

Figure 1.1 Diagrams showing the variations of electron energy with wave number (momentum) in (a) Ge, (b) Si, and (c) GaAs along the [100] and [111] directions in k space. Electrons are located near the minimum of the conduction band, whereas holes are located near the maximum of the valence band. The band structures of Ge and Si are examples of indirect-gap semiconductors, whereas that of GaAs represents a direct bandgap semiconductor. Δ is the spin-orbit splitting (from S. Wang, *Fundamentals of Semiconductor Theory and Device Physics*, Prentice Hall, Englewood Cliffs, NJ, 1989).

and InP have high electron mobilities and velocities, properties that are extremely important for the development of high-speed electronic devices. Their direct bandgaps and the consequent high radiative efficiency make them important optoelectronic materials. The bandgaps and lattice constants of common III-V binary compounds are depicted in Fig. 1.2.

It is instructive to find out what makes a semiconductor direct or indirect. The top of the valence band of most semiconductors occurs at a value of effective momentum, or k , equal to zero. Semiconductors in which the bottom of the conduction band is also at $k = 0$ are direct bandgap materials. Semiconductors in which the bottom of the conduction band occurs at other points in momentum space are indirect bandgap materials. It is evident from the atomic structure of the constituent elements of these semiconductors, described in the next section, that their outermost valence electrons are in s- or p-type orbitals. Although true only for elements in their atomic form, the s- or p-like character is also retained in the crystalline semiconductors. The bands of a semiconductor are a result of the crystal potential that originates from the equilibrium arrangement of atoms in the lattice. If the edge of the conduction band is made up of s-type states, the semiconductor is direct bandgap. If, on the other hand, the lowest conduction band edge is made up of p-type states, then the semiconductor is indirect bandgap.

An attractive feature of the binary compounds is that they can be combined or alloyed to form *ternary* or *quaternary* compounds, or *mixed crystals*. These compounds are made up of three or four group III and group V atoms and are indicated by the tie lines between the binary compounds in Fig. 1.2. Note that by choosing different binary compounds, it is possible to select different bandgaps, and therefore varying

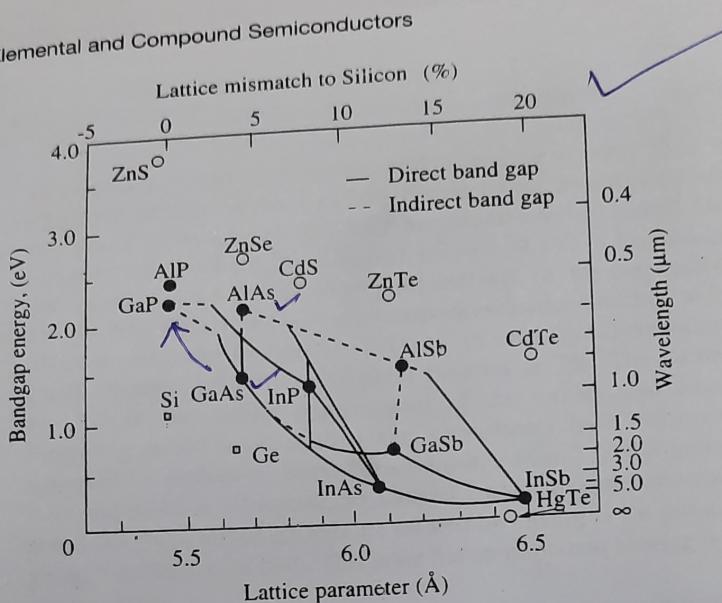


Figure 1.2 Energy bandgap versus lattice constant for common elemental and compound semiconductors. The tie lines joining the binaries represent ternary compositions. The dashed lines represent indirect bandgap material. The vertical dashed line passing through the point representing InP contains the bandgaps for the lattice-matched InGaAlAs and InGaAsP quaternary systems.

emission energies for light sources. However, by alloying it is possible to vary the bandgap *continuously* and monotonically, and together with it the bandstructure, electronic, and optical properties. The formation of ternary and quaternary compounds of varying bandgaps also enables the formation of heterojunctions, which have become essential for the design of high-performance electronic and optoelectronic devices. As an example, the bandgap of the ternary compound $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($0 \leq x \leq 1$) depends on the mole fraction x of AlAs in the solid solution and changes continuously from 1.43 eV (GaAs, $x = 0$) to 2.1 eV (AlAs, $x = 1$). As we shall see later, the bandstructure, electronic, and optical properties of the mixed crystal also change with change in alloy composition, and these are exploited in the design of electronic and optoelectronic devices. Among the common GaAs and InP-based ternary and quaternary compounds, the properties of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ have been most thoroughly investigated. Other important ternary and quaternary compounds are $\text{GaAs}_{1-x}\text{P}_x$, $\text{In}_{1-x}\text{Ga}_x\text{P}$, $\text{In}_x\text{Ga}_y\text{Al}_{1-x-y}\text{As}$, and $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$. The last two are usually grown on InP substrates. The bandgaps and lattice constants of these compounds can be found from the tie lines in Fig. 1.2. The quaternary compounds mentioned above have emerged as being extremely important for optical communication, since their bandgaps correspond to the spectral window in which silica fibers have their lowest loss and dispersion. Several important observations may be made from Fig. 1.2. First, it may be noted that the lattice constants of GaAs (5.6532 Å) and AlAs (5.6611 Å) are almost identical. This implies that all the mixed crystal compositions of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ can be grown *lattice-matched* on GaAs substrates. We shall soon see in Sec. 1.5 that this is very useful because any thickness

of the ternary crystal can be grown without having to worry about strain effects or the generation of dislocations. Similarly certain mixed crystal compositions of the quaternary alloys InGaAlAs and InGaAsP are lattice-matched to InP. These range from the end-point compositions $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ ($E_g = 0.74$ eV) to $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ ($E_g = 1.45$ eV) and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ to InP (1.35 eV), respectively, for the two quaternary systems. Note that the only ternary $\text{In}_x\text{Ga}_{1-x}\text{As}$ composition lattice-matched to InP is with $x = 0.53$. All other compositions from $x = 0$ (GaAs) to $x = 1$ (InAs) are mismatched and the mismatch between these two end-point binaries is 7%. The second point to note in Fig. 1.2 is that certain compositions of the ternary and quaternary compounds, depending on the nature of the binary constituents, have indirect bandgaps. These are indicated by dashed tie lines. For example, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is indirect bandgap for $x \geq 0.43$ and AlAs is, of course, an indirect bandgap semiconductor. Finally, it may be noted that these mixed crystals are formed by mixing in the group III sublattice, or the group V sublattice, or both. This point has an important bearing on the techniques used to grow them.

Many physical parameters of ternary compounds are determined by the parameters of the constituent binaries and vary roughly linearly with composition. For example, the lattice constant, a , of $\text{In}_x\text{Ga}_{1-x}\text{As}$ is given by Vegard's law as

$$a_{\text{In}_x\text{Ga}_{1-x}\text{As}} = x a_{\text{InAs}} + (1 - x) a_{\text{GaAs}} \quad (1.1)$$

Similarly, for a quaternary compound $\text{A}_{1-x}\text{B}_x\text{C}_y\text{D}_{1-y}$, a material parameter Q can be expressed as

$$\begin{aligned} Q(x,y) = & \{x(1-x)[(1-y)T_{12}(x) + yT_{43}(x)] \\ & + y(1-y)[(1-x)T_{14}(y) + xT_{23}(y)]\} \\ & [x(1-x)+y(1-y)]^{-1} \end{aligned} \quad (1.2)$$

where T_{ij} is the material parameter for the ternary alloy formed by binaries i and j . The relevant parameters of GaAs and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ together with those for Si, for the purpose of comparison, are listed in Appendix 1.

1.2 BONDING IN SOLIDS

In the *solid state*, also referred to as *condensed matter*, the atoms forming the solid are held together by bonding forces. The atoms also maintain a finite, fixed distance from each other. If the array of atoms have long-range order or *periodicity*, the resulting solid is crystalline, and we will study the properties of crystals in the next section. The periodic array of atoms leads the way to the energy band models and conduction properties. However, before going into all that, we should understand the nature of the forces that hold the atoms together in their equilibrium positions. There are in general two types of forces, attractive and repulsive, which are both functions of the interatomic distance z . At large distances the attractive forces dominate, and therefore the atoms are drawn nearer to each other. At small interatomic distances the repulsive forces dominate, and the atoms are pushed further apart. In equilibrium the forces of attraction $F_A(z)$, and repulsion, $F_R(z)$, must balance to establish the equilibrium atomic spacing. In other words:

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In a ternary alloy, the lattice constant is linearly dependent on the composition, as expressed in Eq. 1.1. The linear relationship of the lattice constant generally holds for quaternary alloys too. However, other parameters of a mixed alloy do not, in general, obey this linear relationship. The bandgap E_g , for example, is usually given by an empirical relationship:

$$\checkmark E_g(x) = E_{go} + bx + cx^2 \quad (1.15)$$

where E_{go} is the bandgap of the lower bandgap binary, b is a fitting parameter, and c is called the bowing parameter, which may be calculated theoretically or determined experimentally. The bowing in the bandgap arises from increasing disorder due to alloying. In fact, there is always a probability of finding regions with a bandgap equal to that of the low-bandgap constituent in the epitaxial material. In a new material, the variation of bandgap with composition may not be known. A simple approach is to compute the alloy bandgap from the weighted bandgaps of the constituents A and B according to the equation $E_g(x) = xE_g^A + (1 - x)E_g^B$. This is known as the *virtual crystal approximation*. As we shall soon see, it is not only the variation of bandgap with composition, but also the energy variation of the higher-lying bandstructure with composition, that is extremely important for the understanding of material properties. This variation for the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system is depicted in Fig. 1.14. The figure shows the variation of the Γ , L, and X conduction bands with alloy composition x , and the energy disposition of the conduction valleys of the two end-point binaries. The relevant energies are approximately given by

$$\begin{aligned} E_g^\Gamma(x) &= 1.425 + 1.247x \quad (\text{direct: } x \leq 0.45) \\ &= 1.425 + 1.247x + 1.147(x - 0.45)^2 \quad (\text{indirect: } x > 0.45) \end{aligned}$$

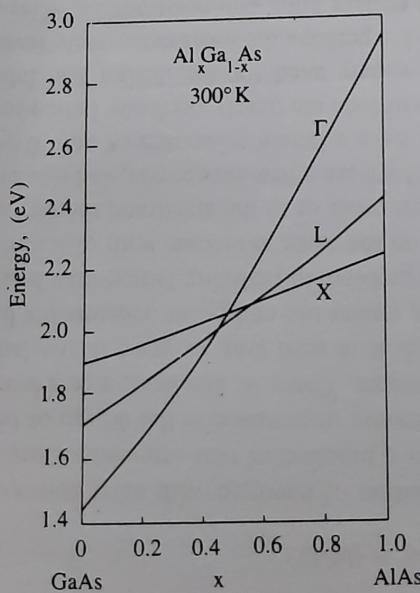
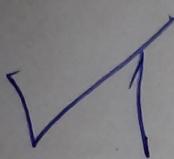


Figure 1.14 Compositional dependence of the direct (Γ) and indirect (X and L) conduction band minima in the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ mixed crystals.



$$\begin{aligned}\mathcal{E}_g^X(x) &= 1.9 + 0.125x + 0.143x^2 \\ \mathcal{E}_g^L(x) &= 1.708 + 0.642x\end{aligned}\quad (1.16)$$

The monotonic variation of bandgap with alloy composition allows us to realize *heterojunctions*, which is a junction of two semiconductors of unequal bandgap. Heterojunctions are of paramount importance in the design of high-performance electronic and optoelectronic devices. There is, however, a problem, which becomes evident upon examining Fig. 1.2. It is seen that, in general, the lattice constant of the alloy varies with composition, unless the end-point constituents have the same lattice constant. This does create a problem in realizing lattice-matched heterojunctions, since no two alloy compositions on the same substrate, with different energy bandgaps, would be lattice-matched to each other or to the substrate, thereby creating the possibility of dislocation generation. There are a few exceptions, and one of them is the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system. GaAs and AlAs have a lattice mismatch of only 0.04%, and therefore all the intermediate alloy compositions are nearly perfectly lattice-matched. This heterostructure material system is widely used for the design and fabrication of near-infrared sources and detectors and is perhaps the most extensively investigated. Looking at Fig. 1.2, it is evident that the ternary alloy compositions $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ ($\mathcal{E}_g = 0.74$ eV) and $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ ($\mathcal{E}_g = 1.45$ eV) are both lattice-matched to InP. The $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ heterojunction on InP has the advantage over the GaAs/AlGaAs one in that the energy bandgap of InGaAs is close to the region of low-loss and low-dispersion of optical fibers. In addition, it is seen that the quaternary alloys InGaAsP (with InP and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ as the end-point materials) and InGaAlAs (with $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and $\text{In}_{0.52}\text{Al}_{0.48}\text{As}$ as the end-point materials) are also lattice-matched to InP and are technologically very important for optical fiber communication. There are other alloy systems lattice-matched to GaSb substrates that will be important for far infrared sources and detectors, but some of them have miscibility gaps in the phase diagram. As we shall see in the next section, one does not always have to work under the constraints of lattice-matching, and use of *pseudomorphic* materials does alleviate this problem to some extent.

The process of random alloying causes a perturbation of the periodic potential of the lattice, which manifests itself as an additional scattering mechanism for carriers. The process is characterized by a disorder, or alloy-scattering potential, which is due to the deviation in electronegativity of atoms caused by the deviation of the covalent radius due to alloying. If A- and B-type atoms are arranged randomly in space in a lattice and U_A and U_B are the corresponding short-range atomic potentials, then it is convenient to be able to calculate an average weighted potential for bandstructure calculations. In one technique, by using the virtual crystal approximation, the random potential is replaced by an average weighted periodic potential

$$U_{\text{alloy}}(\mathbf{r}) = xU_A(\mathbf{r}) + (1 - x)U_B(\mathbf{r}) \quad (1.17)$$

for an alloy $A_xB_{1-x}C$. For example, in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, the alloy-scattering potential can be approximated as

$$U_{\text{Al}_x\text{Ga}_{1-x}\text{As}} = 0.46 + 0.01x$$

tion using fibers, the materials of choice are InP-based lattice-matched materials, or GaAs- and InP-based mismatched materials. For short-distance optical fiber systems, GaAs/AlGaAs is used, since the fiber losses at $0.8 \mu\text{m}$ remain within acceptable limits. Fibers are now being developed for use at longer wavelengths, where there is a lot of potential for the Sb-containing compounds. Similarly, as semiconductor sources are developed for radiation in the visible part of the spectrum, using III-V and II-VI compounds, appropriate guiding materials will also be developed. For free-space communication, both long and short wavelength materials can be used, and other system requirements and advantages determine the choice of materials. In what follows, we will briefly discuss the bandgaps and other important properties of binary III-V compounds and their ternary and quaternary derivatives. The bandgaps and lattice constants of the common III-V binary compounds are seen in Fig. 1.2. The compositional dependence of the energy gap of some important ternary derivatives are listed in Table 1.5.

Among the large bandgap III-V compounds, GaP and $\text{GaAs}_x\text{P}_{1-x}$ are important for the manufacture of visible LEDs. The compositional dependence of the direct and indirect energy gaps of the $\text{GaAs}_{1-x}\text{P}_x$ alloys is depicted in Fig. 1.21. These alloys and heterostructures with different compositions are grown on GaAs or GaP substrates. $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ ($E_g = 1.96 \text{ eV}$) and $\text{Al}_{0.51}\text{In}_{0.49}\text{P}$ ($E_g = 2.45 \text{ eV}$) and their heterojunction lattice-matched to GaAs are important for the development of sources and detectors in the visible region of the spectrum. The $\text{GaAs}-\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ heterojunction is important for bipolar devices and may be important for phototransistors.

The large bandgap nitrides, namely AlN, GaN, and InN, have gained tremendous importance as optoelectronic materials and in particular for the design of blue light emitters. Depending on which substrate is used for the epitaxy of these compounds, they crystallize in the wurtzite or cubic (zincblende) forms. The wurtzite structure is obtained for growth on SiC or sapphire, while the cubic form is obtained for growth on GaAs. The former has been studied more extensively. The bandgap and lattice constant

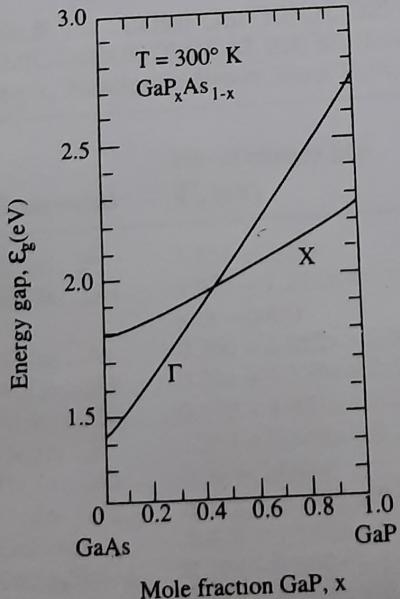
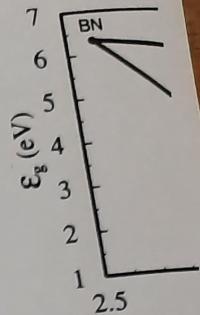


Figure 1.21 Compositional dependence of the direct-energy gap Γ and indirect-energy gap X for $\text{GaP}_x\text{As}_{1-x}$ (from M. R. Lorenz and A. Onton, *Proc. Int. Conf. Phys. Semiconduct.*, 10th, Cambridge, MA (S. P. Keller, J. C. Hensel, and F. Stern, eds.), 444, U.S. Atomic Energy Comm., Washington, D.C., 1970).

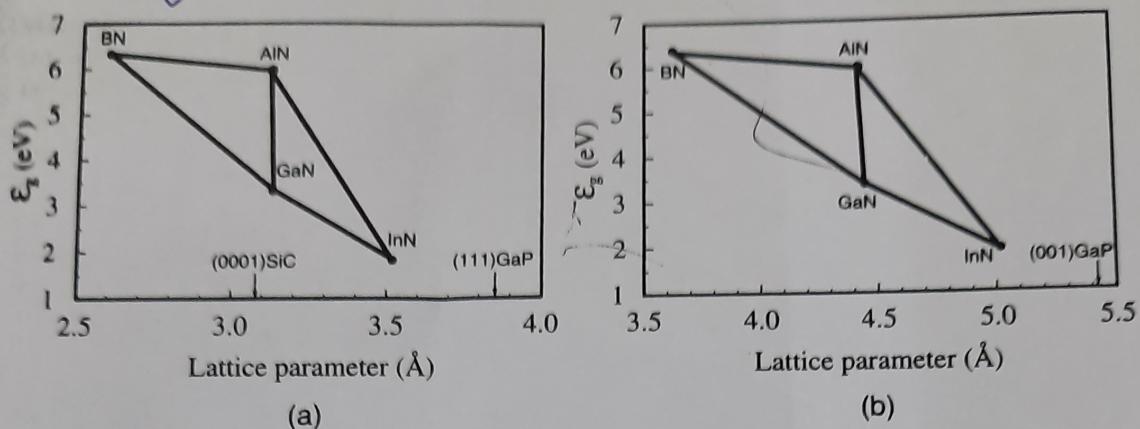


Figure 1.22 Bandgaps and lattice constants of (a) wurtzite, and (b) zincblende nitrides.

of these compounds for the two crystalline forms are shown in Fig. 1.22. The ternary derivatives of these binary compounds are also important for heterojunctions and it is interesting to note that a range of compositions of the quaternary compound AlGaAsN, corresponding to the visible part of the optical spectrum, are lattice-matched to Si. The foremost difficulty associated with the epitaxy of nitrides has been the low sticking coefficient of N and the consequent large density of N vacancies. These vacancies behave electrically as donors, making *p*-type doping and the realization of *p-n* junctions difficult.

TABLE 1.5 COMPOSITIONAL DEPENDENCE OF THE ENERGY GAP OF TERNARY III-V SEMICONDUCTORS AT 300°K^a (from H. C. Casey and M. B. Panish, *Heterostructure Lasers*, Academic Press, New York, 1978).

Compound	Direct energy gap E_g (eV)	Indirect energy gap, E_g (eV)	
		X minima	L minima
Al _x In _{1-x} P	1.351 + 2.23x	—	—
Al _x Ga _{1-x} As	1.425 + 1.247x + 1.147 × (x - 0.45) ²	1.900 + 0.125x + 0.143x ²	1.708 + 0.642x
Al _x In _{1-x} As	0.360 + 2.012x + 0.698x ²	—	—
Al _x Ga _{1-x} Sb	0.726 + 1.129x + 0.368x ²	1.020 + 0.492x + 0.077 ²	0.799 + 0.746x + 0.334x ²
Al _x In _{1-x} Sb	0.172 + 1.621x + 0.43x ²	—	—
Ga _x In _{1-x} P	1.351 + 0.643x + 0.786x ²	—	—
Ga _x In _{1-x} As	0.36 + 1.064x	—	—
Ga _x In _{1-x} Sb	0.172 + 0.139x + 0.415x ²	—	—
GaP _x As _{1-x}	1.424 + 1.150x + 0.176x ²	—	—
GaAs _x Sb _{1-x}	0.726 - 0.502x + 1.2x ²	—	—
InP _x As _{1-x}	0.360 + 0.891x + 0.101x ²	—	—
InAs _x Sb _{1-x}	0.18 - 0.41x + 0.58x ²	—	—

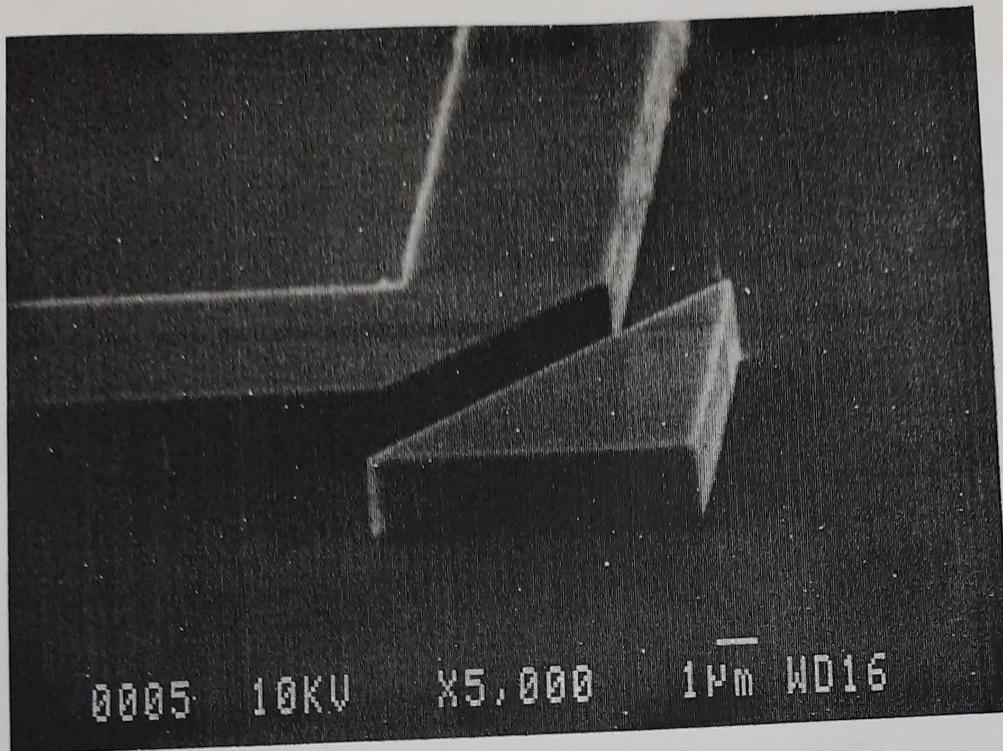


Figure 1.39 Scanning electron microscope image of $2.5\mu\text{m}$ deep corner mirror facet produced in a GaAs/AlGaAs laser heterostructure by reactive ion etching with an ECR source.

- Materials for optoelectronics and compatibility with transmission media.
- Alloy and strained semiconductors.
- Epitaxial techniques for crystal growth.
- Device processing techniques.

PROBLEMS

- 1.1 Discuss, with suitable diagrams, the difference between ionic and covalent bonding.
- 1.2 Draw a cubic unit cell and sketch the (111) and (211) planes. Also indicate the [110] direction.
- 1.3 Given that the unit cell edge of a cubic crystal, $a = 2.62 \text{ \AA}$, at what angles can the [100] and [110] reflections of monochromatic X-rays be observed for $\lambda = 1.54 \text{ \AA}$?
- 1.4 On a planar projection of a cubic lattice with dots to represent lattice sites, draw lines to represent the intersection of (100), (110), and (210) planes. If the lattice constant is a , what is the separation between successive intersection lines in the three cases?

- 1.5 Determine the packing fraction of
 (a) simple cubic lattice
 (b) face-centered cubic lattice
 (c) diamond lattice
 assuming that the atoms are rigid spheres.
- 1.6 What is the number of (a) nearest neighbors, and (b) second nearest neighbors for the FCC, BCC, and diamond crystal lattices?
- 1.7 The lattice constants of Si and GaAs are 5.43 and 5.65 Å, respectively. The atomic weights of Si, Ga, and As are, respectively, 28.1, 69.7, and 74.9. Avogadro's number is 6.02×10^{23} . Calculate the densities of Si and GaAs. [Hint: Si has 8 atoms per unit cell and GaAs has 4 Ga atoms and 4 As atoms per unit cell.]
- 1.8 Calculate the number density of Si atoms in the Si lattice and the number density of As atoms in the GaAs lattice.
- ✓ 1.9 Calculate the number density of In atoms in the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ lattice. Use the information in Appendix 1.
- ✓ 1.10 Calculate the Γ -L conduction band crossover in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ using the virtual crystal approximation. How does the crossover composition compare with that calculated by taking bowing of the Γ band energy into account, as given by Eq. 1.16?
- 1.11 (a) Find the number of surface atoms on the (100) surface of InP.
 (b) Calculate the distance between nearest Al neighbors in a AlAs crystal.
- ✓ 1.12 Using Eqs. 1.1 and 1.2, calculate lattice constant and dielectric constant of
 (a) $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$
 (b) $\text{InAs}_{0.4}\text{P}_{0.6}$
 (c) $\text{In}_{0.8}\text{Ga}_{0.2}\text{As}_{0.4}\text{P}_{0.6}$
- ✓ 1.13 From Fig. 1.14 it is evident that in $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, the X- and L-minima are very close to the Γ minimum. As a result, if the electrons in the Γ minimum of this alloy are given a small amount of energy, they may transfer to the X- and L-valleys. Do you know of, or can you suggest, some consequences and applications of this phenomenon? Since a momentum change is also involved in such a transfer, where is this momentum derived from?
- 1.14 It is decided to use InP-based materials and heterojunctions for a laser to emit at $1.3 \mu\text{m}$ for an optical fiber communication link. With reference to Fig. 1.2, mention the approximate compositions of low- and high-bandgap materials that can form a suitable heterojunction and the low-bandgap material is the active material for the laser.
- 1.15 At the critical thickness, it can be assumed that a two-dimensional dislo-