Chapter 3
Properties of Nanostructures

In Chapter 2, the reduction of the extent of a solid in one or more dimensions was shown to lead to a dramatic alteration of the overall behavior of the solids. Generally, the physical properties of any given material can be characterized by some critical length, e.g., thermal diffusion length and attenuation distance. What makes nanoparticles very interesting and endows them with their remarkable properties is that their dimensions are smaller than a relevant critical length. Accordingly, the electron states of nanostructures are quantized, leading to new and usually striking electrical, thermal, magnetic, optical, and mechanical properties at the nanoscale. Accordingly, nanostructures are of both basic and practical interest since their physico-chemical properties can be tailored by controlling their size and shape at the nanoscale, leading to improved and/or novel applications.

The energy spectrum (i.e., the ensemble of discrete eigenenergies) of a quantum well, quantum wire, or quantum dot can be engineered by controlling (i) the size and shape of the confinement region and (ii) the strength of the confinement potential. The resulting control over the physico-chemical properties of the nanostructures is limited only by the accuracy of the experimental techniques used for the fabrication of the low-dimensional structures (Chapter 4). The situation is not unlike that of quantum phenomena, many of which were described at the beginning of the 20th century but could not be demonstrated until the 1960s to 1970s when appropriate nanofabrication techniques were developed.

Not only is fabrication at the nanoscale limited by the available techniques, but other practically unavoidable factors such as imperfections—known to influence the properties of any material—may have very significant impacts on the properties of nanomaterials. As such, size dispersion, shape dispersion, defects, residual stresses, impurities, etc., are of great importance for devices of reduced dimensionality. These factors may, in many instances, create a gap between expectation and realization.

As in Chapter 2, the reader who is not interested in the details on how the electrical, thermal, magnetic, optical, and mechanical properties change at the nanoscale may prefer to skip to Section 3.7, wherein the most significant properties are summarized.

3.1 Band Diagrams

In order to understand many of the properties of nanostructured materials, a basic knowledge of band diagrams is required, along with knowledge of such concepts as bandgap energy, direct/indirect bandgaps, holes, and excitons. A band diagram depicts the energy of an allowed state of a charge-carrying particle in a particular material as a function of its momentum or, equivalently because of wave–particle duality, as a function of the wave vector $\vec{k}$. The magnitude of the wave vector is the wave number denoted by k. In a band diagram, the allowed energy states are grouped into bands, the valence band and the conduction band being the most important bands for the description of the properties of many materials. As the wave vector is a 3D quantity, band diagrams should be 4D plots. However, very often only 2D and 3D plots for specific ranges of the wave vector direction are drawn; furthermore, symmetries often allow 3D plots to be developed as 2D plots.

Figure 3.1 presents typical 1D band diagrams for direct- and indirect-bandgap semiconductors, the direction of the wave vector being fixed, but not its magnitude. The two basic features that play an important role in the behavior of any material can be gleaned from a band diagram: (i) the bandgap energy E_g and (ii) whether the bandgap is direct or indirect. The bandgap is an energy range wherein no states are allowed for charge carriers to occupy. As the bandgap energy is defined as the difference in energy between the lowest point of the conduction band and the highest point of the valence band, E_g is the vertical distance between these two bands in the band diagram. Typical values of the bandgap energy at room temperature are: $E_g(\text{Si}) = 1.11$ eV, $E_g(\text{Ge}) = 0.66$ eV, $E_g(\text{GaAs}) = 1.43$ eV, $E_g(\text{CdS}) = 2.42$ eV, and $E_g(\text{InP}) = 1.27$ eV.

The traversal of bandgaps by charge carriers involves the net exchange of energy between the charge carriers on the one hand and photons and/or phonons on the other. Photons of energy $\hbar\omega$ are quanta of light. Phonons of energy $\hbar\omega$ are also
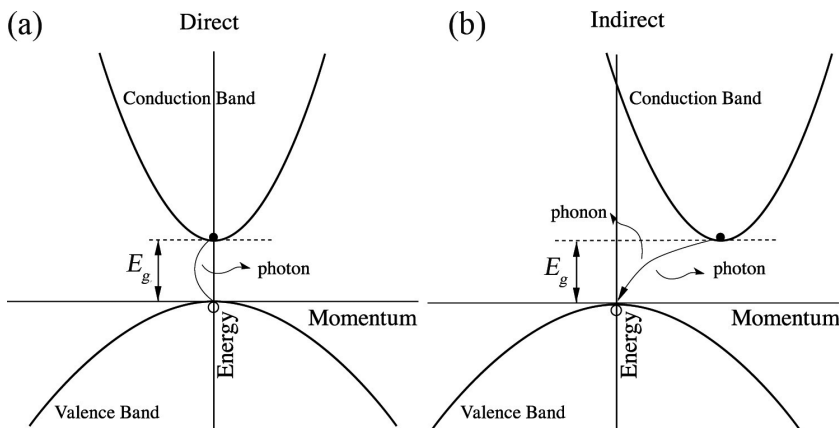

Figure 3.1 One-dimensional band diagrams containing (a) direct and (b) indirect bandgaps. These 2D plots are called 1D band diagrams because the direction of the wave vector (or momentum) has been fixed, but its magnitude is allowed to vary.

quantum particles, being defined as quanta of excitation of the crystalline-lattice-vibration modes of angular frequency ω. The concept of a phonon arises from a quantum-mechanical treatment of lattice vibrations in a solid, after assuming that a lattice-vibration mode is analogous to a simple harmonic oscillation. Phonons play an important role in the behavior of solids by affecting their optical, electrical, and thermal properties through interactions with photons, electrons, neutrons, etc.

A bandgap can be either direct or indirect. In a direct-bandgap material the maximum energy of the valence band and the minimum of the conduction band occur at the same value of the momentum, as depicted in Fig. 3.1(a). Either photons supply the necessary energy for a particle to climb to conduction band from the valence band, or photons are emitted during the transition of the particle from the conduction band to the valence band. No phonons participate in the transitions from the conduction/valence band to the valence/conduction band. Most III–V compound semiconductors, such as GaAs, are direct-bandgap semiconductors and are widely used for optoelectronic applications.

An indirect-bandgap semiconductor is one in which the maximum energy of the valence band and the lowest energy of the conduction band occur at different values of the momentum, as shown in Fig. 3.1(b). Since momentum (in addition to energy) must be conserved in any interband transition, phonons need to participate in these transitions, making these transitions less likely (or less efficient) in indirect-bandgap semiconductors. Silicon and germanium are examples of indirect-gap semiconductors, with limited practical use in optoelectronics.

Energy bands are populated by charge carriers, i.e., electrons and holes. Holes are virtual entities that can be thought as electron vacancies. The charge of a hole is opposite in sign but equal in magnitude to that of an electron. The effective mass of a hole is somewhat different from that of an electron, their respective effective masses being dependent on the curvatures of the valence and conduction bands.

An exciton is a quasi-particle comprising an electron and a hole bound to each other. As an exciton's energy is slightly below the bandgap energy, transitions of slightly lower energy than E_g become possible. Excitons can move through a material and transport energy, although they do not transport charge as they are electrically neutral. Typical binding energies of excitons are E_{ex} (Si) = 14.7 meV, E_{ex} (Ge) = 4.15 meV, E_{ex} (GaAs) = 4.2 meV, E_{ex} (CdS) = 29.0 meV, and E_{ex} (InP) = 4.0 meV.

3.2 Electrical-Transport Properties

The changes that occur in the electronic properties as the length scale is reduced are mainly related to the increasing influence of the wavelike properties of the electrons and the scarcity of scattering centers. As one or more dimensions become comparable with the de Broglie wavelengths of electrons (see Section 2.1), the discrete nature of the energy states becomes apparent, although a fully discrete energy spectrum is observed only in systems that are confined in all three dimensions. The finite spacing of energy states as a result of quantum-mechanical

confinement engenders fundamental and technologically important phenomena, which are being explored for electronic nanodevices.

Although electrical transport occurs through the motion of both electrons and holes, the remainder of this section is focused on electrons but can be adapted to holes. The confinement of charge carriers in two or fewer dimensions results in quantized energy levels, as discussed in Chapter 2. The confinement of electrons to a 2D structure consisting of a conducting strip of width w and length l amounts to the creation of a 2D electron gas (2DEG). Its conductance is given by

$$G = \sigma \frac{w}{l},\qquad(3.1)$$

and its conductivity by

$$\sigma = \frac{\rho_s e^2 \tau}{m^*},\qquad(3.2)$$

where e is the charge of an electron and τ is a relaxation time that takes into account the delay due to the collisions of electrons with the structure. The physical definition of G is the ratio of the total current to the voltage drop across a sample of length l in the direction of current flow. For a 3D electron gas (3DEG), this relationship can be used when replacing w by the cross-sectional area A orthogonal to the current flow. Similar expressions are also valid for the thermal transport of energy, as discussed in Section 3.3.

Novel size-dependent effects emerge as the dimensions w (or A) and l are reduced toward atomic dimensions in the nanometer range. The relationship expressed by Eq. (3.1) holds in the diffusive-transport regime where both w and l are greater than the mean free path λ_e of the electrons. As the width of the strip decreases, quantum-mechanical effects begin to emerge. The quantum-mechanical confinement of an electron in a strip of width w leads to the discretization of energy levels given by $E_n = \hbar^2/2m^*(n\pi/w)^2$, $(n = 1, 2, 3, \ldots.)$, per Eq. (2.10), where m^* is the effective mass of the electron and $\hbar$ is the reduced Planck constant. The conductance is determined by the number of these w-dependent transverse confined states that are occupied. Thus, rather than a simple linear dependence of G on w, quantum mechanics forces a particular dependence of G on w. As w is altered, the energy spectrum changes, as does the number of occupied states below the Fermi energy level E_F, which is the highest energy level occupied by electrons (or, more precisely, fermions) at $T = 0$ K; hence, the conductance changes as well. Thus, the quantum-mechanical effect of reducing the dimension w is the change of conductance in discrete steps, much like a staircase.

Quantization of conductance can be observed even at room temperature in some special cases, but in general this effect is exhibited at very low temperatures. In a short quasi-1D channel formed between two regions of a 2DEG in an AlGaAs/GaAs heterostructure by the action of metallic gate electrodes deposited on top of the layered structure, as shown in Fig. 3.2(a), the conductance increases
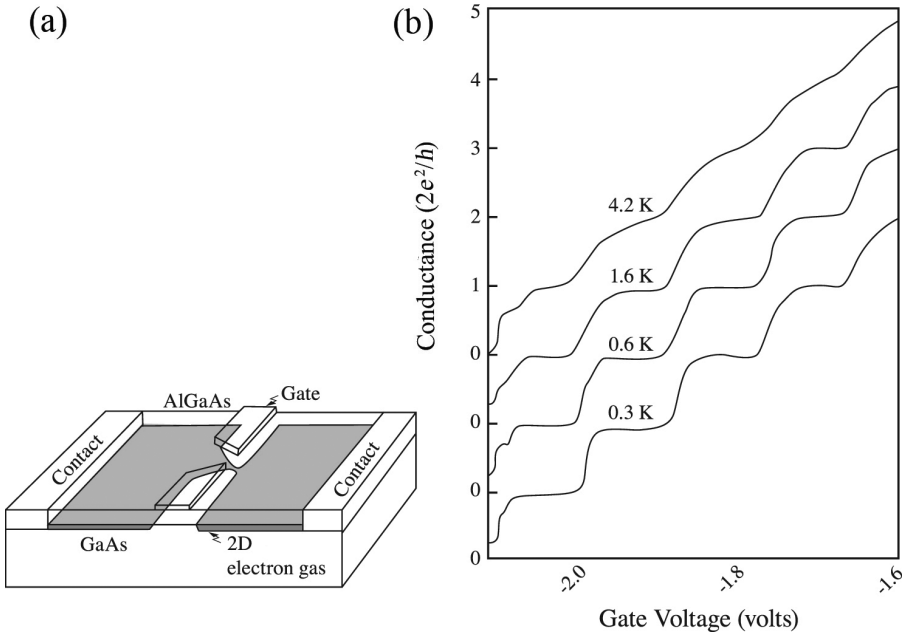
(a)

(b)

Figure 3.2 (a) Schematic representation of a quantum point contact, defined in a high-mobility 2D electron gas at the interface of a GaAs/AlGaAs heterojunction. The point contact is formed when a negative voltage is applied to the gate electrodes on top of the AlGaAs layer. Transport measurements are made by employing contacts to the 2D electron gas at either side of the constriction. (b) Conductance quantization of a quantum point contact in units of $2e^2/h$. As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise. The resulting conductance steps are smeared out when the thermal energy becomes comparable to the energy separation of the modes. [Reprinted with permission from van Houten and Beenakker.[1] © 2005, American Institute of Physics.]

in discrete steps as the electron density in the channel is increased. Figure 3.2(b) shows a sequence of steps in the conductance of a constriction in a 2DEG, as the width *w* is varied by the application of a voltage across the gate.

The effect on the conductance *G* of reducing the length *l* is a particularly interesting phenomenon. If the ohmic regime were to hold in Eq. (3.1), the reduction of *l* toward zero would make *G* increase without limit, and the resistance would decrease to zero. However, there is always a finite residual resistance. In the ballistic transport regime $l < \lambda_e$, electrons can propagate without losing their initial momentum since scattering events can be neglected. The expression for ballistic conductance including two-spin orientation (spin degeneracy) in the ideal case becomes

$$G = \frac{2e^2}{h}. \tag{3.3}$$

This relationship is usually called the Landauer formula.

Accordingly, the ballistic conductance of a 1D channel is quantized in units of the conductance quantum $G_0 = 2e^2/h = 7.748 \times 10^{-5}\ \Omega^{-1}$, which is twice the reciprocal of the resistance quantum $R_0 = h/e^2 = 2.581 \times 10^4\ \Omega$. The Landauer formula for quantum transport can be generalized to a network in which several wires connect a barrier with reservoirs, leading to an expression that sums over the contribution of each channel. Then, with N_c being the number of channels available for transport (i.e., the number of transverse modes with energies below the Fermi energy of the electrodes or electron reservoirs), we have

$$G = N_c \frac{2e^2}{h}. \tag{3.4}$$

This leads to quantized conductance and well-defined steps in the measured resistance as either the Fermi energy or the effective width of the wire is changed. Thus, while the classical conductance depends linearly on the width ($G \propto w$), the quantum-mechanical conductance increases in discrete steps of $2e^2/h$ as w increases enough to permit one more transverse-quantization state to be occupied and hence available for conduction.

Quantization is very important for quantum wires of small cross-sectional dimensions and depends on how conduction electrons interact with the atoms of a material. In practice, semiconductor wires unambiguously show conductance quantization for large cross-sectional dimensions ($\sim$100 nm) because the electronic states due to confinement are spatially extended. As a result, their Fermi wavelengths $\lambda_F = hc/E_F$ are large, which means that adjacent energy states are not widely separated since E_F is inversely proportional to λ_F. Hence, the energy state of an electron can be resolved only at a cryogenic temperature (few Kelvin) where the thermal excitation energy is lower than the interstate energy gaps. For metals, quantization corresponding to the lowest energy state is only observed for atomic wires. Its wavelength being thus extremely small, a metallic atomic wire has widely separated energy states, which allows resistance quantization to be easily observed at room temperature.

Conduction in highly confined 0D structures, such as quantum dots, is very sensitive to the presence of other charge carriers and, hence, the charge state of the dot. Transport through quantum dots shows striking effects due to the electron's wave nature and its finite charge. If a particular quantum dot is fully decoupled from its environment, it confines a well-defined number N of electrons. For weak coupling, deviations due to tunneling through the barriers are small, leading to discrete values of the total electrostatic energy of the quantum dot. This energy can be estimated as $N(N-1)e^2/2C$, where C is the capacitance of the quantum dot. Thus, Ne^2/C is the amount of energy required to increase the number of confined electrons by one. This additional energy is discretely spaced in units of e^2/C. If this charging energy exceeds the thermal energy k_BT, where k_B is the Boltzmann constant and T is the temperature, the electrons cannot tunnel on and off the quantum dot by thermal excitations alone, and transport can be blocked, which is referred to as a Coulomb blockade.