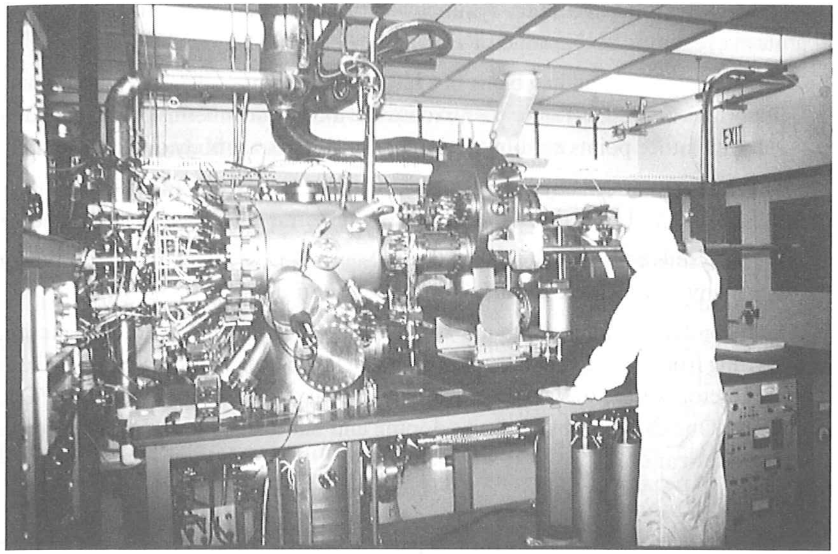


Figure 1–17
Molecular beam epitaxy facility in the Microelectronics Research Center at the University of Texas at Austin.

changes in doping or in crystal composition (e.g., changing from GaAs to AlGaAs) can be obtained by controlling shutters in front of the individual beams. Using slow growth rates (≤ 1 µm/h), it is possible to control the shutters to make composition changes on the scale of the lattice constant. For example, Fig. 1–16b illustrates a portion of a crystal grown with alternating layers of GaAs and AlGaAs only four monolayers thick. Because of the high vacuum and close controls involved, MBE requires a rather sophisticated setup (Fig. 1–17). However, the versatility of this growth method makes it very attractive for many applications.

As MBE has developed in recent years, it has become common to replace some of the solid sources shown in Fig. 1–16 with gaseous chemical sources. This approach, called *chemical beam epitaxy*, or *gas-source MBE*, combines many of the advantages of MBE and VPE.

SUMMARY

1.1 Semiconductor devices are at the heart of information technology. Elemental semiconductors such as Si appear in column IV of the periodic table, while compound semiconductors such as GaAs consist of elements symmetrically around column IV. More complicated alloy semiconductors are used to optimize optoelectronic properties.

1.2 These devices are generally made in single-crystal material for best performance. Single crystals have long-range order, while polycrystalline and amorphous materials have short-range and no order, respectively.

1.3 Lattices are determined by symmetry. In 3-D, these are called Bravais lattices. When we put a basis of atom(s) on the lattice sites, we get a crystal. Common semiconductors have an fcc symmetry with a basis of two identical or different atoms, resulting in diamond or zinc blende crystals, respectively.

1.4 The fundamental building block of a lattice is a *primitive* cell with lattice points at its corners. Sometimes it is easier to describe the crystal in terms of a larger "unit" cell with lattice points not only at the corners, but also at body or face centers.

1.5 Translating unit cells by integer numbers of basis vectors can replicate the lattice. Planes and directions in a lattice can be defined in terms of Miller indices.

1.6 Real crystals can have defects in 0-, 1-, 2-, and 3-D, some of which are benign, but many of which are harmful for device operation.

1.7 Semiconductor bulk crystals are grown from a melt by the Czochralski method, starting from a seed. Single-crystal epitaxial layers can be grown on top of semiconductor wafers in various ways, such as vapor-phase epitaxy, MOCVD, or MBE. One can thereby optimize doping and band-structure properties for device fabrication.

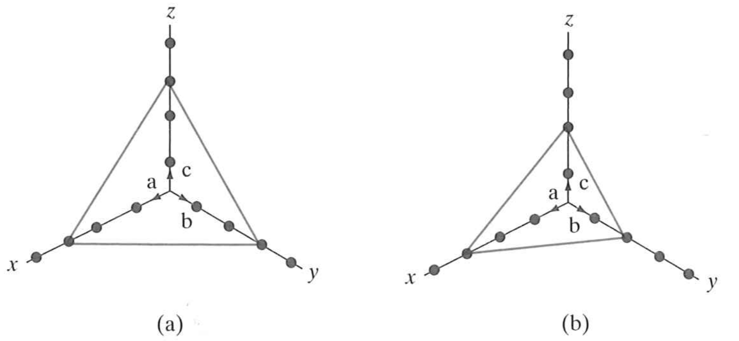
PROBLEMS

1.1 Using Appendix III, which of the listed semiconductors in Table 1–1 has the largest band gap? The smallest? What are the corresponding wavelengths if light is emitted at the energy E_g? Is there a noticeable pattern in the band gap energy of III–V compounds related to the column III element?

1.2 Find the fraction of the fcc unit cell volume filled with hard spheres.

1.3 Label the planes illustrated in Fig. P1–3.

Figure P1–3



(a) (b)

1.4 Calculate the densities of Si and GaAs from the lattice constants (Appendix III), atomic weights, and Avogadro's number. Compare the results with densities given in Appendix III. The atomic weights of Si, Ga, and As are 28.1, 69.7, and 74.9, respectively.

1.5 The atomic radii of In and Sb atoms are approximately 1.44 Å and 1.36 Å, respectively. Using the hard-sphere approximation, find the lattice constant of InSb (zinc blende structure), and the volume of the primitive cell. What is the atomic density on the (110) planes? (Hint: The volume of the primitive cell is

1.6 A crystal with a simple cubic lattice and a monoatomic basis has an atomic radius of 2.5 Å and an atomic weight of 5.42. Calculate its density, assuming that the atoms touch each other.

1.7 Sketch a view down a ⟨110⟩ direction of a diamond lattice, using Fig. 1–9 as a guide. Include lines connecting nearest neighbors.

1.8 Show by a sketch that the bcc lattice can be represented by two interpenetrating sc lattices. To simplify the sketch, show a ⟨100⟩ view of the lattice.

1.9 (a) Find the number of atoms/cm^2 on the (100) surface of a Si wafer.

(b) What is the distance (in Å) between nearest In neighbors in InP?

1.10 The ionic radii of Na^+ (atomic weight 23) and Cl^- (atomic weight 35.5) are 1.0 and 1.8 Å, respectively. Treating the ions as hard spheres, calculate the density of NaCl. Compare this with the measured density of 2.17 g/cm^3.

1.11 Sketch an *sc* unit cell with lattice constant $\mathbf{a} = 4$ Å, whose diatomic basis of atom A is located at the lattice sites, and with atom B displaced by ($\mathbf{a}$/2,0,0). Assume that both atoms have the same size and we have a close-packed structure (i.e., nearest neighbor atoms touch each other). Calculate

(i) the packing fraction (i.e., fraction of the total volume occupied by atoms),

(ii) the number of B atoms per unit *volume*,

(iii) the number of A atoms per unit *area* on (100) planes.

1.12 How many atoms are found inside a unit cell of an sc, a bcc, and an fcc crystal? How far apart in terms of lattice constant a are the nearest neighbor atoms in each case, measured from center to center?

1.13 Draw a cube such as Fig. 1–7, and show four {111} planes with different orientations. Repeat for {110} planes.

1.14 Find the maximum fractions of the unit cell volume that can be filled by hard spheres in the sc, fcc, and diamond lattices.

1.15 Calculate the densities of Ge and InP from the lattice constants (Appendix III), atomic weights, and Avogadro's number. Compare the results with the densities given in Appendix III.

1.16 Beginning with a sketch of an fcc lattice, add atoms at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ from each fcc atom to obtain the diamond lattice. Show that only the four added atoms in Fig. 1–8a appear in the diamond unit cell.

1.17 Assuming that the lattice constant varies linearly with composition x for a ternary alloy (e.g., see the variation for InGaAs in Fig. 1–13), what composition of $AlSb_xAs_{1-x}$ is lattice-matched to InP? What composition of $In_xGa_{1-x}P$ is lattice-matched to GaAs? What is the band gap energy in each case?

(*Note*: Such linear variations of crystal properties (e.g., lattice constant and band gap) with mole fraction in alloys is known as *Vegard's law*. A second-order polynomial or quadratic fit to the data is called the *bowing* parameter.)

1.18 A Si crystal is to be pulled from the melt and doped with arsenic ($k_d = 0.3$). If the Si weighs 1 kg, how many grams of arsenic should be introduced to achieve

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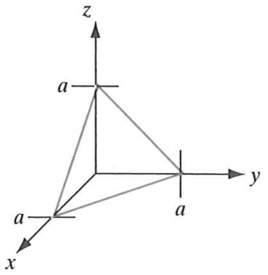
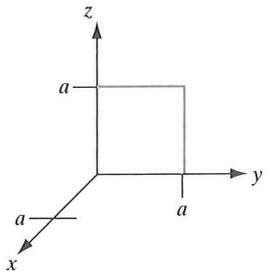
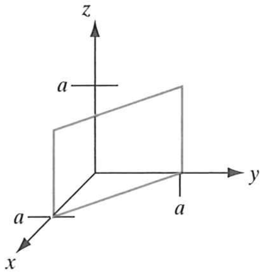
SELF QUIZ

Question 1

(a) Label the following planes using the correct notation for a cubic lattice of unit cell edge length *a* (shown within the unit cell).



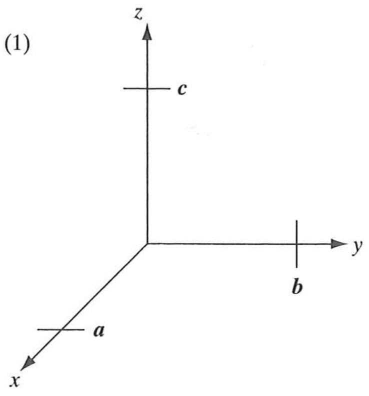




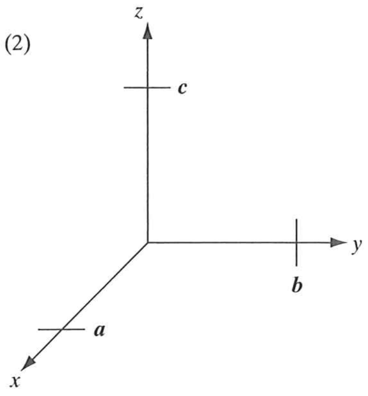
(b) Write out all of the equivalent $\langle 100 \rangle$ directions using the correct notation.

(c) On the two following sets of axes, (1) sketch the [011] direction and (2) a (111) plane (for a cubic system with primitive vectors ***a***, ***b***, and ***c***).

(1)



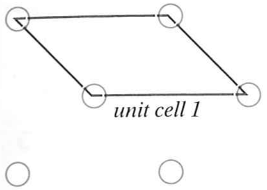
(2)

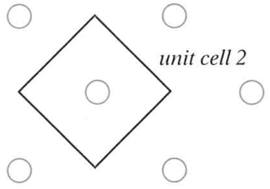


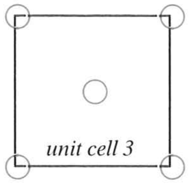
Question 2

(a) Which of the following three unit cells are *primitive cells* for the two-dimensional lattice? Circle the correct combination **in bold** below.

1 / 2 / 3 / 1 and 2 / 1 and 3 / 2 and 3 / 1, 2, and 3

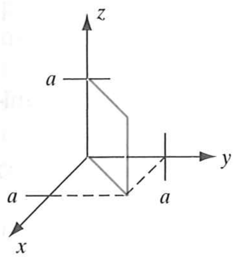


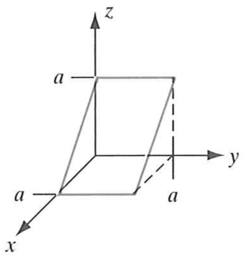


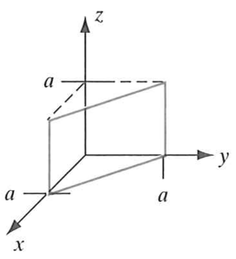


(b) The following planes (shown within the first quadrant for $0 < x,y,z < a$ only, with the dotted lines for reference only) are all from what one set of *equivalent* planes? Use correct notation:

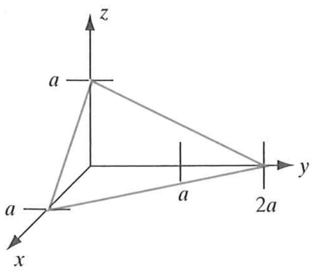
answer:

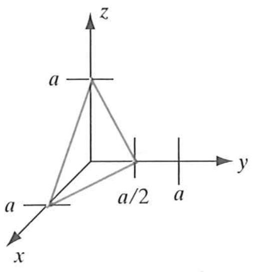


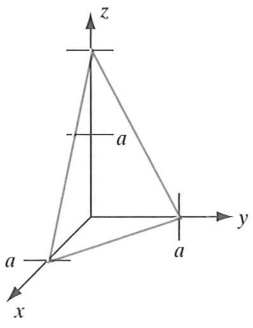




(c) Which of the following three planes (shown within the first quadrant only) is a (121) plane? Circle the correct diagram.

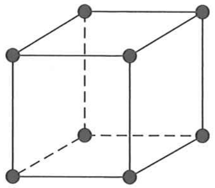


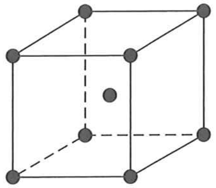


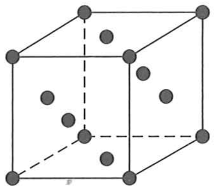


Question 3

(a) Diamond and zinc blende crystal structures are both composed of a Bravais lattice with a two-atom basis. Circle the correct unit cell for this Bravais lattice.







(b) Which statement below is true?

1. GaAs has a ***diamond / zinc blende*** crystal structure.
2. Si has a ***diamond / zinc blende*** crystal structure.

Question 4

Give some examples of zero-dimensional, one-dimensional, two-dimensional, and three-dimensional defects in a semiconductor.

Question 5

(a) What is the difference between a primitive cell and a unit cell? What is the utility of both concepts?

(b) What is the difference between a lattice and a crystal? How many different 1-D lattices can you have?

Question 6

Consider growing InAs on the following crystal substrates: InP, AlAs, GaAs, and GaP. For which case would the *critical thickness* of the InAs layer be greatest? You may use Fig. 1–13 from your text.

GaP / GaAs / AlAs / InP

Chapter 2

Atoms and Electrons

OBJECTIVES

1. Understand the wave-particle duality of nature in quantum mechanics
2. Study the Bohr model of atoms
3. Apply the Schrödinger equation to simple problems
4. Understand the electronic structure of atoms and the periodic table
5. Understand how semiconductor properties are determined

Since this book is primarily an introduction to solid state devices, it would be preferable not to delay this discussion with subjects such as atomic theory, quantum mechanics, and electron models. However, the behavior of solid state devices is directly related to these subjects. For example, it would be difficult to understand how an electron is transported through a semiconductor device without some knowledge of the electron and its interaction with the crystal lattice. Therefore, in this chapter we shall investigate some of the important properties of electrons, with special emphasis on two points: (1) the electronic structure of atoms, and (2) the interaction of atoms and electrons with excitation, such as the absorption and emission of light. By studying electron energies in an atom, we lay the foundation for understanding the influence of the lattice on electrons participating in current flow through a solid. Our discussions concerning the interaction of light with electrons form the basis for later descriptions of changes in the conductivity of a semiconductor with optical excitation, properties of light-sensitive devices, and lasers.

First, we shall investigate some of the experimental observations which led to the modern concept of the atom, and then we shall give a brief introduction to the theory of quantum mechanics. Several important concepts will emerge from this introduction: the electrons in atoms are restricted to certain energy levels by quantum rules; the electronic structure of atoms is determined from these quantum conditions; and this "quantization" defines certain allowable transitions involving absorption and emission of energy by the electrons.