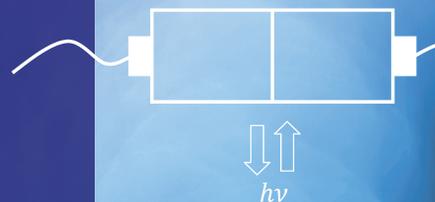# Principles of Solar Cells, LEDs and Diodes

The role of the PN junction

ADRIAN KITAI

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Principles of Solar Cells, LEDs and Diodes

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The role of the PN junction

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Dedicated to my wife Tomoko

Contents

Introduction

Semiconductor devices have revolutionized the way we work and live. Transistors are thought of as one of the most important developments of the twentieth century and they have given rise to the computer age as well as to compact, reliable electronics found in everything from televisions to cell phones.

An even more fundamental semiconductor device exists, however. It is the semiconductor diode or p-n junction diode. Diodes had been developed before the transistor and were used for rectification whereby alternating current can be converted to direct current by employing the unidirectional property of diodes: current normally only flows efficiently in one direction through a diode, and current flow is blocked in the opposite direction. This property of diodes is exploited in power supplies as well as in many other circuits such as those found in radios and limiters. Since an understanding of diodes is required to explain the principles of transistors, diodes are frequently presented as a stepping stone to the transistor.

In the twenty-first century, however, two new major industries are undergoing very rapid developments based directly on the p-n junction diode. Photovoltaic (PV) solar cells and light emitting diodes (LEDs) are both p-n junctions that are designed and optimized to either absorb or emit light. In both cases, an energy conversion process between photons and electrons occurs within a p-n junction.

The consequences of this development constitute a revolution in two major industrial sectors:

1. Energy production has relied on hydrocarbons and nuclear power, and although these will continue to be important, the direct conversion of solar radiation into useful power is the key to a long-term, sustainable energy supply. Ninety-seven percent of all renewable energy on earth is in the form of solar radiation. The beginning of the twenty-first century has seen the abrupt growth of a global solar photovoltaic industry in conjunction with the involvement of governments worldwide, and unprecedented growth in PV production and deployment is now underway. The worldwide consumption of silicon semiconductor material for the entire microelectronics industry is being overtaken by its use for solar cells alone.

2. Electric lighting was achieved by the incandescent lamp in the early twentieth century. In the second half of the twentieth century a significant movement to fluorescent lamps and discharge lamps in which a gas is excited into a plasma that radiates energy more efficiently than a tungsten filament occurred. The twenty-first century will give rise to the virtual displacement of both incandescent lamps and fluorescent lamps by LED lamps. In preparation for this revolution, the world's major lighting companies have

acquired LED research, development and production capabilities. LEDs have already
achieved lower power consumption and longer life in small, rugged packages than either
incandescent or fluorescent lamps. They also eliminate heavy metals such as mercury
used in fluorescent lamps.

The purpose of this book, therefore, is to introduce the physical concepts required
for a thorough understanding of p-n junctions starting with semiconductor fundamentals
and extending this to the practical implementation of semiconductors in both PV and
LED devices. The treatment of a range of important semiconductor materials and device
structures is also presented.

The book is aimed at senior undergraduate levels (years three and four). An introduc-
tory background in quantum mechanics is assumed, together with general knowledge of
junior mathematics, physics and chemistry; however, no background in electronic mate-
rials is required. As such this book is designed to be relevant to all engineering students
with an interest in semiconductor devices and not specifically to electrical or engineering
physics/engineering science students only. This is intentional since solar cells and LEDs
involve a wide range of engineering disciplines and should not be regarded as belonging to
only one branch of engineering.

In Chapter 1, the physics of solid state electronic materials is covered in detail starting
from the basic behaviour of electrons in crystals. The quantitative treatment of electrons and
holes in energy bands is presented along with the important concepts of excess carriers that
become significant once semiconductor devices are either connected to sources of power
or illuminated by light. A series of semiconductor materials and their important properties
is also reviewed. The behaviour of semiconductor surfaces and trapping concepts are also
introduced since they play an important role in solar cell and LED device performance.

In Chapter 2, the basic physics and important models of a p-n junction device are
presented. The approach taken is to present the diode as a semiconductor device that can be
understood from the band theory covered in Chapter 1. Various types of diode behaviour,
including tunnelling, metal-semiconductor contacts and heterojunctions, are presented as
well as reverse breakdown behaviour.

Chapter 3 introduces the theory of photon emission and absorption, a topic that books
on semiconductor devices frequently pay less attention to. The standard description that
a photon is created when an electron and a hole recombine, or a photon is absorbed
when an electron and a hole are generated, is not adequate for a deeper understanding of
photon emission and absorption processes. In this chapter the physics of photon creation
is explained with a minimum of mathematical complexity, and these concepts are much
better understood by following radiation theory and describing the oscillating dipole both
classically and using simple quantum mechanics. A section of Chapter 3 describes the
exciton relevant to inorganic semiconductors as well as the molecular exciton for organic
semiconductors. In addition lineshapes predicted for direct-gap semiconductors are derived.
Finally the subject of photometric units introduces the concepts of luminance and colour
coordinates that are essential to a discussion of organic and inorganic light emitting diodes.

Chapter 4 covers inorganic solar cells. The concepts regarding the p-n junction introduced
in Chapter 2 are further developed to include illumination of the p-n junction and the simplest
possible modelling is used to illustrate the behaviour of a solar cell. Then a more realistic
solar cell structure and model are presented along with the attendant surface recombination

and absorption issues that must be understood in practical solar cells. A series of solar cell technologies are reviewed starting with bulk single and multicrystalline silicon solar cell technology. Amorphous silicon materials and device concepts are presented. Solar cells made using other semiconductors such as CdTe are introduced followed by multijunction solar cells using layered, lattice-matched III-V semiconductor stacks.

Chapter 5 on inorganic LEDs considers the basic LED structure and its operating principles. The measured lineshape of III-V LEDs is compared with the predictions of Chapter 3. LEDs must be engineered to maximize radiative recombination, and energy loss mechanisms are discussed. The series of developments that marked the evolution of current, high-efficiency LED devices is presented starting from the semiconductors and growth techniques of the 1960s, and following trends in succeeding decades that brought better materials and semiconductor growth methods to the LED industry. The double heterojunction is introduced and the resulting energy well is analysed on the basis of the maximum current density that can be accommodated before it becomes saturated. LED optical outcoupling, which must also be maximized to achieve overall efficiency, is modelled and strategies to optimize outcoupling are discussed. Finally the concept of spectral down-conversion using phosphor materials and the white LED are introduced.

Chapter 6 introduces new concepts required for an understanding of organic semiconductors in general, in which conjugated molecular bonding gives rise to π bands and HOMO and LUMO levels in organic semiconductors. The organic LED is introduced by starting with the simplest single active layer polymer-based LED followed by successively more complex small-molecule LED structures. The roles of the various layers, including electrodes and carrier injection and transport layers, are discussed and the relevant candidate molecular materials are described. Concepts from Chapter 3, including the molecular exciton and singlet and triplet states are used to explain efficiency limitations in the light generation layer of small-molecule OLEDs. In addition the opportunity to use phosphorescent host-guest light emitting layers to improve device efficiency is explained. The organic solar cell is introduced and the concepts of exciton generation and exciton dissociation are described in the context of the heterojunction and the bulk heterojunction. The interest in the use of fullerenes and other related nanostructured materials is explained for the bulk heterojunction.

All the chapters are followed by problem sets that are designed to facilitate familiarity with the concepts and a better understanding of the topics introduced in the chapter. In many cases the problems are quantitative and require calculations; however, a number of more conceptual problems are presented and are designed to give the reader experience in using the Internet or library resources to look up further information. These problems are of particular relevance in Chapters 4, 5 and 6, in which developments in solar cells and LEDs are best understood by referring to the recent literature once the basic concepts are understood.

Adrian Kitai

Acknowledgements

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Semiconductor Physics

Objectives

1. Understand semiconductor band theory and its relevance to semiconductor devices.
2. Obtain a qualitative understanding of how bands depend on semiconductor materials.
3. Introduce the concept of the Fermi energy.
4. Introduce the concept of the mobile hole in semiconductors.
5. Derive the number of mobile electrons and holes in semiconductor bands.
6. Obtain expressions for the conductivity of semiconductor material based on the electron and hole concentrations and mobilities.
7. Introduce the concepts of doped semiconductors and the resulting electrical characteristics.
8. Understand the concept of excess, non-equilibrium carriers generated by either illumination or by current flow due to an external power supply.
9. Introduce the physics of traps and carrier recombination and generation.
10. Introduce alloy semiconductors and the distinction between direct gap and indirect gap semiconductors.

1.1   Introduction

A fundamental understanding of electron behaviour in crystalline solids is available using the *band theory of solids.* This theory explains a number of fundamental attributes of electrons in solids including:

 (i) concentrations of charge carriers in semiconductors;
 (ii) electrical conductivity in metals and semiconductors;
(iii) optical properties such as absorption and photoluminescence;
(iv) properties associated with junctions and surfaces of semiconductors and metals.

The aim of this chapter is to present the theory of the band model, and then to exploit it to describe the important electronic properties of semiconductors. This is essential for a proper understanding of p-n junction devices, which constitute both the photovoltaic (PV) solar cell and the light-emitting diode (LED).

1.2   The Band Theory of Solids

There are several ways of explaining the existence of energy bands in crystalline solids. The simplest picture is to consider a single atom with its set of discrete energy levels for its electrons. The electrons occupy quantum states with quantum numbers n, l, m and s denoting the energy level, orbital and spin state of the electrons. Now if a number N of identical atoms are brought together in very close proximity as in a crystal, there is some degree of spatial overlap of the outer electron orbitals. This means that there is a chance that

any pair of these outer electrons from adjacent atoms could trade places. The Pauli exclusion principle, however, requires that each electron occupy a unique energy state. Satisfying the Pauli exclusion principle becomes an issue because electrons that trade places effectively occupy new, *spatially extended* energy states. The two electrons apparently occupy the same spatially extended energy state.

In fact, since outer electrons from all adjacent atoms may trade places, outer electrons from *all* the atoms may effectively trade places with each other and therefore a set of outermost electrons from the *N* atoms all appear to share a spatially extended energy state that extends through the entire crystal. The Pauli exclusion principle can only be satisfied if these electrons occupy a set of *distinct*, spatially extended energy states. This leads to a set of slightly different energy levels for the electrons that all originated from the same atomic orbital. We say that the atomic orbital splits into an *energy band* containing a set of electron states having a set of closely spaced energy levels. Additional energy bands will exist if there is some degree of spatial overlap of the atomic electrons in lower-lying atomic orbitals. This results in a set of energy bands in the crystal. Electrons in the lowest-lying atomic orbitals will remain virtually unaltered since there is virtually no spatial overlap of these electrons in the crystal.

The picture we have presented is conceptually a very useful one and it suggests that electrical conductivity may arise in a crystal due to the formation of spatially extended electron states. It does not directly allow us to quantify and understand important details of the behaviour of these electrons, however.

We need to understand the behaviour in a solid of the electrons that move about in the material. These mobile charge carriers are crucially important in terms of the electrical properties of devices. An electron inside an infinitely large vacuum chamber is a free electron, but a mobile electron in a solid behaves very differently.

We can obtain a more detailed model as follows. The mobile electrons in a crystalline semiconductor are influenced by the electric potential in the material. This potential has a spatial periodicity on an atomic scale due to the crystal structure. For example, positively charged atomic sites provide potential valleys to a mobile electron and negatively charged atomic sites provide potential peaks or barriers. In addition, the semiconductor is finite in its spatial dimensions and there will be additional potential barriers or potential changes at the boundaries of the semiconductor material.

The quantitative description of these spatially extended electrons requires the use of wavefunctions that include their spatial distribution as well as their energy and momentum. These wavefunctions may be obtained by solving Schrödinger's equation. The following section presents a very useful band theory of crystalline solids and the results.

1.3   The Kronig–Penney Model

The *Kronig–Penney model* is able to explain the essential features of band theory.

First, consider an electron that can travel within a one-dimensional periodic potential $V(x)$. The periodic potential can be considered as a series of regions having zero potential energy separated by potential energy barriers of height V_0, as shown in Figure 1.1, forming a simple periodic potential with period $a + b$. We associate $a + b$ also with the lattice constant of the crystal. Note that the electric potential in a real crystal does not exhibit the

$$V(x)$$
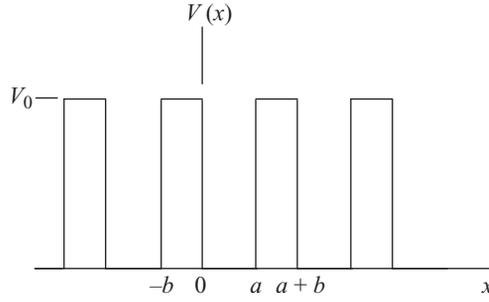
Figure 1.1   *Simple one-dimensional potential V(x) used in the Kronig–Penney model*

idealized shape of this periodic potential; however, the result turns out to be relevant in any case, and Schrödinger's equation is much easier to solve starting from the potential of Figure 1.1.

In order to obtain the electron wavefunctions relevant to an electron in the crystalline solid, $V(x)$ is substituted into the time-independent form of Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x) = E\psi(x) \tag{1.1}$$

where $V(x)$ is the potential energy and E is total energy.

For $0 \leq x \leq a$ we have $V = 0$ and the general solution to Equation 1.1 yields:

$$\psi(x) = Ae^{iKx} + Be^{-iKx} \tag{1.2a}$$

where

$$E = \frac{\hbar^2 K^2}{2m} \tag{1.2b}$$

For $-b \leq x \leq 0$ we have

$$\psi(x) = Ce^{Qx} + De^{-Qx} \tag{1.3a}$$

where

$$V_0 - E = \frac{\hbar^2 Q^2}{2m} \tag{1.3b}$$

Boundary conditions must be satisfied such that $\psi(x)$ and $\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}$ are continuous functions. At $x = 0$, equating (1.2a) and (1.3a), we have

$$A + B = C + D \tag{1.4a}$$

and equating derivatives of (1.2a) and (1.3a),

$$iK(A - B) = Q(C - D) \tag{1.4b}$$

An important additional constraint on the required wavefunctions results from the periodicity of the lattice. The solution to Equation 1.1 for any periodic potential must also have the form of a *Bloch function*:

$$\psi(x) = u_k(x)e^{ikx} \tag{1.5}$$

Here, k is the wavenumber of a plane wave. There are no restrictions on this wavenumber; however, $u_k(x)$ must be a periodic function with the same periodicity as the lattice.

Consider two x-values separated by one lattice constant, namely $x = -b$ and $x = a$. Now, Equation 1.5 states that $\psi(x + a + b) = \psi(x)e^{ik(a+b)}$. At $x = -b$ this may be written as:

$$\psi(a) = \psi(-b)e^{ik(a+b)} \tag{1.6}$$

The boundary conditions to satisfy $\psi(x)$ and $\frac{d\psi(x)}{dx}$ being continuous functions at $x = a$ may now be written by substituting ψ from Equations 1.2 and 1.3 into Equation 1.6:

$$Ae^{iKa} + Be^{-iKa} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \tag{1.7a}$$

and substituting the corresponding derivatives:

$$iK(Ae^{iKa} - Be^{-iKa}) = Q(Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \tag{1.7b}$$

Equations 1.4a, 1.4b, 1.7a and 1.7b constitute four equations with four unknowns A, B, C and D. A solution exists only if the determinant of the coefficients of A, B, C and D is zero (Cramer's rule). This requires that

$$\frac{Q^2 - K^2}{2QK}\sinh QB \sin Ka + \cosh Qb \cos Ka = \cos k(a + b) \tag{1.7c}$$

This may be simplified if the limit $b \rightarrow 0$ and $V_0 \rightarrow \infty$ is taken such that bV_0 is constant (see Problem 1.1). We now define

$$P = \frac{Q^2ba}{2}$$

Since $Q \gg K$ and $Qb \ll 1$ we obtain

$$\cos ka = P\frac{\sin Ka}{Ka} + \cos Ka \tag{1.8}$$

Here k is the wavevector of the electron describing its momentum $p = \hbar k$ and

$$K = \frac{1}{\hbar}\sqrt{2mE} \tag{1.9}$$

which means that K is a term associated with the electron's energy.

Now, Equation 1.8 only has solutions if the righthand side of Equation 1.8 is between -1 and $+1$, which restricts the possible values of Ka. The righthand side is plotted as a function of Ka in Figure 1.2.
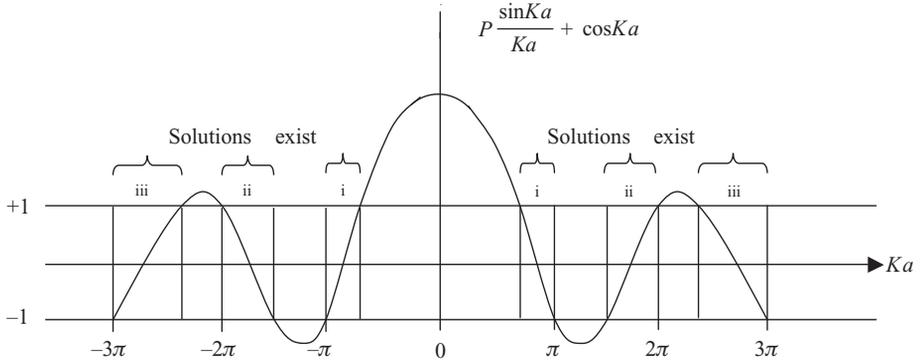
Figure 1.2   *Graph of righthand side of Equation 1.8 as a function of* P *for* P = 2

Since *K* and *E* are related by Equation 1.9, these allowed ranges of *Ka* actually describe *energy bands* (allowed ranges of *E*) separated by *energy gaps* (forbidden ranges of *E*). *Ka* may be re-plotted on an energy axis, which is related to the *Ka* axis by the square root relationship of Equation 1.9. It is convenient to view *E* on a vertical axis as a variable dependent on *k*. Note that $k = \frac{n\pi}{a}$ for integer values of *n* at the edges of each energy band where the left side of Equation 1.8 is equal to ±1. These critical values of *k* occur at the boundaries of what are called *Brillouin zones*. A sketch of *E* versus *k* is shown in Figure 1.3, which clearly shows the energy bands and energy gaps.

Let us now plot the free electron graph for *E* versus *k*. Solving Equation 1.1 for a free electron with *V* = 0 yields the solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$
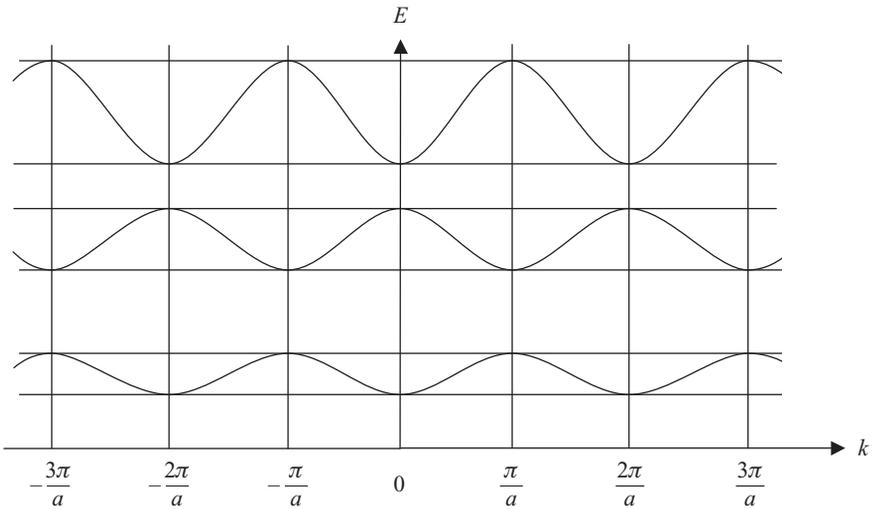
Figure 1.3   *Plot of* E *versus* k *showing how* k *varies within each energy band and the existence of energy bands and energy gaps. The vertical lines at* k = n$\frac{\pi}{a}$ *are Brillouin zone boundaries*
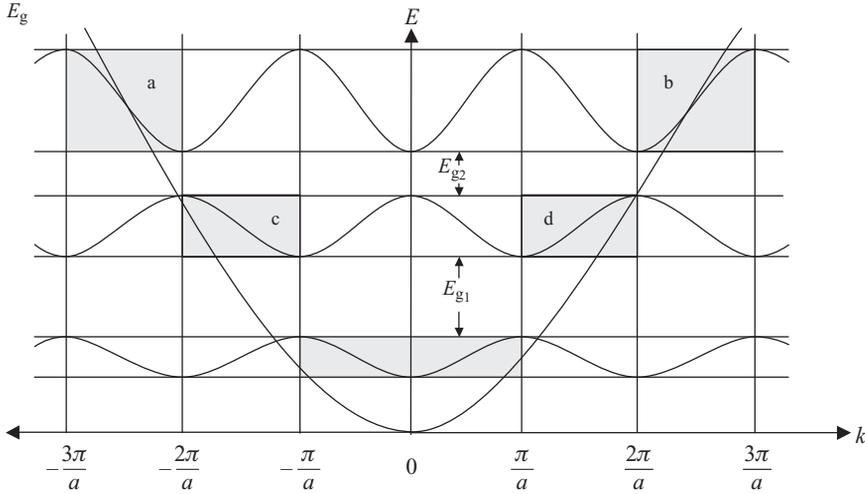
Figure 1.4 *Plot of* E *versus* k *comparing the result of the Kronig–Penney model to the free electron parabolic result*

where

$$E = \frac{\hbar^2 k^2}{2m} \tag{1.10}$$

This parabolic E versus k relationship is plotted superimposed on the curves from Figure 1.3. The result is shown in Figure 1.4.

Taking the limit $P \to 0$, and combining Equations 1.8 and 1.9, we obtain:

$$E = \frac{\hbar^2 k^2}{2m}$$

which is identical to Equation 1.10. This means that the dependence of E on k in Figure 1.4 approaches a parabola as expected if the amplitude of the periodic potential is reduced to zero. In fact, the relationship between the parabola and the Kronig–Penney model is evident if we look at the solutions to Equation 1.4 within the shaded regions in Figure 1.4 and regard them as portions of the parabola that have been broken up by energy gaps and distorted in shape. For a weak periodic potential (small P) the solutions to Equation 1.4 would more closely resemble the parabola. We refer to Equation 1.10 as a *dispersion relation* – it relates energy to the wavenumber of a particle.

At this point, we can draw some very useful conclusions based on the following result: *The size of the energy gaps increases as the periodic potential increases in amplitude in a crystalline solid.* Periodic potentials are larger in amplitude for crystalline semiconductors that have small atoms since there are then fewer atomically bound electrons to screen the point charges of the nuclei of the atoms. In addition, periodic potentials increase in amplitude for compound semiconductors as the ionic character of the crystal bonding increases. This will be illustrated in Section 1.10 for some real semiconductors.

To extend our understanding of energy bands we now need to turn to another picture of electron behaviour in a crystal.

1.4   The Bragg Model

Since electrons behave like waves, they will exhibit the behaviour of waves that undergo reflections. Notice that in a crystal with lattice constant a, the Brillouin zone boundaries occur at

$$k = \frac{n\pi}{a} = \frac{2\pi}{\lambda}$$

which may be rearranged to obtain

$$2a = n\lambda$$

The well-known Bragg condition relevant to waves that undergo strong reflections when incident on a crystal with lattice constant a is

$$2a \sin\theta = n\lambda$$

Now, if the electron is treated as a wave incident at $\theta = 90°$ then we have

$$2a = n\lambda$$

which is precisely the case at Brillouin zone boundaries. We therefore make the following observation: Brillouin zone boundaries occur when the electron wavelength satisfies the requirement for strong reflections from crystal lattice planes according to the Bragg condition. The free electron parabola in Figure 1.4 is similar to the Kronig–Penney model in the shaded regions well away from Brillouin zone boundaries; however, as we approach Brillouin zone boundaries, strong deviations take place and energy gaps are observed.

There is therefore a fundamental connection between the Bragg condition and the formation of energy gaps. The electrons that satisfy the Bragg condition actually exist as *standing waves* since reflections will occur equally for electrons travelling in both directions of the x axis, and standing waves do not travel. Provided electrons have wavelengths not close to the Bragg condition, they interact relatively weakly with the crystal lattice and behave more like free electrons.

The E versus k dependence immediately above and below any particular energy gap is contained in four shaded regions in Figure 1.4. For example, the relevant shaded regions for E_{g2} in Figure 1.4 are labelled a, b, c and d. These four regions are redrawn in Figure 1.5. Energy gap E_{g2} occurs at $k = \pm\frac{2\pi}{a}$. Since this is a standing wave condition with both electron velocity and electron momentum $p = \hbar k$ equal to zero, E_{g2} is redrawn at $k = 0$ in Figure 1.5. Since we are only interested in relative energies, the origin of the energy axis is moved for convenience, and we can arbitrarily redefine the origin of the energy axis. Figure 1.5 is known as a *reduced zone scheme*.

1.5   Effective Mass

We now introduce the concept of *effective mass* m^* to allow us to quantify electron behaviour. Effective mass changes in a peculiar fashion near Brillouin zone boundaries, and generally is not the same as the free electron mass m. It is easy to understand that the effective acceleration of an electron in a crystal due to an applied electric field will depend
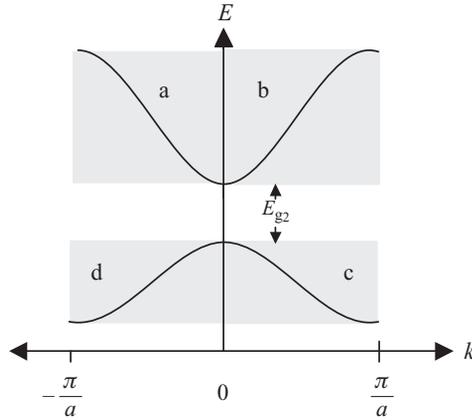
Figure 1.5 *Plot of* E *versus* k *in reduced zone scheme taken from regions a, b, c and d in* Figure 1.4

strongly on the nature of the reflections of electron waves off crystal planes. Rather than trying to calculate the specific reflections for each electron, we instead modify the mass of the electron to account for its observed willingness to accelerate in the presence of an applied force.

To calculate m^* we start with the free electron relationship

$$E = \frac{1}{2}mv_g^2$$

where v_g is the group velocity of the electron. Upon differentiation with respect to k,

$$\frac{\mathrm{d}E}{\mathrm{d}k} = mv_g\frac{\mathrm{d}v_g}{\mathrm{d}k} \qquad (1.11)$$

Since $p = \hbar k = mv_g$ we can write

$$\frac{v_g}{k} = \frac{\mathrm{d}v_g}{\mathrm{d}k} = \frac{\hbar}{m} \qquad (1.12)$$

Combining Equations 1.11 and 1.12 we obtain

$$\frac{\mathrm{d}E}{\mathrm{d}k} = v_g\hbar$$

or

$$v_g = \frac{1}{\hbar}\frac{\mathrm{d}E}{\mathrm{d}k} \qquad (1.13)$$

Note that the group velocity falls to zero at the Brillouin zone boundaries where the slope of the E versus k graph is zero. This is consistent with the case of a standing wave.

Now, using Newton's law,

$$F = \frac{\mathrm{d}p}{\mathrm{d}t} = \hbar\frac{\mathrm{d}k}{\mathrm{d}t} \qquad (1.14)$$

From Equations 1.13 and 1.14, we can write

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk\,dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} = \frac{F}{\hbar^2}\frac{d^2E}{dk^2}$$

(1.15)

If we assign m^* to represent an effective electron mass, then Newton's law tells us that

$$\frac{dv_g}{dt} = \frac{F}{m^*}$$

Upon examination Equation 1.15 actually expresses Newton's law provided we define

$$m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$$

(1.16)

Since $\frac{d^2E}{dk^2}$ is the curvature of the plot in Figure 1.5, it is interesting to note that m^* will be negative for certain values of k. This may be understood physically: if an electron that is close to the Bragg condition is accelerated slightly by an applied force it may then move even closer to the Bragg condition, reflect more strongly off the lattice planes, and effectively accelerate in the direction opposite to the applied force.

We can apply Equation 1.16 to the free electron case where $E = \frac{\hbar^2k^2}{2m}$ and we immediately see that $m^* = m$ as expected. In addition at the bottom or top of energy bands illustrated in Figure 1.5, the shape of the band may be approximated as parabolic for small values of k and hence a constant effective mass is often sufficient to describe electron behaviour for small values of k. This will be useful when we calculate the number of electrons in an energy band.

1.6   Number of States in a Band

The curves in Figure 1.5 are misleading in that electron states in real crystals are discrete and only a finite number of states exist within each energy band. This means that the curves should be regarded as closely spaced dots that represent quantum states. We can determine the number of states in a band by considering a semiconductor crystal of length L and modelling the crystal as an infinite-walled potential box of length L with a potential of zero inside the well. See Example 1.1.

Example 1.1

An electron is inside a potential box of length L with infinite walls and zero potential in the box. The box is shown below.
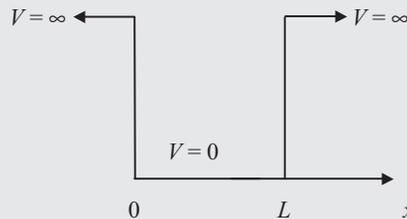
(a) Find the allowed energy levels in the box.
(b) Find the wavefunctions of these electrons.

Solution

(a) Inside the box, from Schrödinger's equation, we can substitute $V(x) = 0$ and we obtain

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x)$$

Solutions are of the form

$$\psi(x) = A\exp\frac{i\sqrt{2mE}}{\hbar}x + B\exp\frac{-i\sqrt{2mE}}{\hbar}x$$

In regions where $V = \infty$ the wavefunction is zero. In order to avoid discontinuities in the wavefunction we satisfy boundary conditions at $x = 0$ and at $x = L$ and require that $\psi(0) = 0$ and $\psi(L) = 0$. These boundary conditions can be written

$$0 = A + B \text{ or } B = -A$$

and

$$0 = A\exp\frac{i\sqrt{2mE}}{\hbar}L + B\exp\frac{-i\sqrt{2mE}}{\hbar}L$$

$$= A\left(\exp\frac{i\sqrt{2mE}}{\hbar}L - \exp\frac{-i\sqrt{2mE}}{\hbar}L\right) = C\sin\frac{\sqrt{2mE}}{\hbar}L$$

where C is a constant. Now $\sin\theta$ is zero provided $\theta = n\pi$ where n is an integer and hence

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi$$

A discrete set of allowed energy values is obtained by solving for E to obtain

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

(b) The corresponding wavefunctions may be found by substituting the allowed energy values into Schrödinger's equation and solving:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = \frac{n^2\pi^2\hbar^2}{2mL^2}\psi(x)$$

> now
>
> $$\frac{d^2 \psi(x)}{dx^2} = -\frac{n^2 \pi^2}{L^2} \psi(x)$$
>
> and hence
>
> $$\psi_n(x) = A \sin \left(\frac{n\pi}{L} x \right)$$

From Example 1.1 we obtain

$$\psi_n(x) = A \, \sin \frac{n\pi}{L} x \tag{1.17}$$

where n is a quantum number, and

$$k = \frac{n\pi}{L}, n = 1, 2, 3 \dots$$

As n increases we will inevitably reach the k value corresponding to the Brillouin zone boundary from the band model

$$k = \frac{\pi}{a}$$

This will occur when

$$\frac{n\pi}{L} = \frac{\pi}{a}$$

and therefore $n = \frac{L}{a}$. The maximum possible value of n now becomes the macroscopic length of the semiconductor crystal divided by the unit cell dimension, which is simply the number of unit cells in the crystal, which we shall call N. Since electrons have an additional quantum number s (spin quantum number) that may be either $\frac{1}{2}$ or $-\frac{1}{2}$, the maximum number of electrons that can occupy an energy band becomes

$$n = 2N$$

Although we have considered a one-dimensional model, the results can readily be extended into two or three dimensions and we still obtain the same result. See Problem 1.3.

We are now ready to determine the actual number of electrons in a band, which will allow us to understand electrical conductivity in semiconductor materials.

1.7   Band Filling

The existence of $2N$ electron states in a band does not determine the actual number of electrons in the band. At low temperatures, the electrons will occupy the lowest allowed energy levels, and in a semiconductor like silicon, which has 14 electrons per atom, several low-lying energy bands will be filled. In addition, the highest occupied energy band will be full, and then the next energy band will be empty. This occurs because silicon has an even number of valence electrons per unit cell, and when there are N unit cells, there will