Chapter 1

Phonons in nanostructures

There are no such things as applied sciences, only applications of sciences.

*Louis Pasteur*, 1872

1.1 Phonon effects: fundamental limits on carrier mobilities and dynamical processes

The importance of phonons and their interactions in bulk materials is well known to those working in the fields of solid-state physics, solid-state electronics, optoelectronics, heat transport, quantum electronics, and superconductivity.

As an example, carrier mobilities and dynamical processes in polar semiconductors, such as gallium arsenide, are in many cases determined by the interaction of longitudinal optical (LO) phonons with charge carriers. Consider carrier transport in gallium arsenide. For gallium arsenide crystals with low densities of impurities and defects, steady state electron velocities in the presence of an external electric field are determined predominantly by the rate at which the electrons emit LO phonons. More specifically, an electron in such a polar semiconductor will accelerate in response to the external electric field until the electron’s energy is large enough for the electron to emit an LO phonon. When the electron’s energy reaches the threshold for LO phonon emission – 36 meV in the case of gallium arsenide – there is a significant probability that it will emit an LO phonon as a result of its interaction with LO phonons. Of course, the electron will continue to gain energy from the electric field.

In the steady state, the processes of electron energy loss by LO phonon emission and electron energy gain from the electric field will come into balance and the electron will propagate through the semiconductor with a velocity known as the saturation velocity. As is well known, experimental values for this saturated drift velocity generally fall in the range $10^7$ cm s$^{-1}$ to $10^8$ cm s$^{-1}$. For gallium arsenide this velocity is about $2 \times 10^7$ cm s$^{-1}$ and for indium antimonide $6 \times 10^7$ cm s$^{-1}$.
For both these polar semiconductors, the process of LO phonon emission plays a major role in determining the value of the saturation velocity. In non-polar materials such as Si, which has a saturation velocity of about $10^7 \text{ cm s}^{-1}$, the deformation-potential interaction results in electron energy loss through the emission of phonons. (In Chapter 5 both the interaction between polar-optical-phonons and electrons – known as the Fröhlich interaction – and the deformation-potential interaction will be defined mathematically.)

Clearly, in all these cases, the electron mobility will be influenced strongly by the interaction of the electrons with phonons. The saturation velocity of the carriers in a semiconductor provides a measure of how fast a microelectronic device fabricated from this semiconductor will operate. Indeed, the minimum time for the carriers to travel through the active region of the device is given approximately by the length of the device – that is, the length of the so-called gate – divided by the saturation velocity. Evidently, the practical switching time of such a microelectronic device will be limited by the saturation velocity and it is clear, therefore, that phonons play a major role in the fundamental and practical limits of such microelectronic devices. For modern integrated circuits, a factor of two reduction in the gate length can be achieved in many cases only through building a new fabrication facility. In some cases, such a building project might cost a billion dollars or more. The importance of phonons in microelectronics is clear!

A second example of the importance of carrier–phonon interactions in modern semiconductor devices is given by the dynamics of carrier capture in the active quantum-well region of a polar semiconductor quantum-well laser. Consider the case where a current of electrons is injected over a barrier into the quantum-well region of such a laser. For the laser to operate, an electron must lose enough energy to be ‘captured’ by the quasi-bound state which it must occupy to participate in the lasing process. For many quantum-well semiconductor lasers this means that the electron must lose an energy of the order of a 100 meV or more. The energy loss rate of a carrier – also known as the thermalization rate of the carrier – in a polar-semiconductor quantum well is determined by both the rate at which the carrier’s energy is lost by optical-phonon emission and the rate at which the carrier gains energy from optical-phonon absorption. This latter rate can be significant in quantum wells since the phonons emitted by energetic carriers can accumulate in these structures. Since the phonon densities in many dimensionally confined semiconductor devices are typically well above those of the equilibrium phonon population, there is an appreciable probability that these non-equilibrium – or ‘hot’ – phonons will be reabsorbed. Clearly, the net loss of energy by an electron in such a situation depends on the rates for both phonon absorption and phonon emission. Moreover, the lifetimes of the optical phonons are also important in determining the total energy loss rate for such carriers. Indeed, as will be discussed in Chapter 6, the longitudinal optical (LO) phonons in GaAs and many other polar materials decay into acoustic phonons through the Klemens’ channel. Furthermore, over a wide
1.2 Devices with nanostructure components

range of temperatures and phonon wavevectors, the lifetimes of longitudinal optical phonons in GaAs vary from a few picoseconds to about 10 ps (Bhatt et al., 1994). (Typical lifetimes for other polar semiconductors are also of this magnitude.) As a result of the Klemens’ channel, the ‘hot’ phonons decay into acoustic phonons in times of the order of 10 ps. The LO phonons undergoing decay into acoustic phonons are not available for absorption by the electrons and as a result of the Klemens’ channel the electron thermalization is more rapid than it would be otherwise; this phenomenon is referred to as the ‘hot-phonon-bottleneck effect’.

The electron thermalization time is an important parameter for semiconductor quantum-well lasers because it determines the minimum time needed to switch the laser from an ‘on’ state to an ‘off’ state; this occurs as a result of modulating the electron current that leads to lasing. Since the hot-phonon population frequently decays on a time scale roughly given by the LO phonon decay rate (Das Sarma et al., 1992), a rough estimate of the electron thermalization time – and therefore the minimum time needed to switch the laser from an ‘on’ state to an ‘off’ state – is of the order of about 10 ps. In fact, typical modulation frequencies for gallium arsenide quantum-well lasers are about 30 GHz. The modulation of the laser at significantly higher frequencies will be limited by the carrier thermalization time and ultimately by the lifetime of the LO phonon. The importance of the phonon in modern optoelectronics is clear.

The importance of phonons in superconductors is well known. Indeed, the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity is based on the formation of bosons from pairs of electrons – known as Cooper pairs – bound through the mediating interaction produced by phonons. Many of the theories describing the so-called high-critical-temperature superconductors are not based on phonon-mediated Cooper pairs, but the importance of phonons in many superconductors is of little doubt. Likewise, it is generally recognized that acoustic phonon interactions determine the thermal properties of materials.

These examples illustrate the pervasive role of phonons in bulk materials. Nanotechnology is providing an ever increasing number of devices and structures having one, or more than one, dimension less than or equal to about 100 ångstroms. The question naturally arises as to the effect of dimensional confinement on the properties on the phonons in such nanostructures as well as the properties of the phonon interactions in nanostructures. The central theme of this book is the description of the optical and acoustic phonons, and their interactions, in nanostructures.

1.2 Tailoring phonon interactions in devices with nanostructure components

Phonon interactions are altered unavoidably by the effects of dimensional confinement on the phonon modes in nanostructures. These effects exhibit some similarities
to those for an electron confined in a quantum well. Consider the well-known wavefunction of an electron in a infinitely deep quantum well, of width $L_z$ in the $z$-direction. The energy eigenstates $\Psi_n(z)$ may be taken as plane-wave states in the directions parallel to the heterointerfaces and as bound states in an infinitely deep quantum well in the $z$-direction:

$$\Psi_n(z) = e^{i|k| \cdot r_\parallel} \sqrt{\frac{2}{L_z}} \sin k_z z,$$

where $r_\parallel$ and $k_\parallel$ are the position vector and wavevector components in a plane parallel to the interfaces, $k_z = n\pi/L_z$, and $n = 1, 2, 3, \ldots$ labels the energy eigenstates, whose energies are

$$E_n(k_\parallel) = \frac{\hbar^2 (k_\parallel)^2}{2m} + \frac{\hbar^2 \pi^2 n^2}{2m L_z^2}.$$

$A$ is the area of the heterointerface over which the electron wavefunction is normalized. Clearly, a major effect of dimensional confinement in the $z$-direction is that the $z$-component of the bulk continuum wavevector is restricted to integral multiples of $\pi/L_z$. Stated in another way, the phase space is restricted.

As will be explained in detail in Chapter 7, the dimensional confinement of phonons results in similar restrictions in the phase space of the phonon wavevector $q$. Indeed, we shall show that the wavevectors of the optical phonons in a dielectric layer of thickness $L_z$ are given by $q_z = n\pi/L_z$ (Fuchs and Kliever, 1965) in analogy to the case of an electron in an infinitely deep quantum well. In fact, Fasol et al. (1988) used Raman scattering techniques to show that the wavevectors $q_z = n\pi/L_z$ of optical phonons confined in a ten-monolayer-thick AlAs/GaAs/AlAs quantum well are so sensitive to changes in $L_z$ that a one-monolayer change in the thickness of the quantum well is readily detectable as a change in $q_z$. These early experimental studies of Fasol et al. (1988) demonstrated not only that phonons are confined in nanostructures but also that the measured phonon wavevectors are well described by relatively simple continuum models of phonon confinement.

Since dimensional confinement of phonons restricts the phase space of the phonons, it is certain that carrier–phonon interactions in nanostructures will be modified by phonon confinement. As we shall see in Chapter 7, the so-called dielectric and elastic continuum models of phonons in nanostructures may be applied to describe the deformation-potential, Fröhlich, and piezoelectric interactions in a variety of nanostructures including quantum wells, quantum wires, and quantum dots. These interactions play a dominant role in determining the electronic, optical and acoustic properties of materials (Mitin et al., 1999; Dutta and Stroscio, 1998b; Dutta and Stroscio, 2000); it is clearly desirable for models of the properties of nanostructures to be based on an understanding of how the above-mentioned interactions change as a result of dimensional confinement. To this end, Chapters
8, 9 and 10 of this book describe how the dimensional confinement of phonons in nanostructures leads to modifications in the electronic, optical, acoustic, and superconducting properties of selected devices and structures, including intersubband quantum-well semiconductor lasers, double-barrier quantum-well diodes, thin-film superconductors, and the thin-walled cylindrical structures found in the biological structures known as microtubulin. Chapters 8, 9, and 10 also provide analyses of the role of collective effects and non-equilibrium phonons in determining hot-carrier energy loss in polar quantum wires as well as the use of metal–semiconductor structures to tailor carrier–phonon interactions in nanostructures. Moreover, Chapter 10 describes how confined phonons play a critical role in determining the properties of electronic, optical, and superconducting devices containing nanostructures as essential elements. Examples of such phonon effects in nanoscale devices include: phonon effects in intersubband lasers; the effect of confined phonons on the gain of intersubband lasers; the contribution of confined phonons to the valley current in double-barrier quantum-well structures; phonon-enhanced population inversion in asymmetric double-barrier quantum-well lasers; and confined phonon effects in thin film superconductors.
Chapter 2

Phonons in bulk cubic crystals

The Creator, if He exists, has a special preference for beetles.
J.B.S. Haldane, 1951

2.1 Cubic structure

Crystals with cubic structure are of major importance in the fields of electronics and optoelectronics. Indeed, zincblende crystals such as silicon, germanium, and gallium arsenide may be regarded as two face-centered cubic (fcc) lattices displaced relative to each other by a vector \((\frac{a}{4}, \frac{a}{4}, \frac{a}{4})\), where \(a\) is the size of the smallest unit of the fcc structure. Figure 2.1 shows a lattice with the zincblende structure.

A major portion of this book will deal with phonons in cubic crystals. In addition, we will describe the phonons in so-called isotropic media, which are related mathematically to cubic media as explained in detail in Section 7.2. The remaining portions of this book will deal with crystals of würtzite structure, defined in Chapter 3. More specifically, the primary focus of this book concerns phonons in crystalline structures that are dimensionally confined in one, two, or three dimensions. Such one-, two-, and three-dimensional confinement is realized in quantum wells, quantum wires, and quantum dots, respectively. As a preliminary to considering phonons in dimensionally confined structures, the foundational case of phonons in bulk structures will be treated. The reader desiring to supplement this chapter with additional information on the basic properties of phonons in bulk cubic materials will find excellent extended treatments in a number of texts including Blakemore (1985), Ferry (1991), Hess (1999), Kittel (1976), Omar (1975), and Singh (1993).

2.2 Ionic bonding – polar semiconductors

As is well known, the crystal structure of silicon is the zincblende structure shown in Figure 2.1. The covalent bonding in silicon does not result in any net transfer of charge between silicon atoms. More specifically, the atoms on the two displaced
2.3 Linear-chain model and macroscopic models

face-centered cubic (fcc) lattices depicted in Figure 2.1 have no excess or deficit of charge relative to the neutral situation. This changes dramatically for polar semiconductors like gallium arsenide, since here the ionic bonding results in charge transfer from the Group V arsenic atoms to the Group III gallium atoms: Since Group V atoms have five electrons in the outer shell and Group III atoms have three electrons in the outer shell, it is not surprising that the gallium sites acquire a net negative charge and the arsenic sites a net positive charge. In binary polar semiconductors, the two atoms participating in the ionic bonding carry opposite charges, \( e^* \) and \(-e^*\), respectively, as a result of the redistribution of the charge associated with polar bonding. In polar materials such ionic bonding is characterized by values of \( e^* \) within an order of magnitude of unity. In the remaining sections of this chapter, it will become clear that \( e^* \) is related to the readily measurable or known ionic masses, phonon optical frequencies, and high-frequency dielectric constant of the polar semiconductor.

2.3 Linear-chain model and macroscopic models

The linear-chain model of a one-dimensional diatomic crystal is based upon a system of two atoms with masses, \( m \) and \( M \), placed along a one-dimensional chain as depicted in Figure 2.2. As for a diatomic lattice, the masses are situated alternately along the chain and their separation is \( a \). On such a chain the displacement of one atom from its equilibrium position will perturb the positions of its neighboring atoms.

![Figure 2.1. Zincblende crystal. The white spheres and black spheres lie on different fcc lattices.](image)

![Figure 2.2. One-dimensional linear-chain representation of a diatomic lattice.](image)
In the simple linear-chain model considered in this section, it is assumed that only nearest neighbors are coupled and that the interaction between these atoms is described by Hooke’s law; the spring constant $\alpha$ is taken to be that of a harmonic oscillator. This model describes many of the basic properties of a diatomic lattice. However, as will become clear in Chapter 6, it is essential to supplement the so-called ‘harmonic’ interactions with anharmonic interactions in order to describe the important process of phonon decay.

### 2.3.1 Dispersion relations for high-frequency and low-frequency modes

To model the normal modes of this system of masses, the atomic displacements along the direction of the chain – the so-called longitudinal displacements of each of the two types of atoms – are taken to be

$$u_{2r} = A_1 e^{i(2rq - \omega t)}$$  \hspace{1cm} (2.1)

and

$$u_{2r+1} = A_2 e^{i[(2r+1)q - \omega t]}$$  \hspace{1cm} (2.2)

where $q$ is the phonon wavevector and $\omega$ is its frequency. In the nearest-neighbor approximation, these longitudinal displacements satisfy

$$m(d^2u_{2r}/dt^2) = -\alpha(u_{2r} - u_{2r-1}) - \alpha(u_{2r} - u_{2r+1}) = \alpha(u_{2r+1} + u_{2r-1} - 2u_{2r})$$  \hspace{1cm} (2.3)

and

$$M(d^2u_{2r+1}/dt^2) = -\alpha(u_{2r+1} - u_{2r}) - \alpha(u_{2r+1} - u_{2r+2}) = \alpha(u_{2r+2} + u_{2r} - 2u_{2r+1}).$$  \hspace{1cm} (2.4)

The signs in the four terms on the right-hand sides of these equations are determined by considering the relative displacements of neighboring atoms. For example, if the positive displacement of $u_{2r}$ is greater than that of $u_{2r-1}$ there is a restoring force $-\alpha(u_{2r+1} - u_{2r})$. Hence

$$-m\omega^2 A_1 = \alpha A_2(e^{iqa} + e^{-iqa}) - 2\alpha A_1$$ \hspace{1cm} (2.5)

and

$$-M\omega^2 A_2 = \alpha A_1(e^{iqa} + e^{-iqa}) - 2\alpha A_2.$$ \hspace{1cm} (2.6)

Eliminating $A_1$ and $A_2$,

$$\omega^2 = \alpha \left( \frac{1}{m} + \frac{1}{M} \right) \pm \alpha \left[ \left( \frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 qa}{mM} \right]^{1/2}.$$ \hspace{1cm} (2.7)

This relationship between frequency and wavevector is commonly called a dispersion relation. The higher-frequency solution is known as the optical mode.
since, for many semiconductors, its frequency is in the terahertz range, which happens to coincide with the infrared portion of the electromagnetic spectrum. The lower-frequency solution is known as the acoustic mode. More precisely, since only longitudinal displacements have been modeled, these two solutions correspond to the longitudinal optical (LO) and longitudinal acoustic (LA) modes of the linear-chain lattice. Clearly, the displacements along this chain can be described in terms of wavevectors \( q \) in the range from \(-\pi/2a\) to \(\pi/2a\). From the solution for \( \omega \), it is evident that over this Brillouin zone the LO modes have a maximum frequency \(2\alpha(1/m + 1/M)^{1/2}\) at the center of the Brillouin zone and a minimum frequency \((2\alpha/m)^{1/2}\) at the edge of the Brillouin zone. Likewise, the LA modes have a maximum frequency \((2\alpha/M)^{1/2}\) at the edge of the Brillouin zone and a minimum frequency equal to zero at the center of the Brillouin zone.

In polar semiconductors, the masses \( m \) and \( M \) carry opposite charges, \( e^* \) and \(-e^*\), respectively, as a result of the redistribution of the charge associated with polar bonding. In polar materials such ionic bonding is characterized by values of \( e^* \) equal to 1, to an order-of-magnitude. When there is an electric field \( E \) present in the semiconductor, it is necessary to augment the previous force equation with terms describing the interaction with the charge. In the long-wavelength limit of the electric field \( E \), the force equations then become

\[
-m\omega^2 u_{2r} = m(d^2u_{2r}/dt^2) = \alpha(u_{2r+1} + u_{2r-1} - 2u_{2r}) + e^* E \\
= \alpha(e^{i2qa} + 1)u_{2r-1} - 2au_{2r} + e^* E \tag{2.8}
\]

and

\[
-M\omega^2 u_{2r+1} = M(d^2u_{2r+1}/dt^2) = \alpha(u_{2r+2} + u_{2r} - 2u_{2r+1}) - e^* E \\
= \alpha(1 + e^{-i2qa})u_{2r+2} - 2au_{2r+1} - e^* E. \tag{2.9}
\]

Regarding the phonon displacements, in the long-wavelength limit there is no need to distinguish between the different sites for a given mass type since all atoms of the same mass are displaced by the same amount. In this limit, \( q \to 0 \). Denoting the displacements on even-numbered sites by \( u_1 \) and those on odd-numbered sites by \( u_2 \), in the long-wavelength limit the force equations reduce to

\[
-m\omega^2 u_1 = 2\alpha(u_2 - u_1) + e^* E \tag{2.10}
\]

and

\[
-M\omega^2 u_2 = 2\alpha(u_1 - u_2) - e^* E. \tag{2.11}
\]

Adding these equations demonstrates that \(-m\omega^2 u_1 - M\omega^2 u_2 = 0\) and it is clear that \(mu_1 = -Mu_2\); thus

\[
-m\omega^2 u_1 = 2\alpha\left(-\frac{m}{M}u_1 - u_1\right) + e^* E \tag{2.12}
\]
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and

\[-M\omega^2 u_2 = 2\alpha \left( u_1 + \frac{m}{M} u_1 \right) - e^* E; \]  

(2.13)

accordingly,

\[-(\omega^2 - \omega_0^2) u_1 = e^* E/m \]  

(2.14)

and

\[-(\omega^2 - \omega_0^2) u_2 = -e^* E/M \]  

(2.15)

where \(\omega_0^2 = 2\alpha (1/m + 1/M)\) is the resonant frequency squared, in the absence of Coulomb effects; that is, for \(e^* = 0\). The role of \(e^*\) in shifting the phonon frequency will be discussed further in the next section.

Clearly, the electric polarization \(P\) produced by such a polar diatomic lattice is given by

\[P = \frac{Ne^* u}{\epsilon(\infty)} = \frac{Ne^* (u_1 - u_2)}{\epsilon(\infty)} = \frac{1}{\epsilon(\infty)} \frac{Ne^*2}{(\omega_0^2 - \omega^2)} \left( \frac{1}{m} + \frac{1}{M} \right) E, \]  

(2.16)

where \(u = u_1 - u_2\), \(N\) is the number of pairs per unit volume, and \(e^*\) is as defined previously. This equation may be rewritten to show that it describes a driven oscillator:

\[(\omega_0^2 - \omega^2) u = e^* \left( \frac{1}{m} + \frac{1}{M} \right) E. \]  

(2.17)

2.3.2 Displacement patterns for phonons

As discussed in subsection 2.3.1, in the limit \(q \to 0\) the displacements, \(u_1\) and \(u_2\), of the optical modes satisfy \(-mu_1 = Mu_2\) and the amplitudes of the two types of mass have opposite signs. That is, for the optical modes the atoms vibrate out of phase, and so with their center of mass fixed. For the acoustic modes, the maximum frequency is \((2\alpha/M)^{1/2}\). This maximum frequency occurs at the zone edge so that, near the center of the zone, \(\omega\) is much less than \((2\alpha/M)^{1/2}\). From subsection 2.3.1, the ratio \(A_2/A_1\) may be expressed as

\[\frac{A_2}{A_1} = \frac{2\alpha \cos qa}{2\alpha - M\omega^2} = \frac{2\alpha - m\omega^2}{2\alpha \cos qa}, \]  

(2.18)

and it is clear that the ratio of the displacement amplitudes is approximately equal to unity for acoustic phonons near the center of the Brillouin zone. Thus, in contrast to the optical modes, the acoustic modes are characterized by in-phase motion of...