

Chapter 1

Modelling of Heterostructures for Low Dimensional Devices

H. Hakan Gürel, Özden Akıncı and Hilmi Ünlü

Abstract Advancement in the theoretical understanding and experimental development of the science and technology of low dimensional electronic and optical devices requires qualitatively reliable and quantitatively precise theoretical modelling of the structural, electronic and optical properties of semiconducting materials and their heterostructures to predict their potential profiles. In this chapter, we review the calculation techniques of electronic band structures of III–V and II–VI compounds and their heterostructures. We focus on the semiempirical tight binding theory (with sp^3 , sp^3s^* , $sp^3d^5s^*$ and sp^3d^5 orbital sets) and density functional theory (DFT), which, in turn, employs the modified Becke-Johnson exchange-correlation potential with a local density approximation (DFT-MBJLDA). We conclude that the density functional theory and semiempirical tight binding theory can easily be employed in relation to charge transport in heterostructure devices as well as in the accurate design and simulation of low dimensional semiconductor electronic and optical devices.

H. Hakan Gürel

Computational Science and Engineering Programme, Information Systems Engineering
Department, Technology Faculty, Kocaeli University, 41380 Kocaeli, Turkey
e-mail: hhakan.gurel@kocaeli.edu.tr

Ö. Akıncı · H. Ünlü (✉)

Computational Science and Engineering Programme, Informatics Institute, İstanbul
Technical University, 34469 Maslak, İstanbul, Turkey
e-mail: hunlu@itu.edu.tr

Ö. Akıncı

e-mail: akincio@gmail.com

H. Ünlü

Department of Physics, Faculty of Science and Letters, İstanbul Technical University, 34469
Maslak, İstanbul, Turkey

1.1 Introduction

Progress in the theoretical understanding and experimental development of the science and technology of semiconductor devices has grown rapidly ever since the invention of first transistor in 1949 [1–6]. Advances in growing semiconductor thin films having differing structural, electronic and optical properties with varying composition and layer thickness (even approaching atomic dimensions) have provided new opportunities and challenges in basic scientific studies and in their device applications in the electronics industry. The combination of advanced growth, characterization and fabrication technologies has led to the production of an impressive number of high performance semiconductor devices for fast signal processing and the discovery of some novel structures that are of special interest to solid state scientists and device engineers. One can now control the alloy composition and doping in ternary and quaternary alloys based on group IV–IV, III–V and II–VI semiconductor compounds over atomic distances, as low as tens of angstroms. These man-made heterostructures, are easily grown as lattice mismatched substrates (e.g. growth of GaAs on Si substrates [5, 6]) by modern crystal growth techniques including molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). The epitaxial layers are so thin that quantum mechanical effects are prominently realized. The resulting contemporary low dimensional semiconductor devices (e.g., heterostructure bipolar transistors (HBTs) and modulation doped field effect transistors (MODFETs), nanowires, quantum dots, etc.) are known to operate much faster than conventional silicon devices (e.g., silicon bipolar junction transistors (BJTs) and metal oxide semiconductor field effect transistors (MOSFETs)); this is crucial for the electronic and optical communication and computer industries.

When the semiconductor composition changes abruptly across the interface between two constituents, the difference in their energy bandgaps is accommodated by the discontinuities in the conduction and valence bands [7, 8]. There are three types of interface formation between a wide bandgap semiconductor and a narrow bandgap semiconductor shown in Figs. 1.1, 1.2 and 1.3;

- (i) **Type I heterostructure:** The bandgap of the barrier semiconductor overlaps (straddling lineup) that of the well and equilibrium Fermi level is near the middle of the bandgap on both sides, as shown in Fig. 1.1. Both an electron and a hole tend to localize in the narrow bandgap quantum well. Such semiconductor heterostructure is useful in optoelectronic applications such as lasers, with both electrons and holes participate to device operation.
- (ii) **Type II heterostructure:** The bandgap of the barrier semiconductor partially overlaps (staggered lineup) that of the well and the equilibrium Fermi level is close to the conduction band (or valence band) on one side while it is near the middle of the bandgap on other side, as shown in Fig. 1.2. The potential energy gradient tends to spatially separate electron and hole on different sides of heterointerface. Large potential barrier in conduction (or valence) band at heterointerface leads to a better electron (hole) confinement in field effect transistors with higher electron (hole) concentration. Position of equilibrium

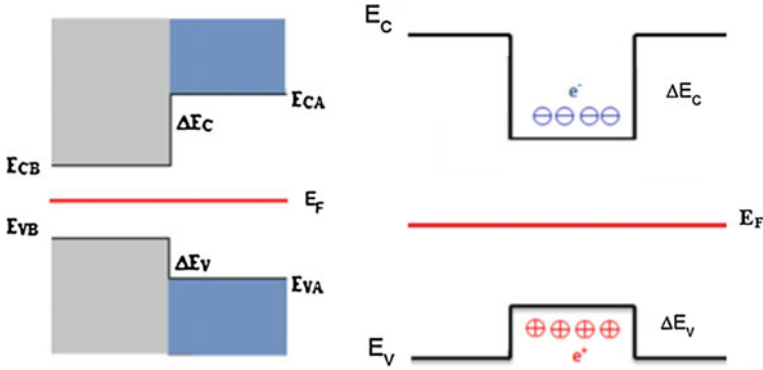


Fig. 1.1 The schematic energy band diagram of Type I heterostructure: electrons and holes localize in the narrow gap quantum well

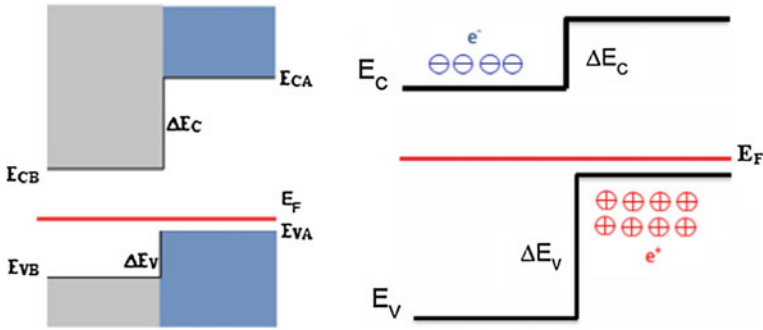


Fig. 1.2 Schematic energy band diagram of Type II heterostructure: the potential energy gradient tends to spatially separate electrons and holes on different sides of heterointerface

Fermi level determines the density of carrier confinement on either side of the heterointerface. When equilibrium Fermi level is close to conduction band of wide bandgap constituent (left) the density of electrons in its conduction band is greater but when it is closer to the valence band of narrow bandgap constituent (right) the number of holes is greater there.

- (iii) **Type III heterostructure:** This is the extreme case of Type II band alignment. The bandgap of the barrier does not overlap at all (broken gap lineup), as shown in Fig. 1.3. The equilibrium Fermi level is well above the conduction band minimum (or well below the valence band maximum) on one side while it is near the middle of the bandgap on the other side. Position of equilibrium Fermi level determines the carrier confinement on either side of the heterointerface. When equilibrium Fermi level is close to conduction band of wide bandgap constituent (left) the number of electrons in its conduction band is greater but when it is closer to the valence band of narrow bandgap constituent (right) the number of holes is greater there.

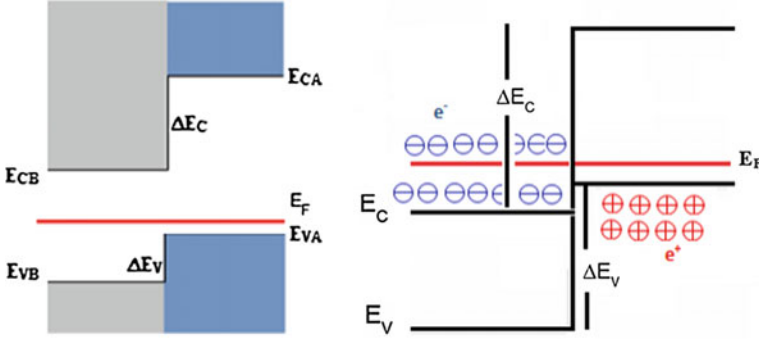


Fig. 1.3 Schematic energy band diagram of Type II heterostructure: the potential energy gradient tends to spatially separate electrons and holes on different sides of heterointerface

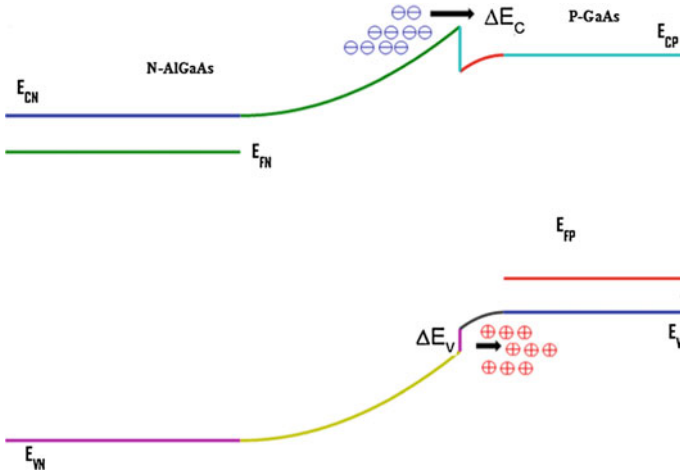
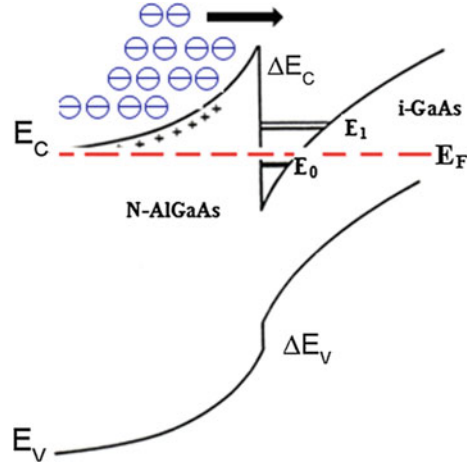


Fig. 1.4 The schematic energy band diagram of a forward biased N-AlGaAs/p-GaAs emitter/base part a of Npn heterojunction bipolar transistor (HBT) in forward active mode

The impact of heterostructures on semiconductor device physics and technology is twofold [1, 2]. The first impact of heterostructures is a high charge carrier injection efficiency that can be obtained in an anisotype heterojunction bipolar transistor (HBT), in which the charge carriers are flowing from a wide bandgap emitter (e.g., AlGaAs) to narrow bandgap base (e.g., GaAs) as shown in Fig. 1.4. When a Np hetero-emitter is forward biased, the potential barrier blocking electron emission from the emitter to the base is lowered and electrons injected from the emitter diffuse across the base and are collected in the collector. Furthermore, holes injected from the base into the emitter are blocked by the valence band offset as $\Delta E_v/kT$.

The second impact of heterostructures involves the confinement of charge carriers in a narrow bandgap two dimensional electron gas (2DEG) quantum well structure to reduce their scattering by parent impurities in a doped wide bandgap

Fig. 1.5 Schematic energy band diagram of an AlGaAs/GaAs 2DEG. The triangular well in a narrow bandgap GaAs well leads to quantization of the allowed energy levels E_0 and E_1 near the heterointerface



barrier layer, as shown in Fig. 1.5. The charge carrier scattering that limits the high speed character of MOSFETs can be minimized by replacing an oxide/semiconductor junction with a widegap/narrowgap semiconductor heterojunction to separate the free charge carriers in a nominally undoped narrow bandgap quantum well (e.g., i-GaAs) from their parent impurities in the doped wide bandgap (e.g., N-AlGaAs) barrier layer, leading to a much higher mobility and a high current from the drain to the source of a MODFET [2, 4].

Conduction and valence band offsets at the AlGaAs/GaAs interface lead to a depletion of electrons from the wide-bandgap AlGaAs barrier and an accumulation of electrons in the narrow-bandgap GaAs channel where they are quantized due to the potential ‘notch’ at the interface. Quantized energy levels are formed in this well, with the lowest level filled and the second level partially or fully filled by electrons, depending on the electron density; the Fermi level lies between the first and the second sub-bands. Free electrons confined in the channel conduct current parallel to the hetero-interface between the source and the drain of a FET when an electric field is applied parallel to the hetero-interface. As the wide bandgap and narrow bandgap semiconductors reach thermal equilibrium, their Fermi levels align at the heterointerface and the resultant energy band structure is as shown in Fig. 1.4 for a Np heterostructure bipolar device and in Fig. 1.5 for a unipolar heterostructure device, respectively.

1.2 Issues in Modelling of Electronic Structure in Heterostructures

Ever since the invention of the first transistor in 1949, device scientists and engineers have witnessed an amazing growth in semiconductor science and technology. Advances in the growth of semiconductor thin films of different structural,

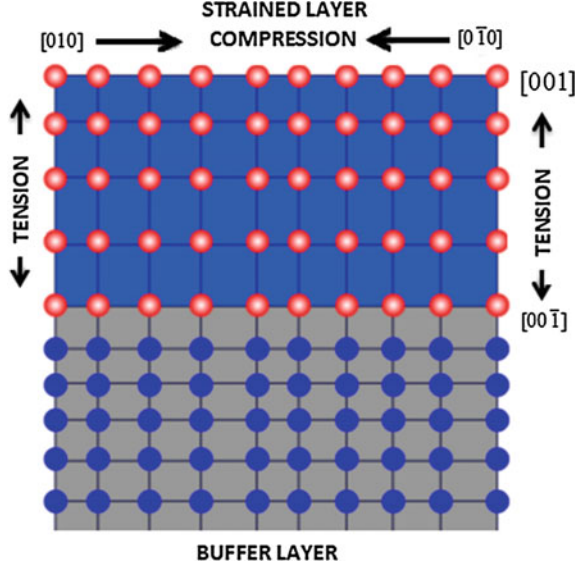
electronic and optical properties and with layer thickness approaching atomic dimensions has provided new opportunities in fundamental science and technology of semiconductors for device applications. Furthermore, contemporary fabrication technologies have further made it possible to reduce the device dimensions to the point where quantum size effects must be described in order to realistically describe the operation and reliably predict the potential and performance of low dimensional semiconductor devices for electronic and optical applications. Such advancement could not have been possible without a qualitatively reliable understanding of the basic physics of semiconducting materials and quantitatively precise potential predictions and performance of devices, leading to new concepts in the semiconductor growth that allowed previously many unknown devices with more complex functionality and much higher densities for electronic and optical applications.

In order to emphasize the importance of heterostructure in low dimensional semiconductor systems it is necessary to understand the interface formation and modelling of the electronic structure of heterostructure constituents. The composition variation in alloy constituent and lattice mismatch between two semiconductors and thermal expansion of lattice constant with the growth temperature will cause strain across the interface that will modify the electronic properties of both materials and consequently, the energy of the moving charge carriers across the interface that influence the device performance [7, 8]. Qualitatively reliable and quantitatively precise modelling and simulation of electronic properties of semiconductor constituents is important for a better prediction of their potential in making low dimensional electronic and optical devices. In the following we will give a brief discussion about the critical structural properties and how they can be implemented in theoretical models for the calculations of electronic properties of heterostructures.

1.2.1 Interface Strain Effects in Heterostructures

When two semiconductors with different lattice constants are grown upon each other, strains will develop across the heterointerface increasing with layer thickness. As long as the thickness of epilayer is kept under a critical thickness, the lattice mismatch will be accommodated by uniform elastic strain, as shown in Fig. 1.6. The interface strain will modify the structural and electronic properties of the constituent semiconductors in directions parallel and perpendicular to the growth direction. Therefore, the lattice matching is known to be important to the electronic properties of semiconductor layers in heteroepitaxy. Until the early 1980s, the studies of heterostructures had focused on semiconducting materials with close lattice matching with a substrate, such as an AlGaAs/GaAs heterostructure quantum well. The constraint on lattice matching in crystal growth is essential for relatively thick epitaxial layers since a large lattice mismatch can cause the occurrence of misfit dislocations with large densities. Such lattice-matched growth will prevent the generation of misfit dislocations that would degrade charge transport and lower device performance.

Fig. 1.6 Strained heteroepitaxy is a result of growth of materials with dissimilar lattice constants



The lattice constant of strained epilayer along the growth direction is equal to that of the substrate and is expanded or compressed in the direction parallel to the interface, shown in Fig. 1.6. Considering the (001) heteroepitaxial growth, elastic theory allows one to decompose the biaxial strain tensor into the sum of hydrostatic and uniaxial strains along the growth direction.

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{f||} = \left(\frac{a_{f||}}{a_{f0}} - 1 \right), \quad \varepsilon_{zz} = \varepsilon_{f\perp} = \left(\frac{a_{f\perp}}{a_{f0}} - 1 \right) = 2 \left(\frac{C_{12}}{C_{11}} \right)_f \varepsilon_{f||} \quad (1.1)$$

where $\varepsilon_{f\perp}$ and $\varepsilon_{f||}$ are the strain components perpendicular and parallel to growth direction. The epilayer lattice constant will be equal to that of the substrate along the growth direction: $a_{f||} = a_s$ and is expanded by the bulk value of its Poisson ratio perpendicular to the growth direction:

$$a_{f\perp} = a_{f0} \left[1 - 2 \left(\frac{C_{12}}{C_{11}} \right)_f \left(\frac{a_{f||}}{a_{f0}} - 1 \right) \right], \quad (1.2)$$

where, a_{f0} is the bulk lattice constant and C_{11} and C_{12} are the bulk elastic stiffness constants of the strained layer. a_s is the bulk lattice constant of the substrate. Equations (1.1) and (1.2), suggest that when a thin layer is deposited on a buffer (or substrate) with large mismatch, the epilayer will be under strain. The lattice constant of the epilayer along and perpendicular to the interface will change to minimize its elastic energy. The interface strains due to lattice mismatch and thermal expansion gradients over the crystal growth temperature can co-exist in heterolayers in low dimensional heterostructures; it is difficult to assign the observed stress to

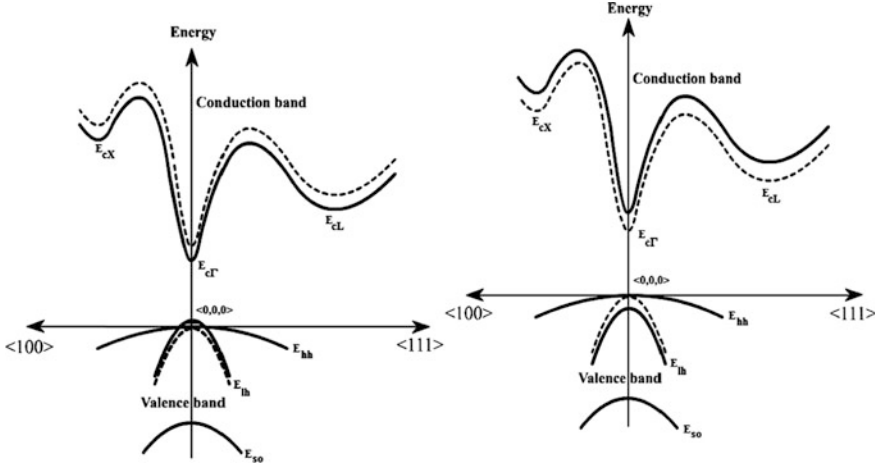


Fig. 1.7 The schematic view of energy band diagram of a semiconductor under tensile strain bandgap decreases (*left*) and compressive strain bandgap increases (*right*). Heavy hole (HH), light hole (LH) and split-off (SO) bands are also shifted with respect to top of the valence band energy

either one or the other. The thermal expansion of lattice constants of epilayer and the substrate with the growth temperature cause the lattice constant parallel and perpendicular to the hetero-interface to change with temperature. High resolution x-ray scattering measurements of GaAs grown on a Si substrate [9] show that the thermal expansion of GaAs perpendicular to the growth direction follows the thermal expansion of a Si substrate $\alpha_{f\parallel}(T) = \alpha_s(T)$ and is therefore smaller than that of bulk GaAs. However, the thermal expansion along the growth direction exceeds the bulk GaAs value by the Poisson ratio as a result of the in-plane constraint;

$$\alpha_{f\perp}(T) = \alpha_f(T) + 2 \frac{C_{12f}}{C_{11f}} [\alpha_f(T) - \alpha_s(T)], \quad (1.3)$$

where $\alpha_s(T)$ and $\alpha_f(T)$ are the bulk linear thermal expansion coefficients of Si and GaAs. Strain across the interface that will modify the electronic properties of both materials, including the band offsets. Compressive (or tensile) strain in epilayer results in an increase (or decrease) in conduction and valence band energy levels [2], as shown in Fig. 1.7.

The uniaxial component of the biaxial strain tensor splits the heavy-hole, light-hole and split-off valence band edges relative to the average valence band edge. The heavy-hole, light-hole and split-off band energies relative to the average valence band edge E_v are

$$E_{vh}(\varepsilon) = E_v(\varepsilon) + \frac{1}{3}\Delta - \frac{1}{2}\delta E, \quad (1.4a)$$

$$E_{vl}(\varepsilon) = E_v(\varepsilon) - \frac{1}{6}\Delta + \frac{1}{4}\delta E + \frac{1}{2}\sqrt{\Delta^2 + \Delta\delta E + \frac{9}{4}\delta E^2}, \quad (1.4b)$$

$$E_{vs}(\varepsilon) = E_v(\varepsilon) - \frac{1}{6}\Delta + \frac{1}{4}\delta E - \frac{1}{2}\sqrt{\Delta^2 + \Delta\delta E + \frac{9}{4}\delta E^2}, \quad (1.4c)$$

where $\delta E = 2b(\varepsilon_{zz} - \varepsilon_{xx}) = 2b(\varepsilon_{\perp} - \varepsilon_{\parallel})$ and b is the shear deformation potential which describes splitting in the valence band energy due to the [001] uniaxial strain. $E_v(\varepsilon)$ is the average valence band maximum under hydrostatic strain. The hydrostatic component of biaxial strain tensor corresponds to the relative volume change of the strained epilayer; $Tr(\varepsilon) = 2\varepsilon_{\perp} + \varepsilon_{\parallel} = \Delta V/V_0 = (V - V_0)/V_0$, which leads to shifts of the conduction band minimums relative to the average valence band maximum at the Γ point.

According to a statistical thermodynamic model in which the conduction electrons and valence holes are treated as charged chemical particles, the conduction and valence band energy levels energy are expressed as a function of pressure at any temperature as [10, 11]

$$E_i(T, P) = E_i(0, P_0) + C_{iP}^0 T(1 - \ln T) - \frac{a_i}{B} \left[P - \frac{P^2}{2B} - \frac{(1 + B')}{6B^2} P^3 \right], \quad (1.5)$$

where i represents the conduction (c) or valence (v) band energy levels, P is the applied pressure, T is the temperature, $E_i(0, P_0)$ are the conduction or valence band edges at Γ , L and X high symmetry points. E_{ci} and E_v are the conduction and valence band edges at Γ , L and X points with deformation potentials $a_{ci} = -B(\partial E_{ci}/\partial P)$ and $a_v = -B(\partial E_v/\partial P)$. B is the bulk modulus; $B' = \partial B/\partial P$ is its derivative. C_{iP}^0 is the standard heat capacity of conduction electrons and valence holes. $C_{cP}^0 = C_{nP}^0 - C_{0P}^0 = C_{pP}^0 + \Delta C_P^0$ and $C_{vP}^0 = C_{pP}^0$ are the standard heat capacities of conduction electrons and valence holes; $C_{nP}^0 = C_{pP}^0 = (5/2)k$, where k is the Boltzmann's constant. $\Delta C_P^0 = C_{nP}^0 + C_{pP}^0 - C_{0P}^0$ is the heat capacity of reaction of free electron and hole formation obtained by fitting (1.6) to the experimental data [12, 13] and empirical pseudopotential bandgap energy [14] and at high symmetry points in the first Brillouin zone of semiconductors:

$$E_{gl}(T, P) = E_{gi} + \Delta C_P^0 T(1 - \ln T) - \frac{a_{gl}}{B} \left[P - \frac{P^2}{2B} - \frac{(1 + B')P^3}{6B^2} \right], \quad (1.6)$$

where $P = -2B_f C_f \varepsilon_{f\parallel}$ and $P = -3B_s \varepsilon_{s\parallel}$ for the epilayer and the substrate, respectively. In the case of (001) pseudomorphic growth, $\varepsilon = \varepsilon_{f\parallel} = (a_{f\parallel} - a_f)/a_f$ is the strain in the epilayer along the growth direction and $C_f = (C_{11} - C_{12})/C_{11}$.

Any interface strain will modify the energy band structure and charge transport in heterobipolar and unipolar devices. It should be noted that as the device dimension is reduced to nanoscale of the order of Bohr radius of charged carriers, the use of continuum elastic theory becomes questionable [15]. In such a case one should use the atomic elasticity theory known as valence force field (VFF) approach [16], especially as the lattice mismatch at heterointerface becomes large.

1.2.2 Composition Effects in Heterostructures

Semiconductor alloys based on IV–VI, III–V and II–VI compounds are important in fabricating low dimensional bipolar and unipolar heterostructure devices since their structural and electronic properties (e.g., lattice constants and bandgaps) can be tailored independently. Therefore, reliable and accurate determination of composition variation of lattice constant and bandgap energies are very important. In the theoretical determination of composition effects on the structural properties such as lattice constants, a virtual crystal approximation (VCA) is often used [17, 18] in which the compositional disorder effect is neglected. Since in VCA the alloy potential is taken as the concentration weighted average of the constituent potentials the bandgap energy is linear function of alloy composition. However, many experimental studies report that the bandgap energies of semiconductor alloys is nonlinear function of composition. Furthermore, it is believed that the compositional disorder, which is related to the differences of electronegativity of atoms forming a ternary semiconductor, plays a major role in determining its bowing of the bandgap energy when lattice mismatch induced strain plays a crucial role in heterostructure electronic properties.

In our recent studies [19–28] the effects of composition and strain on the electronic properties of semiconductor alloy constituents in heterostructures are implemented in the semiempirical tight binding models and first principles DFT with MBJLDA functional in terms of host bond length and distorted bond length by the substitutional impurity without any adjustable parameter. In determining the composition effects on band structures, we do not follow the common practice which employs the so called virtual crystal approximation (VCA) to the TB Hamiltonian matrix elements and bond length, with or without the compositional disorder of the semiconductor alloys, since the detailed treatment requires inclusion of the compositional disorder effect on the electronic properties. Instead, we employ the method of the modified virtual crystal approximation (MVCA) in which one formulates the composition dependence of the bond length of ternary material [19–28]. The MVCA allows one to accurately take into account the effect of disorder-induced nonlinear variation of the lattice constant on the TB parameters used in calculating the band structure properties. The composition dependence of bond length (or lattice constant) of the ABC ternary is written as the sum of

undistorted bond length ($d_{VCA} = (1-x)d_{AC}^0 + xd_{BC}^0$) due to the virtual crystal approximation (VCA) and the distorted bond length ($d_{relax} = x(1-x)\delta_c(d_{BC}^0 - d_{AC}^0)$) due to cation-anion relaxation of binary in ternary [19–28]:

$$d(x) = (1-x)d_{AC}(x) + xd_{BC}(x) = d_{VCA}(x) + x(1-x)\delta_c(d_{AC}^0 - d_{BC}^0), \quad (1.7a)$$

$$d_{BC}(x) = d_{BC}^0 - (1-x)\xi_{AC:B}(d_{BC}^0 - d_{AC}^0), \quad (1.7b)$$

$$d_{AC}(x) = d_{AC}^0 - x\xi_{BC:A}(d_{AC}^0 - d_{BC}^0), \quad (1.7c)$$

where $d_{AC}(x)$ and $d_{BC}(x)$ are the bond lengths of AC and BC binaries in an ABC ternary, d_{AC}^0 and d_{BC}^0 are the undistorted bond lengths of the host materials AC and BC and $\xi_{AC:B}$ and $\xi_{BC:A}$ are two dimensionless relaxation parameters [29],

$$\xi_{AC:B} = \frac{1}{1 + \frac{\alpha_{AC}}{6\alpha_{BC}}(1 + 10\frac{\beta_{AC}}{\alpha_{AC}})}, \quad \xi_{BC:A} = \frac{1}{1 + \frac{\alpha_{BC}}{6\alpha_{AC}}(1 + 10\frac{\beta_{BC}}{\alpha_{BC}})}, \quad (1.7d)$$

δ_c is the difference between dimensionless relaxation parameters: $\delta_c = \xi_{AC:B} - \xi_{BC:A}$. As an example, Fig. 1.8 shows the composition variation of the lattice constants and interface strain in AlGaIn and InGaIn ternaries in AlGaIn/GaN and InGaIn/GaN heterostructures, respectively. Compressive strain at the InGaIn/GaN heterointerface decreases the lattice constant of the InGaIn ternary constituent as composition increases. Whereas tensile strain at the AlGaIn/GaN heterointerface increases the lattice constant of the AlGaIn ternary constituent as composition increases, such an increase or decrease in lattice constant due to interface strain will change the electronic properties of the heterostructure ternary constituents. Therefore, it is essential that we include the compositional disorder effect on the structural and electronic properties of constituents in lattice mismatched heterostructures. Equation (1.7a–1.7d) can then be used to take into account the composition effects on the band structures of the ternary constituent of heterostructures in the theoretical models such as first principles WIEN2K simulations package with the MBJLDA functional embedded in DFT and semiempirical sp^3 , sp^3s^* , $sp^3d^5s^*$ and sp^3d^5 tight binding models.

The diagonal or off-diagonal matrix elements in the NN sp^3d^5 and 2NN sp^3s^* TB Hamiltonian matrix elements for an ABC ternary semiconductor are expressed as [19–28]

$$E_{\alpha/\beta}(x) = (1-x)E_{\alpha/\beta}(AC) + xE_{\alpha/\beta}(BC) + x(1-x)[E_{\alpha/\beta}(AC) - E_{\alpha/\beta}(BC)], \quad (1.8)$$

where $E_{\alpha/\beta}(AC)$ and $E_{\alpha/\beta}(BC)$ represent the fitted energies of the s, p and d states of anion and cation atoms forming the AC and BC binary compounds. This allows

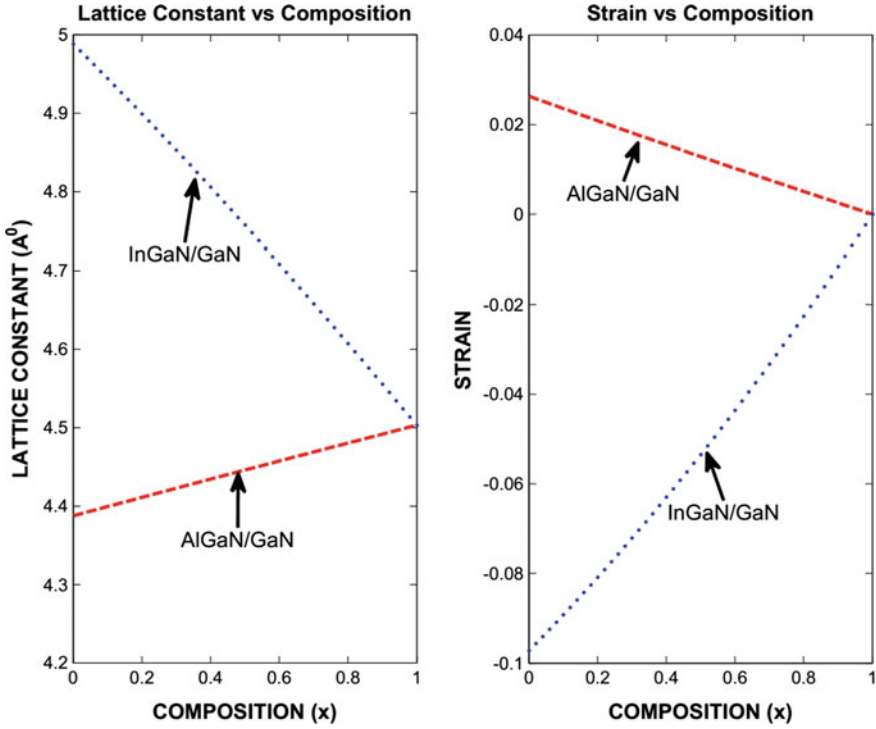


Fig. 1.8 Lattice constant versus alloy composition (*left*) and interface strain versus alloy composition (*right*) for AlGaIn/GaN and InGaIn/GaN GaN heterostructures

one to take into account the composition variations of the diagonal and off-diagonal elements of the TB Hamiltonian matrix for a ternary ABC semiconductor can be taken as a nonlinear function of alloy composition.

1.3 Semiempirical Tight Binding Modeling of Heterostructures

Advances in growing multilayered structures with layer thicknesses approaching atomic dimensions have provided new opportunities and new challenges for the theoretical modelling of electronic structures of low dimensional heterostructures based on the universally accepted fundamental principles of solid state physics and quantum mechanics. The electronic properties of low dimensional bipolar and unipolar semiconductor device structures are often calculated based on the following theoretical models: (i) First principle ab initio methods, such as density functional theory (DFT) [29, 30], (ii) *methods*, such as local/empirical pseudopotential method [14], or (iii) *tight binding* method (also known as the linear

combination of atomic orbitals (LCAO) method) [19–28, 31–38], and *k.p method* [39, 40]. The first principles ab initio methods are computationally expensive and require heavy parallel computations. Since the ab initio models are based on the calculations of ground state properties, they can only give limited physical insight about the energy band structure at high temperatures and pressures.

On the other hand, the semiempirical tight binding models are less expensive than the ab initio methods and can easily be implemented in calculating electronic properties of low dimensional heterostructures such as nanowires or quantum dots. The tight binding model has recently become popular, because of its simplicity and ability to realistically describe the structural and dielectric properties of semiconductors in terms of chemical bonds. The tight binding model is an atomistic approach and is well suited for calculating the electronic band structure of semiconductor heterostructures such as two dimensional quantum wells and zero dimensional quantum dots. In the following Sects. (1.3.1–1.3.4), we will give a detailed discussion of the semiempirical tight binding theory with first and second nearest neighbor (NN and 2NN) sp^3 and sp^3s^* atomic orbitals sets and first nearest neighbor (NN) sp^3d^5 orbitals set with spin-orbit coupling of cation (Al, Ga; In, Cd, Zn) and anion (P, As, Sb, S, Se, Te) atoms for calculating the electronic structure of III–V and II–VI compounds and their heterostructures. We shall later on (Sect. 1.4) compare the semiempirical tight binding models with the density functional theory (DFT) that uses the modified Becke-Johnson exchange-correlation potential with the local density approximation (LDA), called MBJLDA functional, for calculating the band structure of group III–V and II–VI compounds and their alloys.

1.3.1 Semiempirical Sp^3 Tight Binding Modeling

The elementary tight-binding method, also known as the linear combination of atomic-orbitals (LCAO), provides a physically insightful formulation of energy band theory in a crystalline solid, which permits tracing trends from system to system entirely in terms of the fundamental physical features [31–34]. In the semiempirical tight binding theory of semiconductors one assumes that the valence electrons are tightly bound to their nuclei as in the free atom. Anion and cation atoms are brought together until their separations become comparable to the lattice constant of semiconductors, at which point their wave functions will overlap. In the Slater-Koster formalism, the crystal potential of a binary semiconductor is defined as a sum of the symmetrical spherical potentials around each atom. This allows the electronic wave function $\psi_{\alpha k}$ to be written as linear combination of atomic orbitals $\varphi_{\alpha}(k)$ (called the Löwdin orbitals):

$$|\psi_{\alpha k}\rangle = \sum_{\alpha} u_{\alpha} |\varphi_{\alpha}(k)\rangle = \sum_i \frac{e^{i \cdot k \cdot r_i}}{\sqrt{N}} |\varphi_{\alpha}(r - r_i)\rangle, \quad (1.9)$$

where $\mathbf{r}$ is the position of electron with respect to origin of coordinate system is real space, $\mathbf{k}$ is the wave vector, N is the number of atoms, and $\mathbf{r}_i$ is the crystal lattice site. The energy state is given by the eigenvalue of the linear equation written in matrix form [31–34];

$$\sum_{\beta} [H_{\alpha\beta}(k) - S_{\alpha\beta}(k)E] u_{\beta} = 0, \quad (1.10)$$

where E is the eigenvalue and $H_{\alpha\beta} = \langle \varphi_{\alpha}(k) | H | \varphi_{\beta}(k) \rangle$ and $S_{\alpha\beta} = \langle \varphi_{\alpha}(k) | \varphi_{\beta}(k) \rangle$ are the Hamiltonian and overlap matrices, respectively.

$$H_{\alpha\beta} = \begin{bmatrix} H_{cc} & H_{ca} \\ H_{ac} & H_{aa} \end{bmatrix}, \quad S_{\alpha\beta} = \begin{bmatrix} 1 & S_{ca} \\ S_{ac} & 1 \end{bmatrix}, \quad (1.11)$$

Here α correspond to a cation s (p) orbital and β corresponds to an anion s (p) orbital and u_{β} is the wave function coefficient. In the orthogonal sp^3 tight binding formalism in which only the first nearest neighbor interactions are taken into account, the Bloch functions in (1.8) are taken to be orthogonal so that the overlap matrix $S_{\alpha\beta}(k)$ is an identity matrix. There are nine independent matrix elements, namely the four on-site atomic energies, E_{sa}, E_{sc}, E_{pa} and E_{pc} (with a = anion and c = cation) and five hopping terms, $E_{ss}, E_{xx}, E_{sapc}, E_{scpa}$ and E_{xy} . The diagonal elements (E_{sa}, E_{sc}, E_{pa} and E_{pc}) are expressed as the (4×4) matrix

$$H_{aa} = \begin{bmatrix} E_s^a & 0 & 0 & 0 \\ 0 & E_p^a & 0 & 0 \\ 0 & 0 & E_p^a & 0 \\ 0 & 0 & 0 & E_p^a \end{bmatrix}, H_{cc} = \begin{bmatrix} E_s^c & 0 & 0 & 0 \\ 0 & E_p^c & 0 & 0 \\ 0 & 0 & E_p^c & 0 \\ 0 & 0 & 0 & E_p^c \end{bmatrix}, \quad (1.12a)$$

The off-diagonal elements ($E_{ss}, E_{xx}, E_{sapc}, E_{scpa}$ and E_{xy}) are expressed as the (4×4) matrix

$$H_{ac} = \begin{bmatrix} B_0 E_{ss} & B_1 E_{sp} & B_2 E_{ss} & B_3 E_{sp} \\ -B_0 E_{sp} & B_0 E_{xx} & B_3 E_{xy} & B_2 E_{xy} \\ -B_2 E_{sp} & B_3 E_{xy} & B_0 E_{xx} & B_1 E_{xy} \\ -B_3 E_{sp} & B_2 E_{xy} & B_1 E_{xy} & B_0 E_{xx} \end{bmatrix}, \quad (1.12b)$$

$$H_{ca} = \begin{bmatrix} B_0^* E_{ss} & -B_1^* E_{sp} & B_2^* E_{ss} & B_3^* E_{sp} \\ B_1^* E_{sp} & B_0^* E_{xx} & B_3^* E_{xy} & B_2^* E_{xy} \\ B_2^* E_{sp} & B_3^* E_{xy} & B_0^* E_{xx} & B_1^* E_{xy} \\ B_3^* E_{sp} & B_2^* E_{xy} & B_1^* E_{xy} & B_0^* E_{xx} \end{bmatrix},$$

where B_i^* is the complex conjugate of matrix element B_i , defined in (1.15a). The diagonal matrix elements, representing the interactions between the same p-orbitals of cation and anion atoms yield symmetric sums; off-diagonal matrix elements

representing the interactions between different p-orbitals of cation and anion atoms yield asymmetric sums, given as:

$$\langle p_x^c | H | p_x^a \rangle = \langle p_y^c | H | p_y^a \rangle = \langle p_z^c | H | p_z^a \rangle = E_{xx} B_0(k), \quad (1.13a)$$

$$\langle p_x^c | H | p_y^a \rangle = \langle p_y^c | H | p_x^a \rangle = E_{xy} B_3(k), \quad \langle p_y^c | H | p_z^a \rangle = \langle p_z^c | H | p_y^a \rangle = E_{xy} B_1(k), \quad (1.13b)$$

$$\langle p_y^c | H | p_z^a \rangle = \langle p_z^c | H | p_y^a \rangle = E_{xy} B_1(k), \quad \langle p_x^c | H | p_z^a \rangle = \langle p_z^c | H | p_x^a \rangle = E_{xy} B_2(k), \quad (1.13c)$$

Interactions between an s orbital of atom A and the p_x, p_y, p_z orbitals of neighboring atoms B are

$$\langle s^c | H | s^a \rangle = E_{ss} \sum_{n=1}^4 e^{ik \cdot r_n} = E_{ss} B_0(k), \quad \langle s^c | H | p_x^a \rangle = E_{sp} \sum_{n=1}^4 e^{ik \cdot r_n} = E_{sp} B_1(k), \quad (1.14a)$$

$$\langle s^c | H | p_y^a \rangle = E_{sp} \sum_{n=1}^4 e^{ik \cdot r_n} = E_{sp} B_2(k), \quad \langle s^c | H | p_z^a \rangle = E_{sp} \sum_{n=1}^4 e^{ik \cdot r_n} = E_{sp} B_3(k), \quad (1.14b)$$

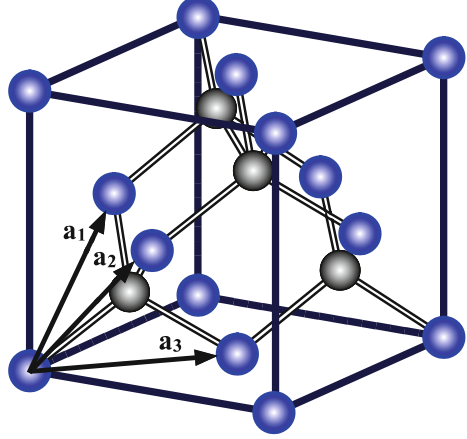
$$B_0(k) = 4 \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) - 4i \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \sin\left(\frac{k_z a}{2}\right), \quad (1.15a)$$

$$B_1(k) = 4 \cos\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \sin\left(\frac{k_z a}{2}\right) + 4i \sin\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right), \quad (1.15b)$$

$$B_2(k) = -4 \sin\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \sin\left(\frac{k_z a}{2}\right) + 4i \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right), \quad (1.15c)$$

$$B_3(k) = -4 \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) - 4i \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) \sin\left(\frac{k_z a}{2}\right), \quad (1.15d)$$

Fig. 1.9 Crystal unit cell group III–V and II–VI compounds with zinc-blende structure



where $i = \sqrt{-1}$ and $r_1 = (a/2)(1, 1, 1)$, $r_2 = (a/2)(1, -1, -1)$, $r_3 = (a/2)(-1, 1, -1)$ and $r_4 = (a/2)(-1, -1, 1)$ are the displacement vectors of nearest neighbors. Figure 1.9 shows the schematic view of unit cells for tetrahedral semiconductors.

In the first nearest neighbor (NN) sp^3 tight binding theory, the acceptable features of electronic band structure of semiconductors are dominated by the diagonal terms (on-site atomic energies: E_{sa} , E_{sc} , E_{pa} and E_{pc}) and off-diagonal terms (E_{ss} , E_{xx} , E_{sapc} , E_{scpa} and E_{xy}) representing the nearest neighbor interactions. The first two off-diagonal elements E_{ss} and E_{xx} can be obtained from the bandgap at the Γ point ($k_x = k_y = k_z = 0$) for which B_1, B_2 and B_3 are all zero, but B_0 is nonzero. The solution of the matrix (1.8) at the Γ point ($k = 0$) then yields

$$E(\Gamma_{1c/v}) = \frac{1}{2}(E_s^a + E_s^c) \pm \sqrt{[(E_s^a - E_s^c)/2]^2 + 16E_{ss}^2}, \quad (1.16)$$

$$E(\Gamma_{15c/v}) = \frac{1}{2}(E_p^a + E_p^c) \pm \sqrt{[(E_p^a - E_p^c)/2]^2 + 16E_{xx}^2}, \quad (1.17)$$

where $E(\Gamma_{15v})$ are $E(\Gamma_{1c})$ the top of the triply degenerate valence band and bottom of the conduction band, respectively. The two unknown parameters E_{ss} and E_{xx} can be determined by inverting (1.7) provided we have accurate s and p energies E_s and E_p for the anion and cation atoms, the bandgap at Γ point and the width of the valence band. The next three off-diagonal matrix elements E_{sapc} , E_{scpa} and E_{xy} are obtained from the bandgap data at the X and L high symmetry points. At the X high symmetry point ($k_x = 1, k_y = k_z = 0$) the Block sums are $B_0 = 0, B_1 = 4i, B_2 = 0$ and $B_3 = 0$, so that conduction and valence band energies are

$$E(X_{3c/v}) = \frac{1}{2}(E_s^a + E_p^c) \pm \sqrt{[(E_s^a - E_p^c)/2]^2 + 16E_{sapc}^2}, \quad (1.18a)$$

$$E(X_{1c/v}) = \frac{1}{2}(E_s^a + E_p^c) \pm \sqrt{[(E_s^a - E_p^c)/2]^2 + 16E_{scpa}^2}, \quad (1.18b)$$

$$E(X_{5c/v}) = \frac{1}{2}(E_p^a + E_p^c) \pm \sqrt{[(E_p^a - E_p^c)/2]^2 + 16E_{xy}^2}, \quad (1.18c)$$

Equations (1.18a) can be inverted for E_{saPc} , E_{scpa} and E_{xy} in terms of the bandgap data at the X symmetry point with appropriate s and p energies. Finally at the L symmetry point ($k_x = k_y = 1, k_z = 0$) the conduction and valence band energies are

$$E(L_{3c/v}) = \frac{1}{2}(E_p^a + E_p^c) \pm \sqrt{[(E_p^a - E_p^c)/2]^2 + 4(E_{xx} + E_{yy})^2}, \quad (1.19)$$

Likewise L energy levels can be improved. It should be noted that fitting of (1.16)–(1.19) to the bandgap data [12, 13] and empirical pseudopotential bandgaps [14] at high symmetry points is reliable only for the valence band but not to the conduction bands; this is vital in studying the electronic structures of low dimensional heterostructures. In this respect we find it useful to use the semiempirical second nearest neighbor (2NN) sp^3 tight binding models [35, 36]. Talwar and Ting [35] incorporate the second nearest neighbor (2NN) interactions of cation and anion atoms in the semiempirical sp^3 tight binding formalism by constructing a nonzero symmetrized (8×8) Hamiltonian matrix with 23 two-center 2NN integrals. The (2NN) sp^3 TB Hamiltonian matrix elements are given as

$$H_{\alpha\beta} = \langle \varphi_\alpha(k) | H | \varphi_\beta(k) \rangle = E_{\alpha\beta} + \sum_{i \neq 0} I_{\alpha\beta}(0, i) e^{ik \cdot r_i} + H''_{\alpha\beta} + H_{so}, \quad (1.20)$$

where $E_{\alpha\beta}$ represents the intra-atomic integrals, coupling atomic orbitals located in the same cell. The second term $I_{\alpha\beta}(0, i)$ is the integral that represents the NN interactions, coupling atomic orbitals located in different cells. Third term represents 2NN interaction integrals. Finally, the last term represents the spin-orbit interactions. In this 2NN sp^3 TB approach there are 23 TB parameters to be determined from the fitting of the TB model energy bands to experimental data [12, 13] and empirical pseudopotential bands at symmetry points [14].

The modified virtual crystal approximation (MVCA) can be implemented in the semiempirical tight binding model [19–28] by using (1.7a–1.7d) and (1.8) for the composition variation of bond length and diagonal and off-diagonal elements in the TB Hamiltonian matrix for ternary constituent of heterostructures. This allows one to take into account the composition variations of the off-diagonal terms in the TB Hamiltonian matrix elements. Likewise, the TB parameters representing the diagonal terms in the Hamiltonian matrix for ABC ternary semiconductor can be taken nonlinear function of composition using (1.8). We can then use the semiempirical NN or 2NN sp^3 TB model calculate the composition effects on electronic properties of ternary/binary heterostructures by taking account of lattice mismatch induced

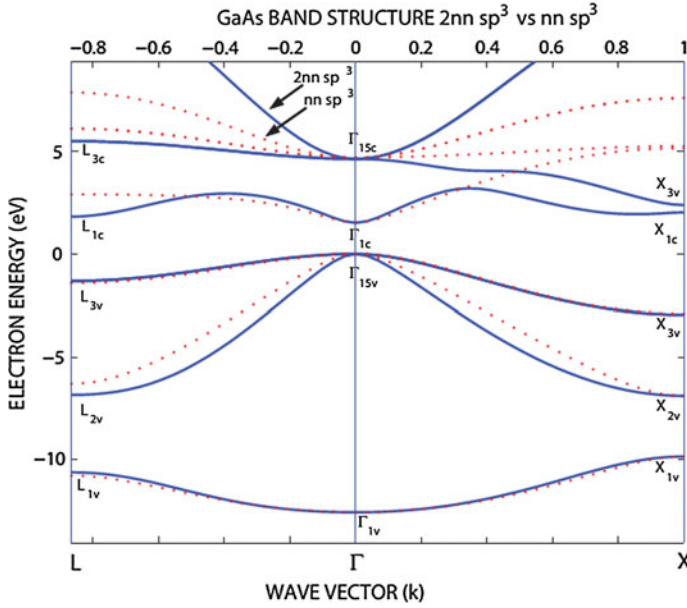


Fig. 1.10 Band structure of GaAs obtained using 2NN sp^3 TB model of Talwar and Ting [35] (dashed lines) and 2NN sp^3 TB model of Loehr and Talwar [36] (solid lines)

interface strain that causes modification of the energy levels of the heterostructure constituents.

Figure 1.10 shows the band diagram of GaAs obtained using the NN and 2NN sp^3 TB model due to the parametrization of Talwar and Ting [35] and Loehr and Talwar [36]. As shown in Fig. 1.10, improvements made in the band structure calculations by the 2NN sp^3 TB model of Loehr and Talwar is visible when it is compared with that of Talwar and Ting at varying values of wave vector over the entire first Brillouin zone, although both produce the experimental bandgap data and empirical pseudopotential bands at symmetry points. However, the low dimensional device performance modeling requires accurate numerical values for the electron and hole masses since they determine the charge transport and device performance. In aiming for this goal, Loehr and Talwar inverted the expressions for energy levels at the Γ , L and X high symmetry point, fitting the electron and hole effective masses, to reduce the number of free tight binding parameters from 23 to 8. The 2NN sp^3 TB parametrization of Loehr and Talwar yields much better conduction band dispersion curves than that of Talwar and Ting. The optimized 2NN sp^3 TB parameters of Loehr and Talwar reproduce the electron mass at the lowest conduction valley and heavy hole effective mass of the valence band at Γ point, in addition to its ability to reproduce the correct values of the critical point energies at the Γ , L and X high symmetry points.

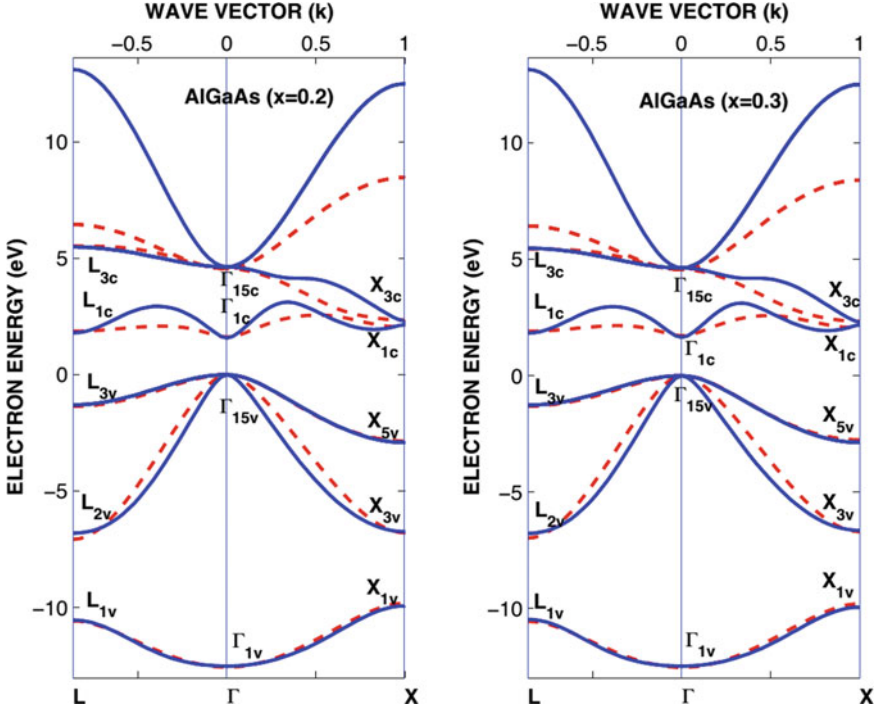


Fig. 1.11 Band structure of AlGaAs with $x = 0.20$ (left) and $x = 0.30$ (right) calculated with the 2NN sp^3 TB parameters of Talwar and Ting [23] (dashed lines) and Loehr and Talwar [24] (solid lines)

Using the tight binding parameters of Talwar and Ting [35] and Loehr and Talwar [36] we calculated the composition effects on band structure of AlGaAs ternary semiconductor and the results are displayed in Fig. 1.11 for $x = 20$ and 30% of aluminum fraction. Furthermore, the composition variation of band gaps of AlGaAs ternary in lattice matched AlGaAs/GaAs heterostructure is shown in Fig. 1.12 (left) and of InGaAs ternary in pseudomorphic InGaAs/GaAs heterostructures is shown in Fig. 1.12 (right), for which band gaps at 0 K are computed using the 2NN sp^3 TB model with the TB parameters of Talwar and Ting and Loehr and Talwar compared with experimental data and empirical pseudopotential model results at symmetry points. As can be seen from Fig. 1.12 (left), there is an excellent agreement between theory and experiment for lattice matched AlGaAs/GaAs heterostructures. However, it should be noted that there is a considerable lattice mismatch across many of the III–V and II–VI ternary/binary heterointerfaces (e.g., InGaAs/GaAs). Interface strain due to lattice mismatch causes a shift in the lattice constant of an epilayer: $a = (1 + \varepsilon)a_0$, where ε is the symmetric strain tensor. Therefore, the bond lengths, defined in (1.7a–1.7d), and TB matrix elements, defined in (1.8), will be modified with strain. The effect of

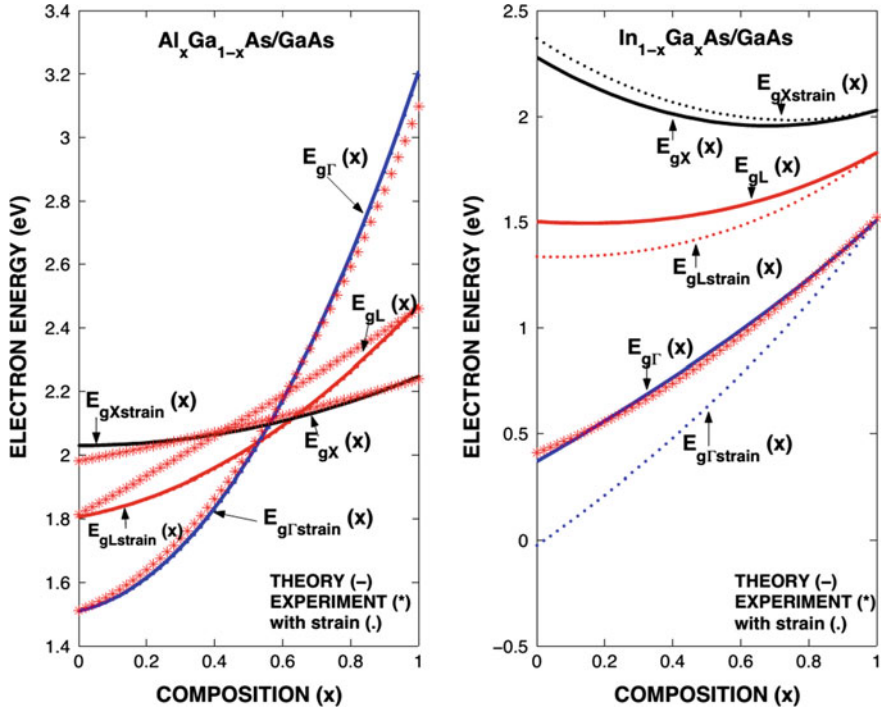


Fig. 1.12 Predicted strain effects on bandgaps of AlGaAs in lattice matched AlGaAs/GaAs (*left*) and of InGaAs in pseudomorphic InGaAs/GaAs (*right*) heterostructures

interface strain is evident in the case of InGaAs/GaAs heterostructure, as seen in Fig. 1.12 (right). There is a large strain shift in the band gaps of the InGaAs ternary constituent in an InGaAs/GaAs heterostructure at symmetry points due to large lattice mismatch that increases with indium mole fraction. There is good agreement between theory and experiment for the InGaAs ternary as bulk at around 0 K.

Qualitatively reliable and quantitatively accurate determination of the strain effects on the energy levels by fitting the off-site tight binding matrix elements to a set of observables is difficult. The off-site TB matrix elements representing nearest neighbor interactions, known as the hopping strength, will be modified with respect to their unstrained values and are often determined by assuming that they obey the Harrison Scaling Law [34]: $V_{ll'm}(\varepsilon) = V_{ll'm}(a/a_0)^{-\eta_{llm}}$, where $V_{ll'm}(\varepsilon)$ is the strained and $V_{ll'm}$ the unstrained value of interaction potential for anion and cation atoms. The exponents η_{llm} are determined to reproduce the strain variations of the band structure of relevant semiconductors under hydrostatic pressure, namely the volume deformation potential $a_{gl} = -B(\partial E_{gl}/\partial P)$ for the corresponding band gap energies $E_{g\Gamma}$, E_{gL} and E_{gX} at symmetry points. Since these bandgaps depend on experimental data, in order to obtain reliable and accurate TB parameters, one must go through a fitting process that depends on the mapping of a large number of orbital coupling

parameters on the set of observables; in many cases there are not many analytical expressions available. One can overcome this difficulty by using a so-called statistical thermodynamic model [10, 11], which considers the conduction electrons and valence holes as distinct electrically chemical species, to study the interface strain effects on the electronic structure of heterostructures at symmetry points, defined by (1.5) and (1.6). In this model, one first expresses the shifts in the conduction and valence band edges at Γ , L and X high symmetry points obtained by using the 2NN sp^3 TB orbitals basis sets as a function of pressure at any lattice temperature and then obtains the refined tight binding matrix elements to find the band structure.

Although the Slater-Koster type semiempirical 2NN sp^3 s tight binding treatment of electronic structures yields a good description of valence band dispersion curves, the conduction band dispersion curves are inaccurately given, especially the indirect band gap at the X symmetry point is not well reproduced. Vogl et al. [34] introduced a nearest neighbour sp^3s^* tight binding model in order to include the influence of excited d-states, which will be discussed next.

1.3.2 Semiempirical Sp^3s^* Tight Binding Modeling

In the semiempirical nearest neighbor sp^3s^* tight binding model of Vogl et al. [41], each atom is described by its outer valence s orbital, three p orbitals and fictitious excited s^* orbital is added to mimic the effects of higher lying d-states. This results in a semiempirical NN sp^3s^* tight binding model with a total of 13 parameters, which are determined by comparing the predicted bandgaps with those produced by empirical pseudopotential model [14] at high symmetry points. Adding the excited s^* state and spin-orbit coupling to sp^3 orbital basis set makes it possible to accurately calculate band dispersion curves at the X high symmetry point. Furthermore, the inclusion of 2NN interactions of cation and anion atoms in the sp^3s^* TB model yields better fit of conduction band dispersion curve at the L symmetry point.

The sub-matrices (diagonal (H_{cc} and H_{aa}) and off-diagonal (H_{ca} and $H_{ac} = H_{ca}^*$) elements of the 2NN sp^3s^* Hamiltonian matrix $H_{\alpha\beta}$ are written as [41]

$$H_{cc} = \begin{bmatrix} E_s^c & -\varepsilon(s, p_x)B_6 & -\varepsilon(s, p_x)B_5 & -\varepsilon(s, p_x)B_4 & 0 \\ -\varepsilon(s, p_x)B_6 & E_p^c & -\varepsilon(p_x, p_y)B_4 & -\varepsilon(p_x, p_y)B_5 & 0 \\ -\varepsilon(s, p_x)B_5 & -\varepsilon(p_x, p_y)B_4 & E_p^c & -\varepsilon(p_x, p_y)B_6 & 0 \\ -\varepsilon(s, p_x)B_4 & -\varepsilon(p_x, p_y)B_5 & -\varepsilon(p_x, p_y)B_6 & E_p^c & 0 \\ 0 & 0 & 0 & 0 & E_{s^*}^c \end{bmatrix}, \quad (1.21a)$$

$$H_{aa} = \begin{bmatrix} E_s^a & \varepsilon(s, p_x)B_6 & \varepsilon(s, p_x)B_5 & \varepsilon(s, p_x)B_4 & 0 \\ \varepsilon(s, p_x)B_6 & E_p^a & \varepsilon(p_x, p_y)B_4 & \varepsilon(p_x, p_y)B_5 & 0 \\ \varepsilon(s, p_x)B_5 & \varepsilon(p_x, p_y)B_4 & E_p^a & \varepsilon(p_x, p_y)B_6 & 0 \\ \varepsilon(s, p_x)B_4 & \varepsilon(p_x, p_y)B_5 & \varepsilon(p_x, p_y)B_6 & E_p^a & 0 \\ 0 & 0 & 0 & 0 & E_{s^*}^a \end{bmatrix}, \quad (1.21b)$$

$$H_{ca} = \begin{bmatrix} B_0E_{ss} & B_1E_{sp} & B_2E_{sp} & B_3E_{sp} & 0 \\ -B_1E_{sp} & B_0E_{xx} & B_3E_{xy} & B_2E_{xy} & -B_1E_{ps^*} \\ -B_2E_{sp} & B_3E_{xy} & B_0E_{xx} & B_1E_{xy} & -B_2E_{ps^*} \\ -B_3E_{sp} & B_2E_{xy} & B_1E_{xy} & B_0E_{xx} & -B_3E_{ps^*} \\ 0 & B_1E_{s^*p} & B_2E_{s^*p} & B_3E_{s^*p} & 0 \end{bmatrix}, H_{ac} = (H_{ca})^*, \quad (1.21c)$$

where $E_s^a, E_s^c, E_p^a, E_p^c, E_{s^*}^a$, and $E_{s^*}^c$ are diagonal elements of $H_{\alpha\beta}$ matrix and represent the on-site atomic energies of cation and anion atoms. $E_{ss}, E_{xx}, E_{s_a p_c}, E_{s_c p_a}, E_{xy}, E_{s^* p}$ and E_{ps^*} are the off-diagonal elements of $H_{\alpha\beta}$ matrix and represent the hopping terms (transfer matrix elements). Finally, $\varepsilon_{sx} = \varepsilon(sc(a), p_x c(a))$ and $\varepsilon_{xy} = \varepsilon(p_x c(a), p_y c(a))$ are the two 2NN transfer matrix elements for the cation and anion atoms. Here s and p refer to the basis states and a and c refer to anion (e.g., As, Sb, N) and cation (e.g., Al, Ga and In) atoms, respectively. In the 2NN sp^3s^* TB Hamiltonian matrix, B_i^* is the complex conjugate of the matrix element B_i which gives the $\mathbf{k}$ wave vector dependence and the first four elements are the same as in (1.15a) and other three are

$$B_4(\mathbf{k}) = 4\text{Sin}(\mathbf{k}_x a)\text{Sin}(\mathbf{k}_y a), \quad (1.22a)$$

$$B_5(\mathbf{k}) = 4\text{Sin}(\mathbf{k}_x a)\text{Sin}(\mathbf{k}_z a), \quad (1.22b)$$

$$B_6(\mathbf{k}) = 4\text{Sin}(\mathbf{k}_y a)\text{Sin}(\mathbf{k}_z a), \quad (1.22c)$$

where $i = \sqrt{-1}$ and displacement vectors of nearest neighbors. Including the spin-orbit coupling the size of the (10×10) 2NN sp^3s^* TB Hamiltonian matrix increases to (20×20) matrix which is diagonalized for each $\mathbf{k}$ vector to obtain the band structure [42]. The spin-orbit effects are included with the 2NN sp^3s^* orbitals set by coupling different spin states of different on-site p orbitals through the spin-orbit interaction. Tight binding parameters of 2NN sp^3s^* orbitals set is obtained by fitting the obtained band gaps given in Table 1.1 to those produced by empirical pseudopotential theory [14]. Having reliable diagonal matrix elements one can make realistic tight binding parametrization of the off-diagonal matrix elements representing the first nearest neighbor (NN) and/or 2NN interactions, which are obtained by focusing on the reproduction of the band gap energies at symmetry points in the energy dispersion curve. As examples of 2NN sp^3s^* tight binding parametrization, the bandgaps given in Table 1.1 [21, 23] for several group III–V compounds may be used to calculate electronic band structure of their heterostructures.

Table 1.1 Bandgaps at symmetry points of AlAs, GaAs, InAs, GaP, AlN, GaN and InN compounds obtained using the 2NN sp^3s^* TB model [21, 23] and experimental data [12] are given in parenthesis

(eV)	GaAs	InAs	GaP	AlN	GaN	InN
$E_{g\Gamma}$	1.52 (1.52)	0.43 (0.42)	2.88 (2.88)	5.99 (6.00)	3.30 (3.27)	0.90 (0.90)
E_{gX}	1.98 (2.03)	2.28 (2.50)	2.33 (2.16)	4.90 (4.80)	4.70 (4.70)	2.83 (3.00)
E_{gL}	1.82 (1.85)	1.61 (1.43)	2.56 (2.79)	8.63	6.10	3.81

Table 1.2 2NN sp^3s^* TB parameters for GaAs, InAs, GaP, AlN, GaN and InN obtained using Table 1.1

(eV)	GaAs	InAs	GaP	AlN	GaN	InN
$E_{s,a}$	-8.4399	-9.5381	-8.1124	-11.505	-12.915	-12.860
$E_{p,a}$	0.9252	0.7733	1.0952	4.3815	3.1697	1.9800
$E_{s,c}$	-2.6569	-2.7219	-2.1976	0.5047	-1.5844	-0.3994
$E_{p,c}$	3.5523	3.5834	4.0851	10.2184	9.0302	8.0200
$E_{s^*,a}$	6.6235	7.2730	8.4796	12.0400	12.2000	10.6300
$E_{s^*,c}$	7.4249	6.6095	7.1563	13.7400	12.2000	13.0000
$4V_{s,s}$	-6.4210	-5.6052	-7.4909	-9.8077	-8.8996	-4.2285
$4V_{x,x}$	1.9850	1.8398	2.1516	6.6900	5.3500	3.9800
$4V_{x,y}$	4.9100	4.3977	5.1213	8.9400	8.6200	7.4100
$4V_{sa,pc}$	4.2390	3.0205	4.2724	7.8500	6.4000	3.8100
$4V_{pa,sc}$	5.15358	5.3894	6.3075	7.6800	7.2400	6.1900
$4V_{s^*a,pc}$	3.80624	3.2191	4.8184	8.0300	7.0600	6.8800
$4V_{pa,s^*c}$	4.7009	3.7234	50534	2.4700	1.8200	3.3600
ε_{xx}	0.2459	0.1441	0.2325	-1.4000	0.9500	0.6150
ε_{xy}	-0.1050	0.0249	-0.2200	6.9000	1.0100	0.7100
λ_a	0.0553	0.1385	0.0578	0.0035	0.0035	0.0035
λ_c	0.1338	0.1290	0.0222	0.0070	0.0410	0.1100

As an example of 2NN sp^3s^* TB parametrization, the diagonal and off-diagonal tight binding parameters for AlAs, GaAs, InAs, GaP, AlN, GaN and InN are given in Table 1.2 [21, 23].

Using the 2NN sp^3s^* TB model the electronic band structures of GaAs, GaN, InN and AlN are calculated [21, 23] and are shown in Fig. 1.13, which reproduce the conduction and valence band structures, including the heavy hole and light hole bands as well as spin-orbit splitting bands. Tight binding interaction parameters $4V_{s^*,p}$ and $4V_{p,s^*}$ were adjusted to fit to the X bands and 2NN interaction parameters ε_{xx} and ε_{xy} to get a good fit to the L bands in reproducing the empirical pseudopotential energy bands [14]. As shown in Fig. 1.13, adding the excited s^* state to the sp^3 orbitals set on the cation and anion atoms with 2NN interactions and

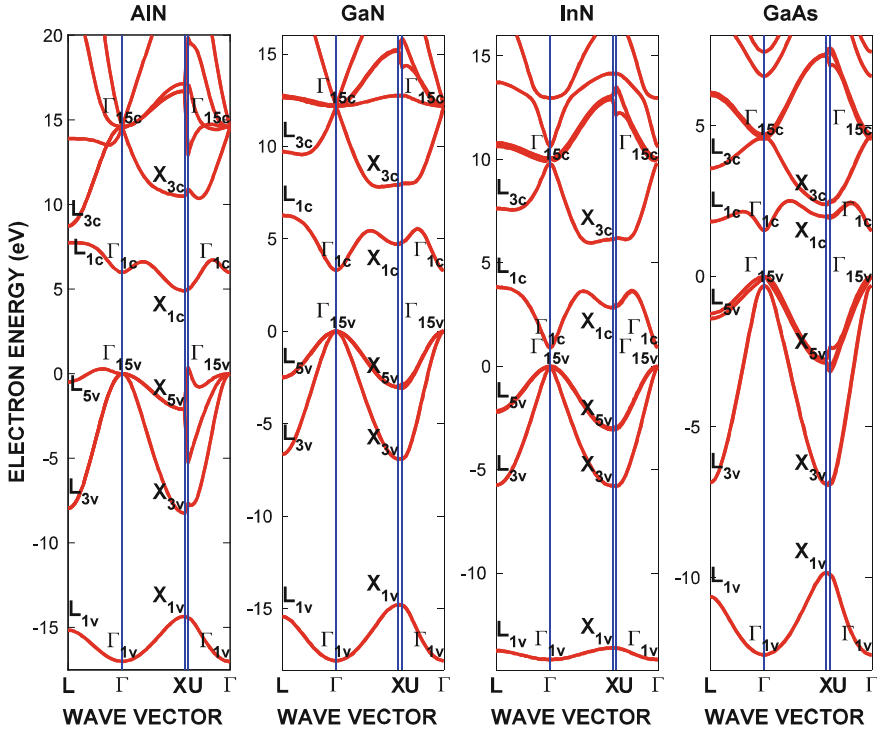


Fig. 1.13 Band structures of AlN, GaN, InN and GaAs obtained using the 2NN sp^3s^* TB parameters given in Table 1.2

spin-orbit coupling of p-states, improves the simulation of the conduction band structure of III–V compounds, especially at the X symmetry point, reproducing the empirical pseudopotential bands at symmetry points of energy dispersion curve, which cannot be done with conventional NN and 2NN sp^3 TB models.

As an example of implementing the modified virtual crystal approximation (MVCA) for the implementation of the composition effects in semiempirical NN or 2NN sp^3s^* tight binding model, the tight binding parameters given in Tables 1.1 and 1.2 are used in the calculations of the electronic structures of AlGa_{1-x}N_x, InGa_{1-x}N_x and GaAs_{1-x}N_x nitride ternaries in k-space for various alloy compositions, as displayed in Fig. 1.14 showing the expected trend in band structures. The main features of the composition effects on the energy band properties of AlGa_{1-x}N_x/Ga_{1-x}N_x, InGa_{1-x}N_x/Ga_{1-x}N_x and GaAs_{1-x}N_x/Ga_{1-x}N_x ternary/binary group III-nitride heterostructures are summarized in Fig. 1.15, in which the principal band gap energies of AlGa_{1-x}N_x, InGa_{1-x}N_x and GaAs_{1-x}N_x ternaries are plotted as functions of interface strain for the entire composition range. As seen from Fig. 1.15, lattice mismatch interface strain effects on the fundamental band gaps at Γ , L and X symmetry points in AlGa_{1-x}N_x/Ga_{1-x}N_x (left), InGa_{1-x}N_x/Ga_{1-x}N_x (middle) and GaAs_{1-x}N_x/Ga_{1-x}N_x (right) heterostructures can be quite large when the band gap (or conduction band) deformation potential is large.

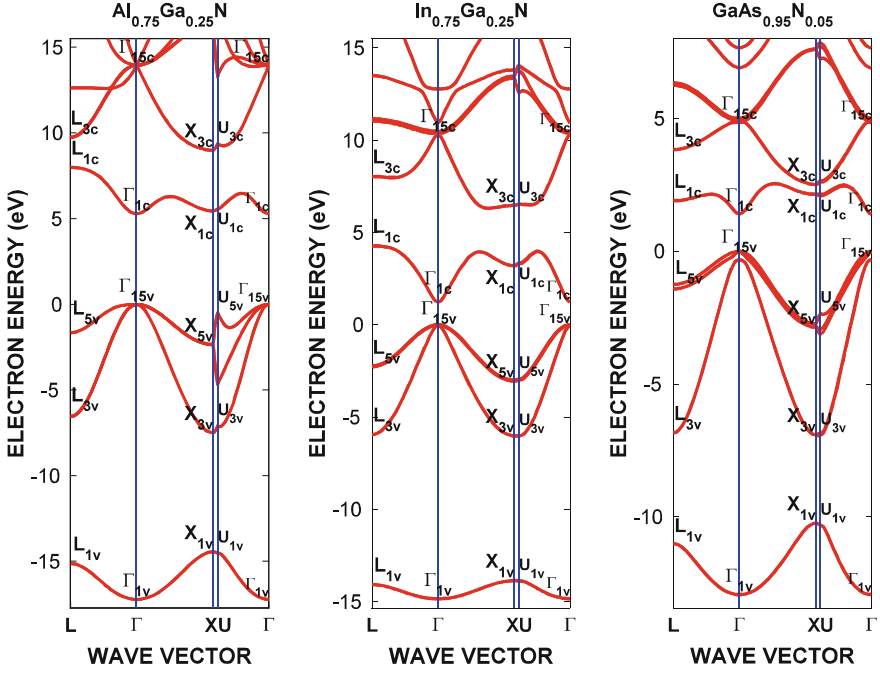


Fig. 1.14 Band structures of AlGaIn, InGaIn and GaAsN obtained using the 2NN sp^3s^* TB orbitals set with optimized energies given in Table 1.2

Predicted fundamental bandgaps of AlGaIn, InGaIn and GaAsN ternaries at the Γ , L and X points, especially at Γ , are in excellent agreement with experiment [12]. The principal band gaps of AlGaIn and InGaIn conventional nitrides increase with composition. However, the band gap of GaAsN diluted nitride at the Γ symmetry point decreases with alloy composition for $x < 0.25$, and then increases for $0.26 < x < 1$, in agreement with experiment. It is gratifying to note that using the optimized 2NN sp^3s^* tight binding model parameters for GaAs, GaN, AlN and InN compounds given in Tables 1.1 and 1.2, we are able to obtain the nonlinear composition dependence of the principal band gaps of AlGaIn, InGaIn and GaAsN ternary semiconductors without any empirical fitting or any adjustable parameter. This observation suggests that by using the optimized 2NN sp^3s^* TB parameters for bulk GaAs, GaN, AlN and InN binary compounds, given in Table 1.2, the 2NN sp^3s^* TB model allows one to determine the nonlinear composition dependence of the principal band gaps of nitride-based ternary semiconductors without any empirical fitting nor any adjustable parameter.

Cadmium and zinc based group II–VI compounds (CdX and ZnX ($X = S, Se, Te$)) and their ternary/binary heterostructures are known to have considerable potential for making optical and photovoltaic devices (e.g., light emitting diodes, laser diodes, infrared detectors, photovoltaic devices, and quantum dots [1, 2]). Therefore, similar calculations were carried out for the electronic band structure of

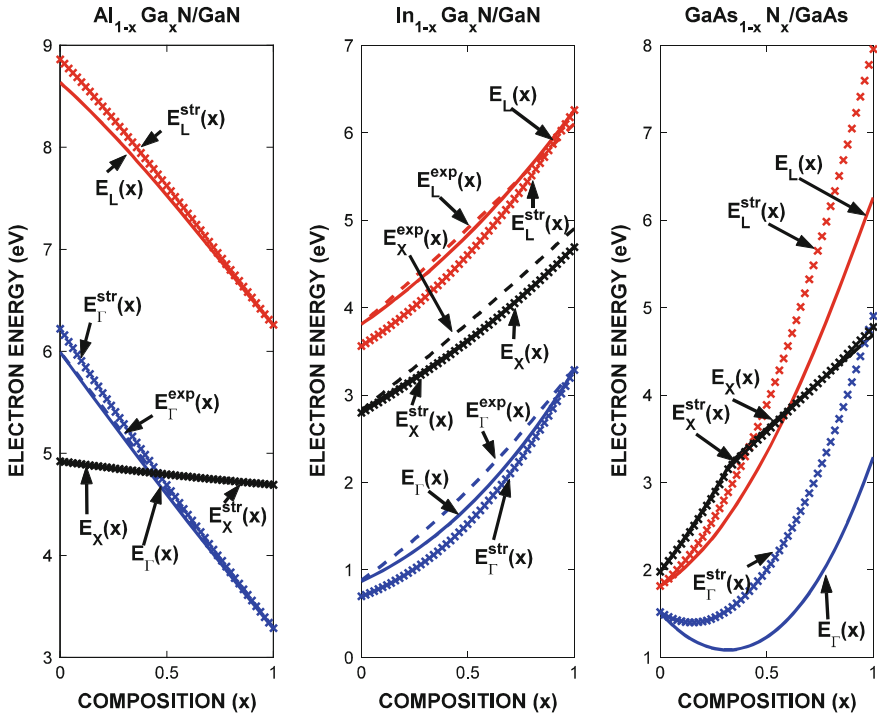


Fig. 1.15 Predicted interface strain effects on the bandgaps of ternaries in AlGaIn/GaN (left), InGaIn/GaN (middle) and GaAsN/GaAs (right) heterostructures compared with experiment [12]

cadmium and zinc based group II–VI compounds (CdX and ZnX ($X = S, Se, Te$)) and their $ZnCdS/CdS$ (left) and $ZnTeS/ZnS$ ternary/binary heterostructures by using the $2NN\ sp^3s^*$ TB parametrization, which yield the same accuracy for the conduction band structure of CdS , $CdSe$, $CdTe$, ZnS , $ZnSe$ and $ZnTe$. Figure 1.16 shows the composition and interface strain effects on band gaps of ternaries in $ZnCdS/CdS$ (left) and $ZnTeS/ZnS$ (right) heterostructures compared with experiment [12]. It should be noted that there is a considerable lattice mismatch across many of the ternary/binary heterointerfaces. Therefore, the composition dependent bond lengths, defined in (1.7a–1.7d), and tight binding matrix elements in the semiempirical $NN\ sp^3s^*$ orbitals set, defined in (1.24), and hence the electronic properties of heterostructure alloy constituents will be modified with respect to their unstrained values. Furthermore, accurate description of the second conduction band and the transverse effective masses at the X- and L-symmetry points are found to be in good agreement with experiment, leading to a reliable and accurate TB model calculation of electronic properties of semiconductors. We should note that the accuracy of $2NN\ sp^3s^*$ TB parametrization depends on the accurate description of band structures of III–V and II–VI compounds by the empirical pseudopotential theory and bandgap data.

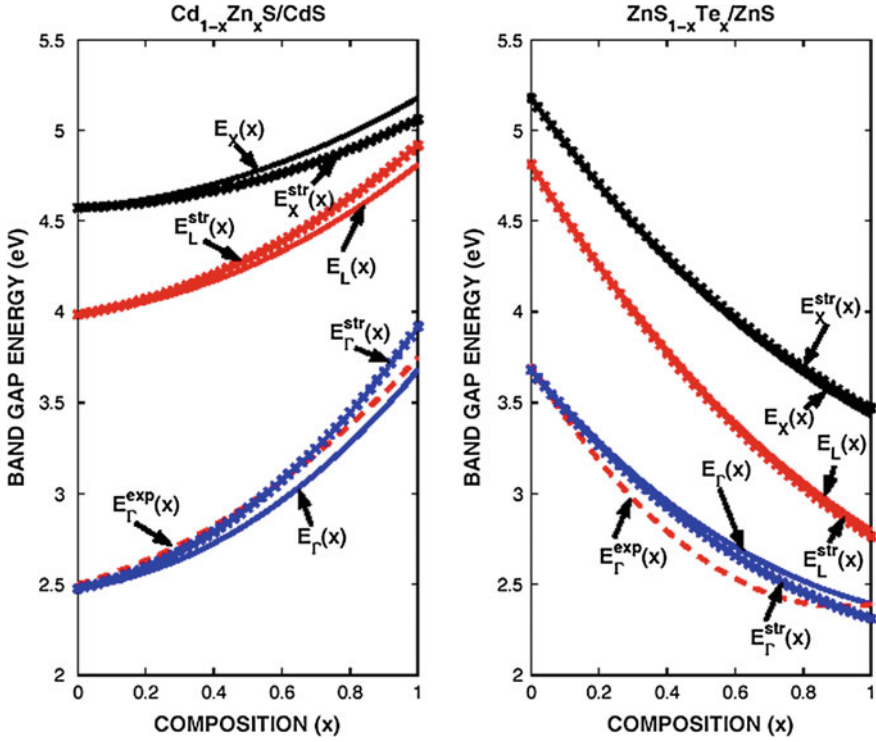


Fig. 1.16 Predicted interface strain effects on band gaps of ternaries in ZnCdS/CdS (*left*) and ZnTeS/ZnS (*right*) heterostructures compared with experiment [12]

Although the inclusion of s^* excited state in the 2NN sp^3 TB model yields accurate calculations of the conduction band structure features at the X high symmetry point, it does so by modelling the average of p-d interactions and is insufficient to determine energy levels above 6.0 eV. Jancu et al. [42, 43] suggested that from a solid state physics point of view, the actual behaviour of excited d-states is not reliably addressed in the sp^3s^* tight binding model of valence band and conduction band dispersion curves involving the Γ , X and L high symmetry points, which will be discussed next.

1.3.3 Semiempirical $Sp^3d^5s^*$ Tight Binding Modeling

In the semiempirical nearest neighbor $sp^3d^5s^*$ tight binding model proposed by Jancu et al. [42, 43], the excited d-states contribute critically to both the valence band maximum at the Γ symmetry point and to the conduction band dispersion curves at the X and L symmetry points and is explicitly included in NN $sp^3d^5s^*$ orbitals set. The band gaps at high symmetry points in the Brillouin zone and

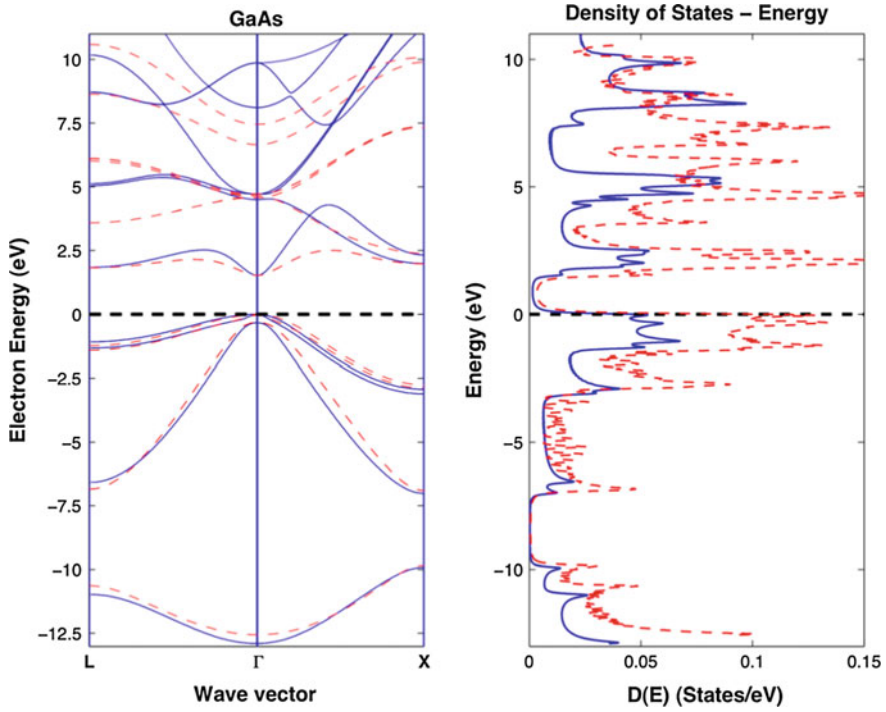


Fig. 1.17 Band structure and density of states of a GaAs compound calculated using the 2NN sp^3s^* (dashed) and NN $sp^3d^5s^*$ (solid) tight binding models

optimized tight binding parameters are given in Tables 1.1 and 1.2 for the 2NN sp^3s^* 2NN TB model and those of the NN $sp^3d^5s^*$ TB model were taken from Jancu et al. [42]. Results of 2NN sp^3s^* TB and NN $sp^3d^5s^*$ TB models are compared in Fig. 1.17 for electronic band structure and density of states of GaAs. As can be seen from Fig. 1.17, both the valence band and conduction band dispersion curves of GaAs obtained by using the NN $sp^3d^5s^*$ TB model overcomes most of the limitations of the earlier 2NN sp^3 and sp^3s^* TB models. As Fig. 1.17 (left) for GaAs show, the NN $sp^3d^5s^*$ TB model overcomes most of the limitations of the earlier of 2NN sp^3 and sp^3s^* 2NN TB models for both valence and conduction band dispersion curves. Furthermore, accurate description of the second conduction band and the transverse effective masses at the X- and L-symmetry points that are in good agreement with experiment suggests that the NN $sp^3d^5s^*$ TB parametrization makes it possible to accurately calculate the electronic and optical properties involving symmetry points at the edge of the Brillouin zone of tetrahedral semiconductors. It is noted here that the NN $sp^3d^5s^*$ TB model is reliable for the calculation of dispersion curves for energies up to 6 eV above the valence band maximum, correctly reproducing the orbital character of band edges, and their

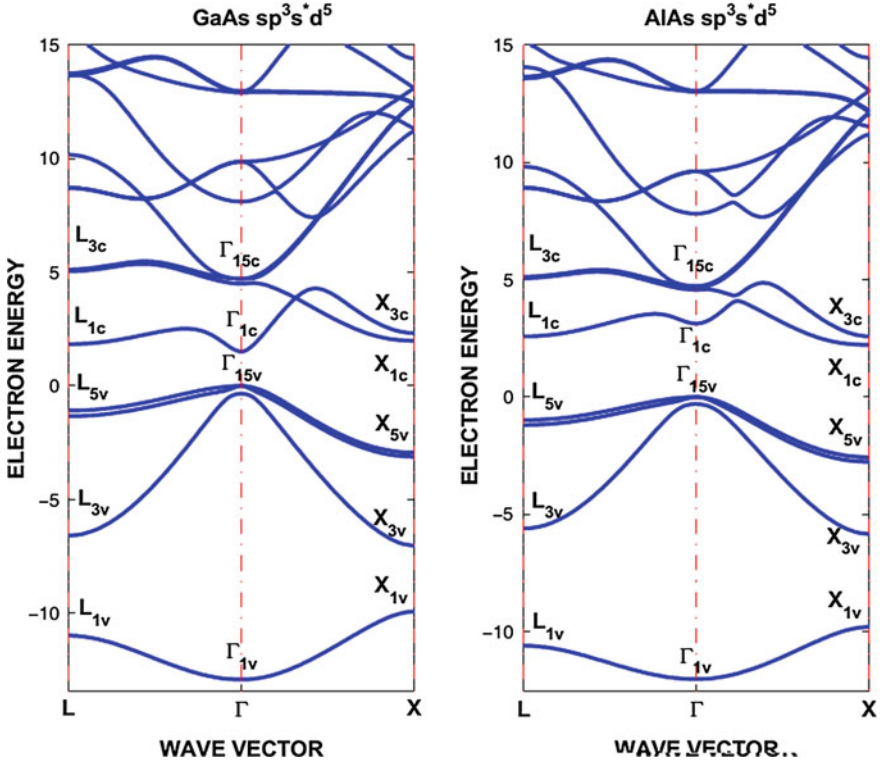


Fig. 1.18 Electronic band structure of AlAs and GaAs obtained using NN $sp^3d^5s^*$ TB model

behavior under strain, at the Γ , X and L symmetry points of the first Brillouin zone of compound semiconductors.

In a search for physically realistic and numerically accurate calculations of band structures of group III–V and II–VI compound semiconductors, Sapra et al. [44] have argued that the adding of an s^* state to an sp^3 orbitals set does not represent the true contribution of d-states to both valence band and conduction band dispersion curves and have shown that the NN sp^3d^5 tight binding model is sufficient to calculate the electronic structure of group III–V and II–VI compounds and suggests that the use of any fictitious s^* state is not needed in tight binding modeling to calculate the energy band structures. However, as can be seen from Fig. 1.18, the use of the more complete nearest neighbor $sp^3d^5s^*$ orbitals set imposes drastically heavier computational requirement on the calculation of electronic band structures of III–V and II–VI compound semiconductors, without affording realistic physical insight to the solid state interpretation of its contribution to the problem.

In the following section we use a semiempirical NN sp^3 tight binding parametrization of the problems of nearest neighbor interactions and spin-orbit

Table 1.3 Bandgaps of CdS, CdSe and ZnS obtained from fitting the NN sp^3d^5 and 2NN sp^3s^* TB models results [24] in the empirical pseudopotential bands [14] and measured band gaps [12, 13] at high symmetry points

Bandgap (eV)	CdS		ZnS		CdSe	
	sp^3s^*	sp^3d^5	sp^3s^*	sp^3d^5	sp^3s^*	sp^3d^5
E_g^T	2.476	2.555	3.680	3.702	1.887	1.937
E_g^X	4.341	4.696	5.103	5.190	3.784	3.779
E_g^L	3.983	5.193	4.810	4.641	3.097	3.027

coupling of p-states taken into account in the calculations of the band structures of III–V and II–VI compound semiconductors.

1.3.4 Semiempirical Sp^3d^5 Tight Binding Modeling

In this section we discuss the semiempirical sp^3d^5 tight binding parametrization with the first nearest neighbor interaction and spin-orbit coupling of p-states taken into account in the calculation of the electronic structure of constituents of semiconductor heterostructures. We write the semiempirical NN sp^3d^5 TB Hamiltonian matrix as [24]

$$H_{\alpha\beta} = \langle \varphi_\alpha(k) | H | \varphi_\beta(k) \rangle = E_{\alpha\beta} + \sum_{i \neq 0} I_{\alpha\beta}(0, i) e^{ik \cdot r_i} + H_{so}, \quad (1.23)$$

where $E_{\alpha\beta}$ is the on-site energy for the β orbital (s, p, d) at the atomic site α (cation and anion); and it represents the intra-atomic integrals, which couple atomic orbitals located in the same cell, and $I_{\alpha\beta}(0, i)$ represents the first nearest neighbor (NN) interaction integrals, known as the hopping term, which couples atomic orbitals located in different cells.

The nine state atomic-like ($s; x, y, z; xy, yz, zx, x^2 - y^2, 3z^2 - r^2$) basis set describes each atom of the semiconductor. $H_{\alpha\beta}$ has 19 independent matrix elements: 9 on-site and 10 off-site elements. The inclusion of spin-orbit coupling to the sp^3d^5 basis set, in which the spin-orbit interaction is given by two parameters; $\lambda_a = \langle x_a \uparrow | H_{so} | z_a \downarrow \rangle$ for anion and $\lambda_c = \langle x_c \uparrow | H_{so} | z_c \downarrow \rangle$ for cation atom, adds two extra tight binding parameters. Therefore, $H_{\alpha\beta}$ has total of 21 independent matrix elements, including the nearest neighbor interaction and spin orbit coupling of p-states. The diagonal and off-diagonal matrix elements are determined by fitting the empirical pseudopotential energy band dispersions to calculated energy band dispersions using the semiempirical NN sp^3d^5 TB parametrization for a given semiconductor. One starts with calculating the electronic band structure by estimating the values of on-site matrix elements and off-site matrix elements and then carries out a least-squares error minimization fitting procedure at a number of high

Table 1.4 Optimized s, p and s* TB parameters for CdS, CdSe and ZnS obtained from fitting the 2NN sp^3s^* TB model [24] to empirical pseudopotential band [14] at symmetry points

(eV)	CdS	ZnS	CdSe
$E_{s,a}$	-11.5300	-11.6100	-9.63
$E_{p,a}$	0.5300	1.4800	1.326
$E_{s,c}$	1.8300	1.1100	0.03
$E_{p,c}$	5.8700	6.5200	4.73
$E_{s^*,a}$	7.1300	8.0800	7.53
$E_{s^*,c}$	6.8700	8.0200	5.72
$4V_{s,s}$	-3.0700	-6.3000	-4.64
$4V_{x,x}$	1.7600	3.1100	2.64
$4V_{x,y}$	4.2300	5.0000	5.36
$4V_{s,p}$	2.1700	5.1600	4.57
$4V_{p,s}$	5.4800	5.1700	5.54
$4V_{s^*,p}$	1.9900	2.8900	3.05
$4V_{p,s^*}$	3.0600	1.7500	2.49
ε_{xx}	0.1000	0.2000	0.0
ε_{xy}	-0.0100	-0.1500	0.0
λ_a	0.0250 [6]	0.0250 [6]	0.1434
λ_c	0.0130 [14]	0.0270 [14]	0.0591

symmetry points in the valence and conduction band dispersion curves to fit band gap energies obtained from the empirical pseudopotential method [14] (Table 1.3).

We now compare the predictions of semiempirical NN sp^3d^5 and 2NN sp^3s^* TB parametrizations, both of which include spin-orbit coupling of p-states [28]. Tables 1.4 and 1.5 give the number of optimized TB parameters for the NN sp^3d^5 and 2NN sp^3s^* TB models. Figure 1.19 compare the electronic band structure of CdS, ZnS and CdSe calculated using NN sp^3d^5 and 2NN sp^3s^* TB models, both reproducing the band gaps as well as the valence band and conduction band dispersion curves at Γ , X and L symmetry points, which cannot be done with conventional NN sp^3 and 2NN sp^3 TB models.

As can be seen from Fig. 1.19 the tight binding model with an sp^3d^5 orbital basis, including the nearest neighbor interactions of cation and anion atoms and spin-orbit coupling of p-states, is adequate to accurately reproduce the band gaps at Γ , X and L symmetry points and both the valence band and conduction band dispersion curves. When compared with the 2NN sp^3s^* TB model, the NN sp^3d^5 TB model better simulates both the valence band and conduction band dispersion curves. This is due to the fact that the inclusion of s*-excited state is included by modeling the average of p-d interactions, and it does not permit the inclusion of excited d-orbitals to a sp^3 orbitals set. Therefore, the actual behavior and contribution of the excited d-states in the band structure calculations is not reliably reproduced, suggesting that the sp^3s^* TB model is of limited value for determination of optical properties of semiconductors involving high symmetry points. We should point out that both TB models with NN sp^3d^5 and 2NN sp^3s^* orbitals sets are

Table 1.5 Optimized s, p and d-TB parameters for CdS, CdSe and ZnS compounds obtained from fitting the NN sp^3d^5 TB model [24] to empirical pseudopotential bands at symmetry points [14]

(eV)	CdS	ZnS	CdSe
s_c	1.8300	1.3600	0.0300
p_c	5.8700	6.5200	4.7300
$d_c(t_2)$	-6.8300	-5.8200	-7.3100
$d_c(e)$	-7.4400	-6.2100	-7.8100
s_a	-11.5300	-14.6100	-9.6300
p_a	0.9300	1.7800	1.3260
$d_a(t_2)$	14.4300	15.5400	15.2600
$d_a(e)$	13.1500	13.6000	14.1000
$ss\sigma$	-0.8440	-1.0050	-1.2600
$sp\sigma$	2.2729	2.5387	2.3989
$pp\sigma$	1.68963	1.3343	1.9789
$pp\pi$	2.5500	4.3775	3.3400
$ps\sigma$	-0.10750	-0.3725	-0.6800
$ds\sigma$	0.0000	-2.5900	-1.2200
$dp\sigma$	-1.1400	-0.0500	-0.0100
$dp\pi$	-1.2900	-2.7800	-1.0900
$sd\sigma$	1.7500	1.3700	1.5200
$pd\sigma$	1.5580	2.1100	1.7800
$pd\pi$	-0.3500	-0.4500	-0.3200
λ_a	0.0250	0.0250	0.1434
λ_c	0.07600	0.0270	0.0591

semiempirical and their basis lies in a good description of the electronic band structures of tetrahedral semiconductors.

1.4 Density Functional Theory Modelling of Heterostructures

The conventional density functional theory (DFT) enables us to have a parameter-free description of structural and electronic properties of semiconductors and has its foundations in the work of Kohn and his collaborators [30, 45]. The variation method is used to calculate the ground state properties of a many-body system with the charge density, expressed in terms of single-particle electronic orbitals

$$n(\vec{r}) = \sum_{i=1}^N \sum_k f_{i,k} |\varphi_{i,k}(\vec{r})|^2, \quad (1.24)$$

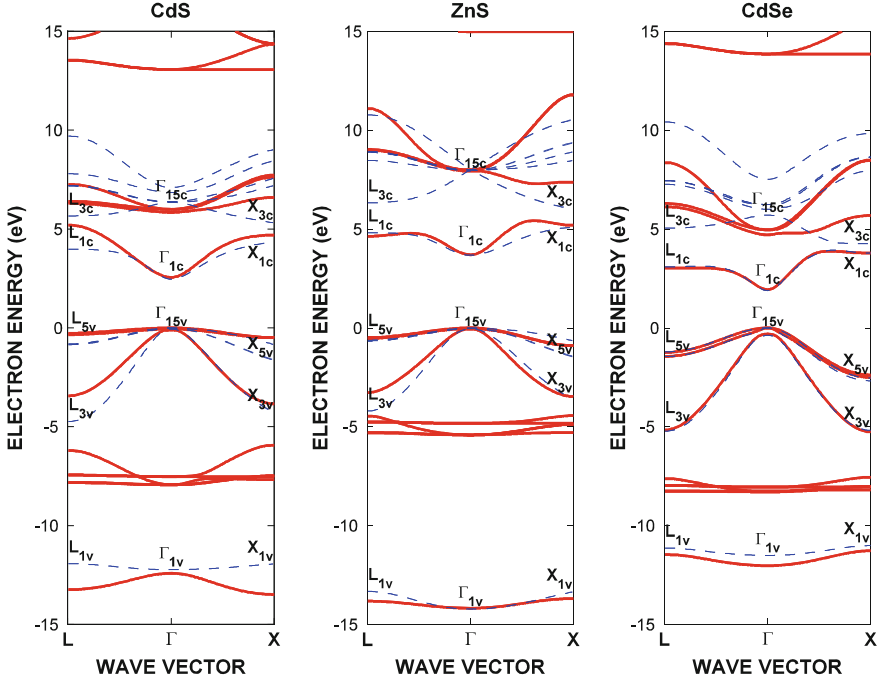


Fig. 1.19 Band structure of CdS, CdSe and ZnS compounds obtained using the 2NN sp^3s^* and NN sp^3d^5 TB models with the tight binding parameters given in Tables 1.4 and 1.5

which plays the central role in the calculation of the structural and electronic properties of semiconductors. The major consequence of the Kohn-Hohenberg-Sham studies [30, 45] is that the single particle states $\varphi_{i,k}(\mathbf{r})$ are determined by the solution of a set of equations similar to the Schrodinger equation:

$$H\varphi_{i,k} = \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}} + V_{\text{eff}} \right) \varphi_{i,k} = E_i \varphi_{i,k}, \quad (1.25)$$

where $\varphi_{i,k}(\mathbf{r})$ are the one-electron wave functions, V_{ext} is the external potential of the nuclei, and $V_{\text{eff}}(\mathbf{r})$ the effective potential defined as

$$V_{\text{eff}}(\mathbf{r}) = V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) = V_H(\mathbf{r}) + \frac{\delta E_{\text{xc}}(n(\mathbf{r}))}{\delta n(\mathbf{r})}, \quad (1.26)$$

where $V_H(\mathbf{r})$ is the Hartree Coulomb term and $E_{\text{xc}}(n(\mathbf{r}))$ is the exchange-correlation functional. Since the electron density $n(\mathbf{r})$ is involved in the definition of effective potential, (1.24) must be solved consistently with (1.25) and (1.26). Although the set of (1.24)–(1.26) yields, in principle, an exact solution to the quantum-mechanical problem, there are approximations involved in the

exchange-correlation potential $V_{xc}(r)$. In this respect, Local Density Approximation (LDA) and Generalized Gradient Approximations (GGA) have proven to be effective for a large number of semiconductors.

The conventional DFT calculations based on (1.24)–(1.26) provide satisfactory results for ground state properties (e.g., total energies, lattice constant, bulk modulus) but give unsatisfactory results for the electronic properties (e.g., band gaps and effective masses) [46]. For example, DFT predicted bandgaps are too small compared to experimental data [12] and predicted by empirical pseudopotential theory [14]. This difficulty can be avoided using various approaches (e.g., GW approximation or hybrid functional) that have been implemented in DFT model calculations. Even with GW and hybrid functionals, conventional DFT results in bandgap error on the order of 10–20 % as compared with experimental data [12]. As a remedy, the exchange-correlation potential contribution to the DFT band gap is shifted by using a so-called “scissor operator”, in accordance with the suggestion of Fiorentini and Balderschi [46]. The difference between the LDA and experimental band gaps (ΔE) scales with the optical dielectric constant ($\Delta E \cong 9.1/\epsilon_\infty$) [26, 27].

Recently, Tran and Blaha [47] proposed a new exchange-correlation potential, called the modified Becke-Johnson density functional (MBJLDA), which combines the Becke-Johnson exchange potential and the local density approximation (LDA) correlation potential in DFT band structure calculations. The MBJLDA functional is an exchange-correlation (XC) potential that is obtained as the functional derivative of the XC-energy functional E_{xc} with respect to the electron density $n(r)$ ($V_{xc}^{MBJ} = \delta E_{xc}[n](r)/\delta n(r)$) taken from LDA. The computational cost of DFT with the MBJLDA functional is comparable with DFT-LDA and DFT-GGA. It yields bandgaps which are in good agreement with experimental data [12, 13] and empirical pseudopotential theory [14]. We calculated the electronic properties of CdX and ZnX (X = S, Se, Te) II–VI compounds and their ternary/binary heterostructures using the WIEN2K [48] simulation package that uses the density functional theory (DFT) with MBJLDA functional in the band structure calculations.

Figure 1.20 exhibits the crystal structure of CdSe and ZnS compounds. CdX and ZnX (X = S, Se, Te) have a zinc-blende crystal structure (space group F-43 m No: 216) in which the Cd/Zn atoms are located at (0, 0, 0) and S (or Se) at (0.25, 0.25, 0.25). Converged results are obtained using 10,000 k points in the first Brillouin zone with $R_{MT}K_{max} = 8.50$, where R_{MT} represents the smallest muffin-tin radius and K_{max} is the maximum size of the reciprocal lattice vectors. LSDA, GGA and MBJLDA, as implemented in the WIEN2K simulations package, are used for exchange and correlation potentials in the calculations. SCF iterations are repeated until the total energy converges to a point less than 10^{-4} Ryd. The WIEN2K simulations with the MBJLDA functional embedded in DFT yields a remarkable improvement over LDA and GGA in the calculation of the structural properties (e.g., lattice constants and bulk modulus) and electronic structure properties (e.g., bandgaps) of the compounds (see Tables 1.6 and 1.7). However, we should point

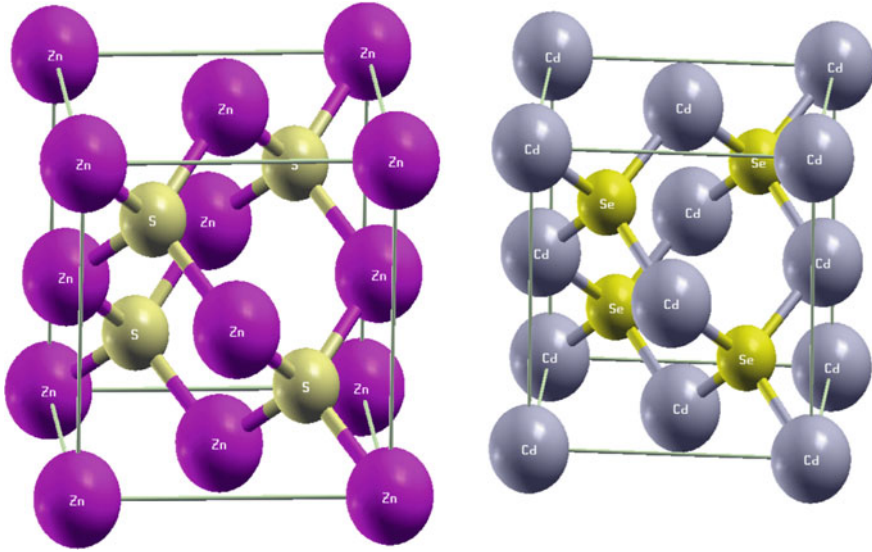


Fig. 1.20 Crystal structure of ZnS and CdSe compounds

Table 1.6 Lattice constant (a_0), bulk modulus (B_0) and its pressure derivative (B'_0) for CdX ($X = S, Se, Te$) and ZnX ($X = S, Se, Te$) calculated using WIEN2K, with DFT-MBJLDA

Property	CdS	CdSe	CdTe	ZnS	ZnSe	ZnTe
$a_0(\text{\AA})$	5.779 ^a	5.994	6.425	5.470	5.540	5.985
	5.839 ^b	6.088	6.500	5.460	5.690	6.039
	5.810 ^c	6.084	6.480	5.320	5.669	6.030
	(5.830) ^d					6.089
B_0	68.765	53.799	47.778	71.474	82.379	54.038
	66.01	56.79	46.76	91.71	73.91	55.56
	64.30	55.53	44.50	77.3	62.50	50.90
		—	—	—	—	—
B'_0	4.375	2.364	5.200	3.550	3.646	4.381
		4.20	4.470		—	5.10
	4.31			5.00	5.00	—
					—	—

a DFT-MBJLDA, *b* 2NN sp^3s^* TBM, *c* NN sp^3d^5 TBM, (...) ^d: Measured lattice constant

out that the MBJLDA only underestimates the band gaps between -2.50 and -7% for CdTe, ZnS, ZnSe, ZnTe and overestimates up to $\sim 4\%$ for CdS and CdSe. In most cases (except ZnS), MBJLDA is in better agreement with experiment than GW and $G'W'$. Bandgap energies at L, Γ and X symmetry points, calculated by using WIEN2K simulations package, with the MBJLDA functional embedded in

Table 1.7 Comparison of calculated bandgap energies of CdX (X = S, Se, Te) and ZnX (X = S, Se, Te)

(eV)	CdS	CdSe	CdTe	ZnS	ZnSe	ZnTe
$E_{g\Gamma}$	2.660 ^a	1.89	1.56	3.66	2.67	2.22
	2.476 ^b	1.887	1.59	3.680	2.83	2.39
	2.555 ^c	1.937	0.76	3.702	1.91	1.53
	(2.55)	(1.82)	(1.60)	(3.82)	(2.82)	(2.39)
E_{gX}	4.28	3.40	2.36	4.48	3.61	2.45
	3.983	3.097	2.46	4.810	3.99	2.80
	5.193	3.027	1.83	4.641	2.14	1.62
E_{gL}	4.71	4.04	3.03	4.42	3.78	2.71
	4.341	3.784	3.57	5.103	4.54	3.43
	4.696	3.779	4.76	5.190	5.04	3.34

a DFT-MBJLDA, *b* 2NN sp^3s^* TBM, NN sp^3d^5 TBM, (...): Measured fundamental bandgap

DFT, and using NN sp^3d^5 and 2NN sp^3s^* TB models, are given in Tables 1.6 and 1.7 for CdS, CdSe, CdTe, ZnS, ZnSe and ZnTe II–VI compounds.

As shown in Table 1.6, MBJLDA functional based DFT calculations of structural properties of compound semiconductors (such as lattice constant, bulk modulus and its pressure derivative) are in good agreement with the experimental data [12]. Furthermore, as shown in Table 1.7, WIEN2K simulations with MBJLDA embedded in DFT are in good agreement with the experimental data in terms of band gaps. Figures 1.21 and 1.22 demonstrate use of MBJLDA functional in WIEN2K simulations package in calculating the electronic band structure of compound semiconductors yields much better results than those of LSDA for CdX (X = S, Se, Te) and GGA band structures for ZnX (X = S, Se, Te). Accurate modeling of band structure properties have a key role in the design of cadmium and zinc chalcogenides based device applications. According to current calculations MBJLDA performed better than other conventional DFT functionals and GW approximations to calculate band structure. For this reason, MBJLDA is a very effective method and it can be used for a wide range of semiconductors. Accurate modelling of band structure has a key role in the design of cadmium and zinc chalcogenides-based device applications.

The comparison of the band structure dispersion curves obtained by using the WIEN2K simulation package with MBJLDA functional embedded in DFT and the semiempirical tight binding theories with NN sp^3d^5 and 2NN sp^3s^* orbitals sets is shown in Fig. 1.23 for CdS and ZnS and in Fig. 1.24 for CdSe, CdTe and ZnSe compound semiconductors, respectively. As displayed in Figs. 1.23 and 1.24, the MBJLDA functional based DFT and semiempirical NN sp^3d^5 and 2NN sp^3s^* orbitals sets TB models accurately reproduce the band gaps and band dispersion curves at high symmetry points when they are compared with empirical pseudopotential calculations for bulk II–VI compounds and their heterostructures. The three different approaches almost equally well reproduce the band gaps at Γ , X and L high symmetry points and valence band and conduction band dispersion curves in

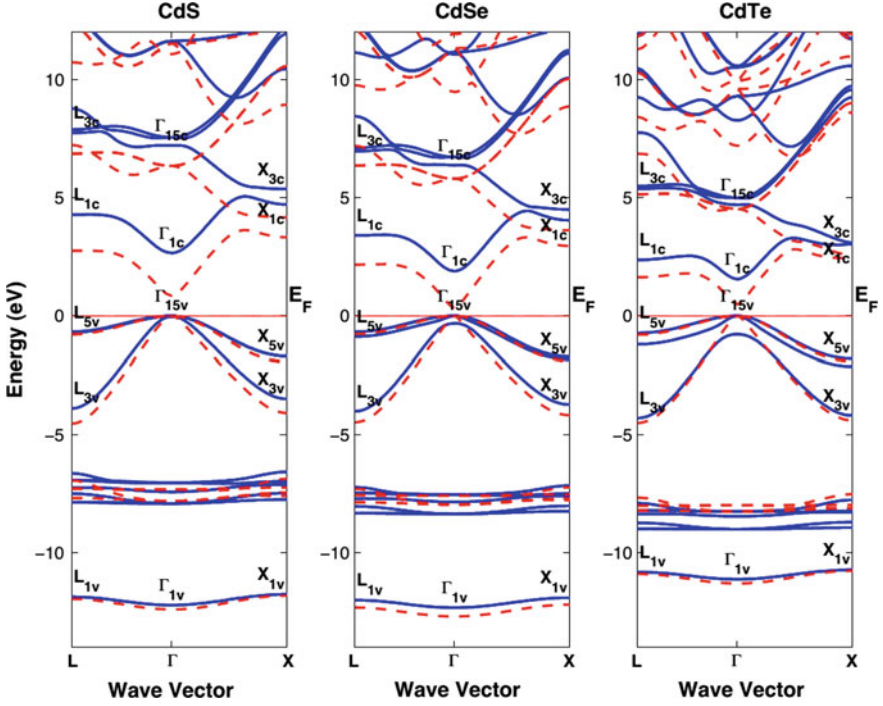


Fig. 1.21 Band structure of CdS, CdSe and ZnS obtained using WIEN2K with DFT-MBJLDA (solid lines) and DFT-LSDA (dashed lines)

the entire Brillouin zone of bulk CdX and ZnX (X = S, Se, Te) II–VI compounds and their heterostructures CdZnS/CdS, CdSe/CdTe and ZnS/CdTe.

We now discuss the use of DFT with MBJLDA functional and of the semiempirical NN sp^3d^5 and 2NN sp^3s^* TB models to calculate the electronic band structures of ZnS/CdS and CdSe/CdTe heterostructures. The predicted composition and interface strain effects on the fundamental band gaps of ZnS/CdS and CdSe in ZnS/CdS and CdSe/CdTe heterostructures are shown in Fig. 1.25 (left, right), respectively. The calculations are carried out using the WIEN2K simulations based on DFT with the MBJLDA functional (dark-solid line) and the semiempirical NN sp^3d^5 TB model (red-solid lines) and 2NN sp^3s^* TB models (dashed-blue lines) with tight binding parameters given in Tables 1.3, 1.4 and 1.5, integrated with the statistical thermodynamic model. (Since the measured band gaps are near 0 K, we ignored the logarithmic term, which accounts for the electron-phonon interactions for temperature dependence.) We can state that strain effect on the fundamental bandgaps can be quite large when the interface strain increases for large deformation potential and high alloy composition. The predicted band gaps, especially at the Γ point, are in excellent agreement with experiment [12].

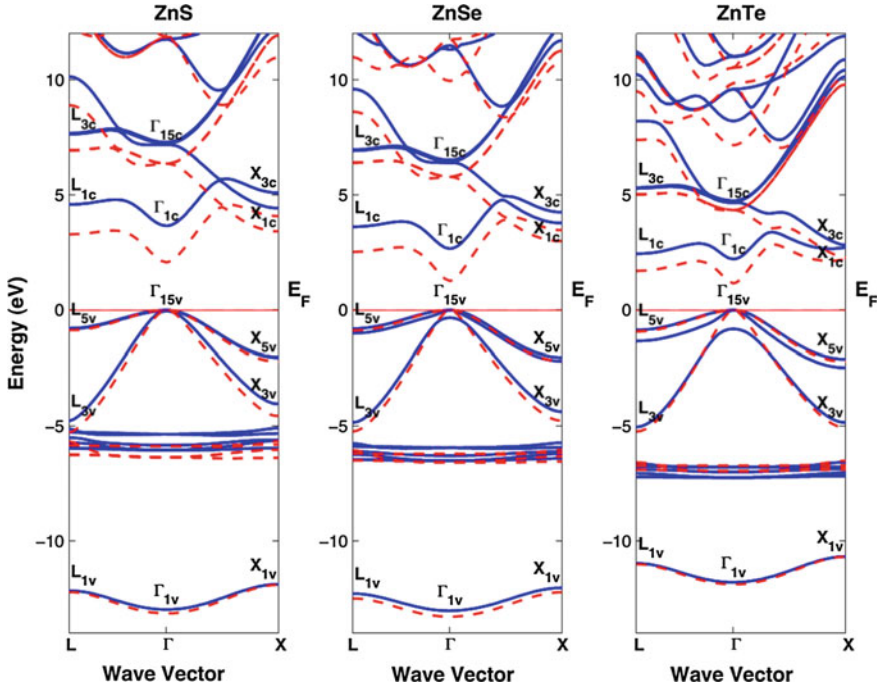


Fig. 1.22 Band structure of ZnS, ZnSe and ZnTe obtained using WIEN2K with DFT-MBJLDA functional (solid lines) and DFT-GGA (dashed lines)

In conclusion, as demonstrated in Figs. 1.23 and 1.24 for CdX and ZnX (X=S, Se, Te) binaries and in 1.25 for ZnSSe and CdSTe ternaries of ZnSSe/ZnSe and CdTe/CdTe heterostructures, the WIEN2K simulations with DFT-MBJLDA functional and semiempirical NN sp^3d^5 and 2NN sp^3s^* TB methods described in this work accurately reproduce the band gaps and band dispersion curves at high symmetry points of Brillouin zone when they are compared with empirical pseudopotential calculations for these binary and ternary semiconductors. The three different approaches almost identically reproduce the band gaps at the Γ , X and L high symmetry points, as well as the valence band and conduction band dispersion curves in the entire Brillouin zones of the bulk CdX and ZnX (X = S, Se, Te) binaries and ZnSSe and CdSTe ternaries of ZnSSe/ZnSe and CdTe/CdTe heterostructures, respectively.

As can be seen from Fig. 1.25, the tight binding model with an sp^3d^5 orbital basis, including the NN interactions of cation and anion atoms and spin-orbit coupling of p-states, is adequate to accurately reproduce the band gaps at the Γ , X and L symmetry points and both the valence band and conduction band dispersion curves, obviating the need for any fictitious excited s^* state in the TB model calculations. When the two semiempirical NN sp^3d^5 and 2NN sp^3s^* tight binding parameterizations are compared with each other, they both give reasonable

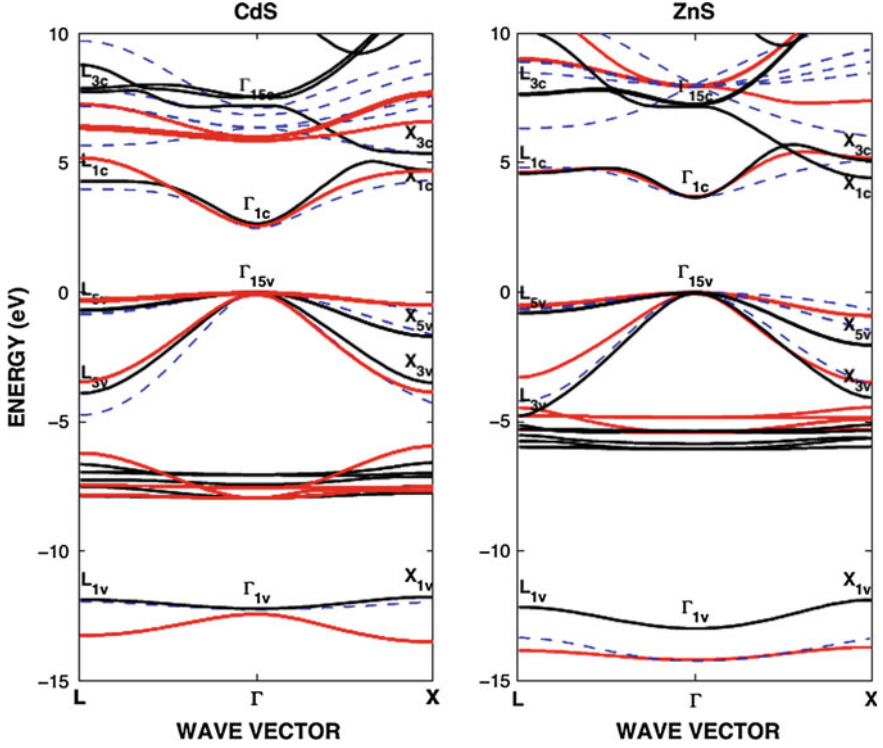


Fig. 1.23 Band structures of CdS and ZnS obtained using WIEN2K with DFT-MBJLDA (dark-solid lines), NN sp^3d^5 TB (red-solid line) and 2NN sp^3s^* TB (dashed-blue line) models

descriptions of the energy levels in the vicinity of the bottom of the conduction band and the top of the valence band of both binary and ternary II–VI compounds. However, the NN sp^3d^5 TB model does better than the 2NN sp^3s^* TB model in accurately reproducing band gaps as well as valence band and conduction band dispersion curves fitted to the empirical pseudopotential calculations at the L high symmetry point of these compounds. Furthermore, since the inclusion of the fictitious s^* excited state is done by modelling the average of p-d interactions, the 2NN sp^3s^* TB parametrization does not permit the inclusion of excited d-orbitals to an sp^3 basis set. Consequently, the actual behavior and contribution of excited d-states in the band structure calculations is reliably and accurately reflected in the NN sp^3d^5 TB model. We should point out that both the NN sp^3d^5 and 2NN sp^3s^* TB models are semiempirical and they rely on a good description of the band structures that are produced exactly by WIEN2K simulations package with MBLDA functional embedded in DFT [47, 48] and empirical pseudopotential theory [14].

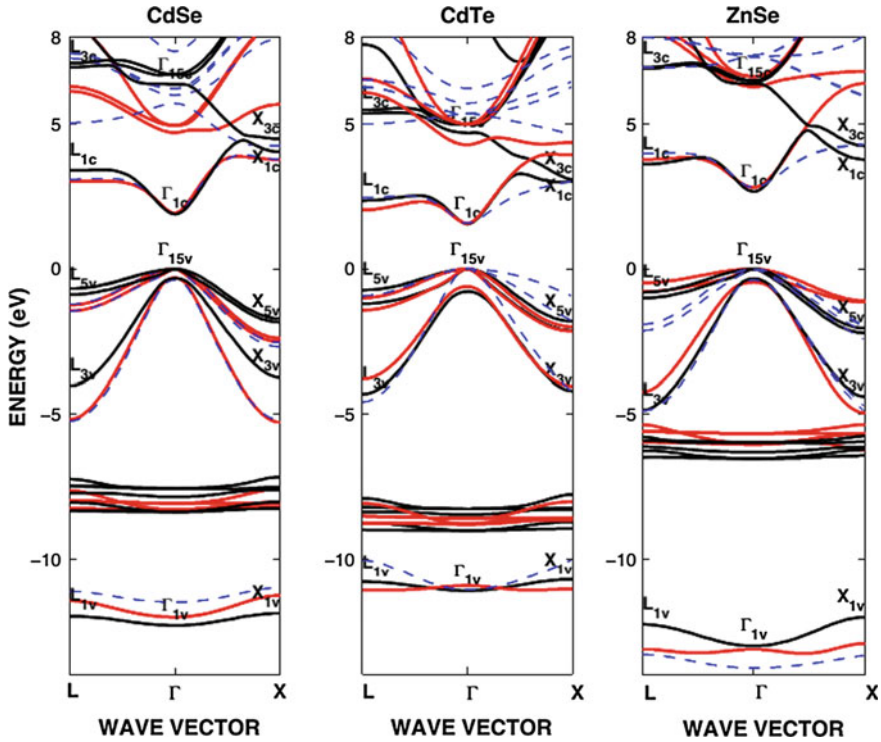


Fig. 1.24 Band structures of CdSe, CdTe and ZnSe obtained using WIEN2K with DFT-MBJLDA (dark-solid lines), NN sp^3d^5 TB (red-solid line) and 2NN sp^3s^* TB (dashed-blue line) models

1.5 Modeling of Band Offsets in Heterostructures

One of the key issues in low dimensional heterostructure semiconductor device technology is the understanding the formation and determining the magnitude of conduction and valence band structure across heterointerfaces (e.g., band offsets), shown in Fig. 1.26.

The potential barriers dominate various device properties such as injection efficiency in heterobipolar devices (e.g., HBTs) and carrier confinement in unipolar devices (e.g., MODFETs), and have received considerable attention among device scientists and engineers over the years. When the semiconductor composition changes abruptly at interface between constituents, the difference in their energy bands is accommodated by the discontinuities in the conduction and valence bands across the interface. In analyzing charge transport in bipolar and unipolar heterostructure devices, the crucial problem is to determine the formation and magnitude of potential barriers relating to conduction bands and valence bands across the heterointerface. In the context of the semiempirical tight binding model

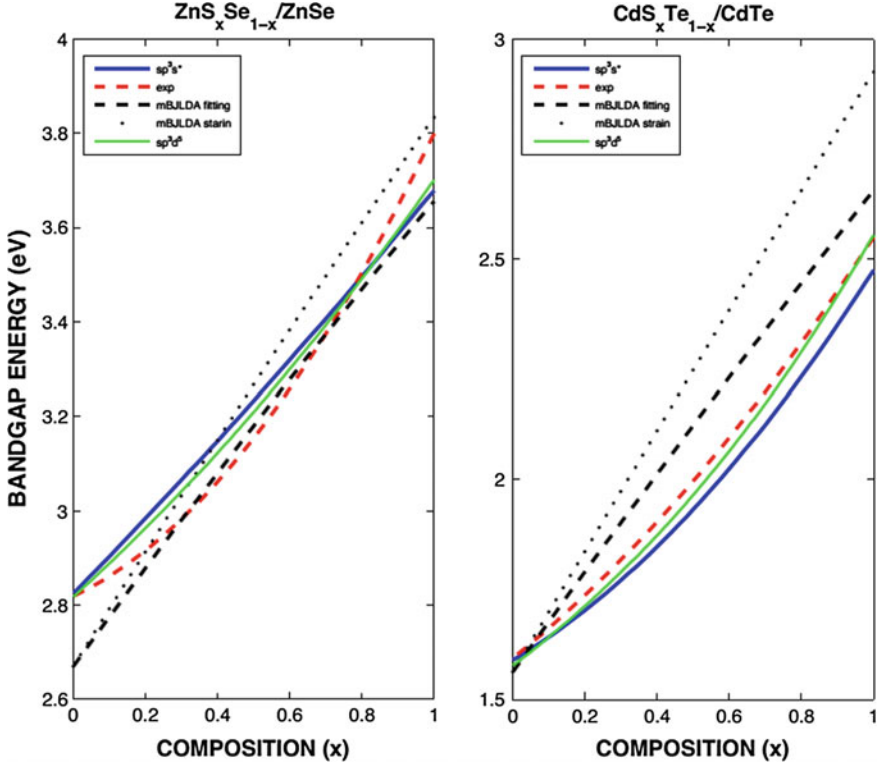


Fig. 1.25 Strain effects on the bandgaps of ZnSSe and CdSTe in ZnSSe/ZnSe and CdSTe/CdTe heterostructures as a function of composition, obtained using the WIEN2K package with DFT-mBJLDA (*dark-solid line*), and the NN sp^3d^5 TB (*red-solid line*) and 2NN sp^3s^* TB (*dashed-blue line*) models for the TB parameters given in Tables 1.3, 1.4 and 1.5

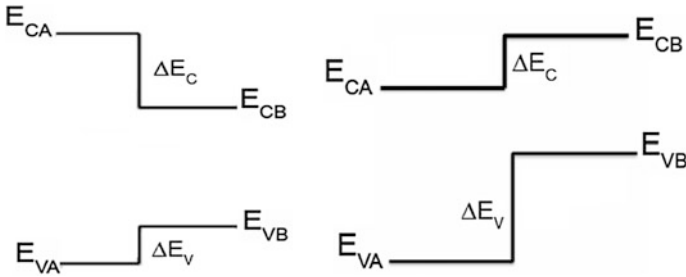


Fig. 1.26 Schematic view of band diagram of Type I (*left*) and Type II (*right*) heterostructures

discussed in Sect. 1.2, the valence band offset across an ABC/AC ternary/binary heterostructure can be obtained by taking the difference between the valence band energies of the constituents that are screened with the optical dielectric constants of the constituents [11]:

$$\Delta E_v = \left(\frac{E_v}{\varepsilon_\infty} \right)_{BC} - \left(\frac{E_v}{\varepsilon_\infty} \right)_{ABC}, \quad (1.27)$$

where $E_v = E_v(\Gamma_{15})$ is top of the valence band at the Γ high symmetry point and $\varepsilon_\infty(ABC)$ and $\varepsilon_\infty(BC)$ are the optical dielectric constants of the ABC ternary and BC binary constituents of heterostructure, respectively:

$$\varepsilon_\infty(ABC) = x\varepsilon_\infty(AC) + (1-x)\varepsilon_\infty(BC) + -x(1-x)\delta_c(\varepsilon_\infty(BC) - \varepsilon_\infty(AC)), \quad (1.28)$$

The conduction band offset for a given Γ , L and X high symmetry point of the Brillouin zone is given as the difference between the respective band gap differences, written as [11]:

$$\Delta E_{ci} = E_{ciABC} - E_{ciBC} = \Delta E_{gi} - \Delta E_v, \quad (1.29)$$

where $E_{ci} = E_{\Gamma_{6c}}, E_{L_{6c}}$ and $E_{X_{6c}}$ are the bottom of the conduction bands at the Γ , L and X high symmetry points, determined using the semiempirical tight binding theory with the sp^3 , sp^3s^* , $sp^3d^5s^*$ or sp^3d^5 orbitals sets. Here $\Delta E_{gi} = E_{gi}(ABC) - E_{gi}(BC)$ is the difference between the band gaps of ABC ternary and BC binary compounds with band gaps $E_{gi}(ABC)$ and $E_{gi}(BC)$, where $E_{gi} = E_{g\Gamma}, E_{gL}$ and E_{gX} are the principal bandgaps at the Γ , L and X symmetry points.

Once the valence band energies and band gaps at high symmetry points are known, it is easy to determine the conduction band offsets of a given heterostructure from (1.29).

The potential barrier in the conduction band and the potential step in the valence band at the interface significantly influence carrier transport and device performance [2], making reliable and accurate modeling of interface energy band structure crucial to designing the functionality of group III–V and II–VI heterostructures and their optimization in low dimensional semiconductor electronic and optical devices. Here, we focus on modeling the effects of composition and interface strain on electronic band structure, band gaps and band offsets of ternary/binary group III–V and II–VI compounds based heterostructures for which experimental data are available for comparison. In this, we compare the predictions of the nearest neighbor (NN) sp^3d^5 tight binding model, with spin-orbit coupling of p-states, to those of the widely used second nearest neighbor (2NN) sp^3s^* model, with spin-orbit coupling of p-states. Tables 1.3, 1.4 and 1.5 give the number of tight binding parameters for the 2NN sp^3s^* TB and NN sp^3d^5 tight TB models used in the calculations. Figure 1.27 shows the composition and strain variations of the band gap difference and valence band offsets at lattice matched AlGaAs/GaAs and pseudomorphic InGaAs/GaAs heterostructures.

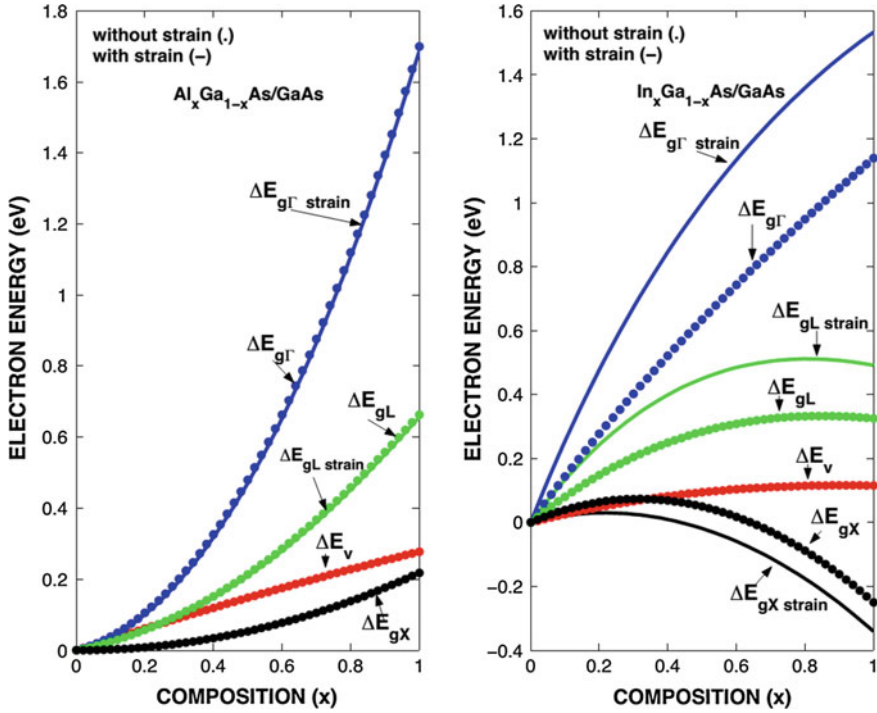


Fig. 1.27 Composition effects on bandgap differences and valence band offsets of lattice matched AlGaAs/GaAs (*left*) and strained InGaAs/GaAs (*right*) heterostructures

The band offsets in III–V nitrides based ternary/binary heterostructures are shown in Fig. 1.28 for AlGaIn/GaN, InGaIn/GaN and GaAsIn/GaAs as functions of interface strain for the entire composition range ($0 \leq x \leq 1$). As shown in Fig. 1.28, the interface strain effect on the valence band offsets in AlGaIn/GaN (left), InGaIn/GaN (middle) and GaAsIn/GaAs (right) dilute nitrides based heterostructures is rather small because of the smaller valence band deformation potentials. However, the interface strain effects on conduction band offsets at the Γ , L and X high symmetry points can be considerably larger because the conduction band deformation potentials are large.

The predicted valence band offsets are in good agreement with experimental findings [12, 13]. As shown in Figs. 1.27 and 1.28, strain effects on the band gap differences and on the conduction band offsets can be quite large since the lattice mismatch increases with an increase in the ternary mole fraction. As we pointed out earlier, there is a considerable lattice mismatch across many of the ternary/binary heterointerfaces. Interface strain due to lattice mismatch causes a shift in the lattice

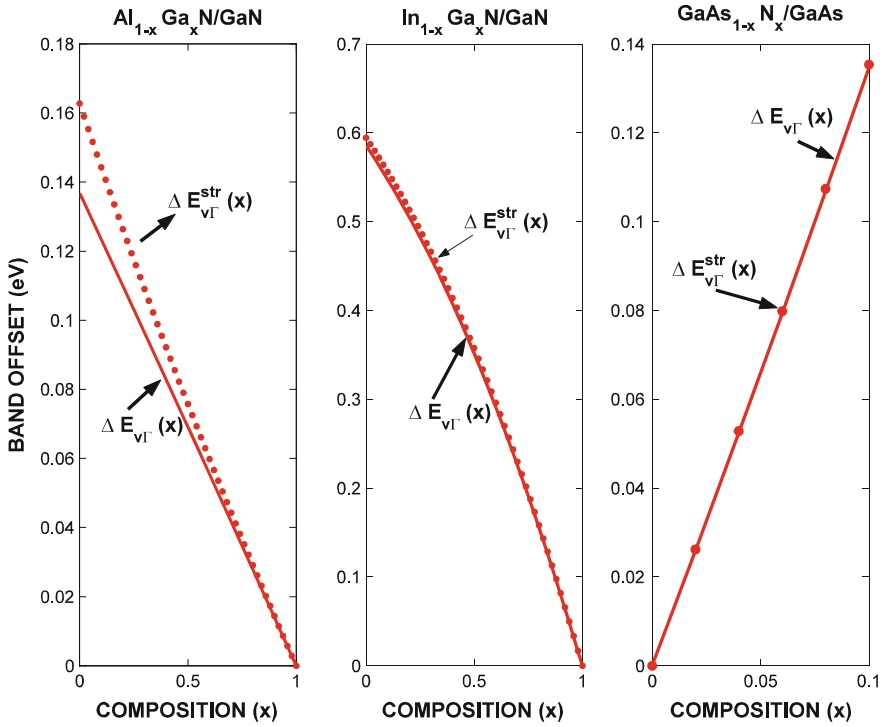


Fig. 1.28 Predicted interface strain effects on the valence band offsets of AlGaIn/GaN (*left*), InGaIn/GaN (*middle*) and GaAsN/GaAs (*right*) heterostructures

constant of the epilayer: $a = (1 + \varepsilon)a_0$, where ε is the symmetric strain tensor. Therefore, the bond lengths and on-site and off-site TB matrix elements will be modified with strain. Consequently, the electronic properties of heterostructures such as conduction and valence band offsets will be modified with respect to their unstrained values. As an example, Fig. 1.29 shows the composition and strain effects on conduction and valence band offsets of CdSTe/CdTe and ZnSSe/ZnSe heterostructures calculated by using the WIEN2K simulation package based on the DFT with MBJLDA functional and semiempirical NN sp^3d^5 and 2NN sp^3s^* TB models for optimized tight binding parameters given in Tables 1.3, 1.4 and 1.5. As can be seen in this comparison, the interface strain effects on the conduction band offsets of ZnSSe/ZnSe and CdSTe/CdTe heterostructures can be quite large when the interface strain increases for large the deformation potential and high alloy composition.

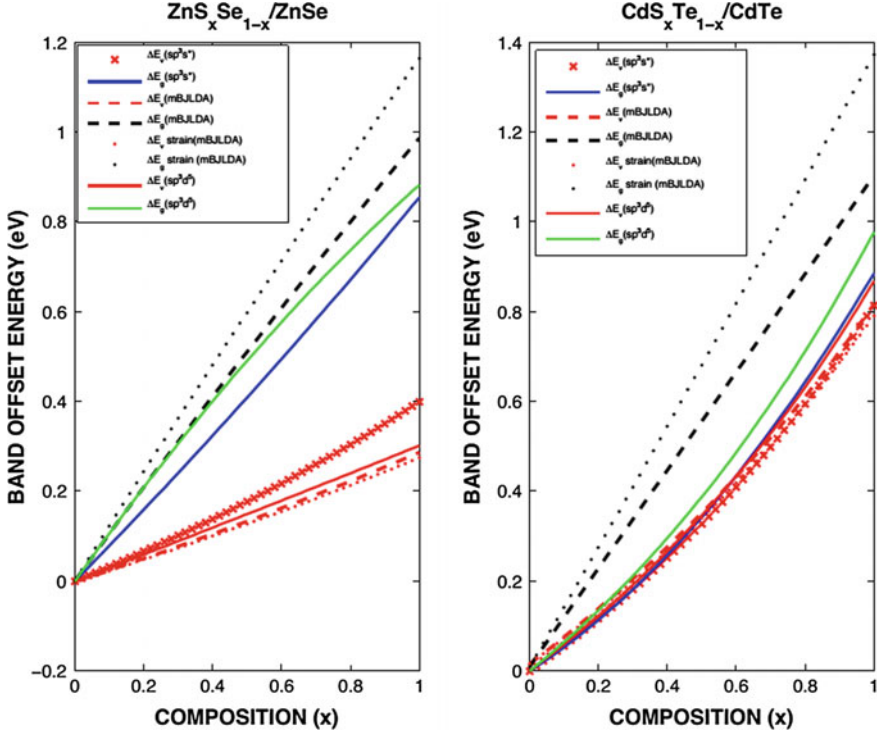


Fig. 1.29 Predicted composition and interface strain effects on the band offsets of ZnSSe/ZnSe and CdSTe/CdTe heterostructures, obtained using the WIEN2K with DFT-MBJLDA (*dark-solid line*) compared with the NN sp^3d^5 (*red-solid line*) and 2NN sp^3s^* (*dashed-blue line*) TB models for parameters given in Tables 1.1 and 1.2 of [30]

1.6 Conclusion

Ever since the invention of the first transistor in 1949, device scientists and engineers have witnessed amazing achievements in the semiconductor science and technology. Advances in the growth of semiconductor thin films with layer thickness approaching atomic dimensions and fabrication of low dimensional electronic and optical devices has provided new opportunities in fundamental science and technology of semiconductors and semiconductor devices. Such advancement could not have been possible without a qualitatively reliable understanding of the basic physics of semiconducting materials and quantitatively precise potential predictions and performance of devices, leading to new concepts in the semiconductor growth that allowed previously many unknown devices with more complex functionality and much higher densities for electronic and optical applications.

This review has presented comparative predictions of electronic band structures of group III–V and II–VI compounds and their heterostructures obtained using the semiempirical tight binding theory based on the 2NN sp^3 , 2NN sp^3s^* , NN sp^3d^{5*} and NN sp^3d^5 orbitals sets in comparison with the WIEN2K simulations package based on the density functional theory (DFT) with the modified modified Becke-Johnson exchange-correlation potential with the local density approximation (LDA), called MBJLDA functional. We conclude that DFT with MBJLDA functional and the semiempirical NN sp^3d^5 TB model are in good agreement with experimental data for band gaps and band offsets and have considerable potential in the design and optimization of group III–V and II–VI compounds and their ternaries used for the fabrication of electronic and optical devices. When compared to the 2NN sp^3s^* TB model, NN sp^3d^5 TB parametrization better simulates both the valence band and conduction band dispersion curves. The actual contribution of the excited d-states in the band structure calculations is reliably reproduced in the case of NN sp^3d^5 orbitals set tight binding parameterization. We conclude that DFT with MBJLDA and semiempirical NN sp^3d^5 TB model show good agreement with experiment for band gaps and band offsets and has a considerable potential in the design and optimization of group III–V and II–VI compounds and their ternaries used for the fabrication of low dimensional electronic and optical devices.

References

1. H. Ünlü, N.J.M. Horing (eds.), *Low Dimensional Semiconductor Structure: Characterization and Applications* (Springer, Heidelberg, 2013)
2. H. Morkoç, H. Ünlü, G. Ji, Principles and technology of MODFETs. Wiley **1**, 2 (1991)
3. H. Ünlü, H. Morkoç, Solid State Technol. **31**, 83 (1988)
4. H. Morkoç, H. Ünlü, in *Semiconductor and Semimetals*, vol. 24 ed. by R. Dingle (1987), p. 135
5. H. Ünlü, H. Morkoç, and S. Iyer, in *Gallium Arsenide Technology*, vol. 2 ed. by D.K. Ferry (1990), p. 231
6. H. Morkoç, H. Ünlü, H. Zabel, N. Otsuka, Solid State Technol. **31**, 71 (1988)
7. H. Kroemer, Proc. IRE **45**, 1535 (1957)
8. H. Kroemer, Rev. Mod. Phys. **73**, 783 (2000)
9. N. Lucas, H. Zabel, H. Morkoç, H. Ünlü, Appl. Phys. Lett. **52**, 2117 (1988)
10. H. Ünlü, Solid State Electron. **35**, 1343 (1992)
11. H. Ünlü, Phys. Status Solidi B **216**, 107 (1999); B **223**, 195 (2001); B **229** 581 (2002); B **235**, 248 (2003)
12. O. Madelung (ed), *Numerical Data and Functional Relationships in Science and Technology*, 17a, Springer, Berlin (1982); ibid 17d, Springer, Berlin (1984)
13. Vurgaftman, I., Meyer, J.R. ve Ram-Mohan, L.R. (2001), J. Appl. Phys. **89**, 5815 (2001)
14. M.L. Cohen, J.R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (2nd edn), Springer, Berlin (1989)
15. C. Pryor, J. Kim, L.M. Wang, A.J. Williamson, A. Zunger, J. Appl. Phys. **83**, 2548 (1998)
16. P. Keating, Phys. Rev. **145**, 637 (1966)
17. K. Shim, H. Rabitz, Phys. Rev. B **57**, 12874 (1998)
18. M. Rabah, B. Sahraoui, B. Bouhafs, B. Abbar, H. Abid, Phys. Stat. Solidi B **238**, 156 (2003)
19. H.H. Gürel, Ö. Akıncı, H. Ünlü, Comput. Mater. Sci. **33**, 269 (2005)

20. Ö. Akıncı, H.H. Gürel, H. Ünlü, *Thin Solid Films* **511–512**, 684 (2006)
21. H.H. Gürel, Ö. Akıncı, H. Ünlü, *Superlattices and Microstructures*, 40 (4–6), 588 (2006)
22. H.H. Gürel, Ö. Akıncı, H. Ünlü, *Physica Status Solidi (c)* **4**(2), 316 (2007)
23. Ö. Akıncı, H.H. Gürel, H. Ünlü, *Physica Status Solidi (c)* **5**(2), 478 (2008)
24. H.H. Gürel, Ö. Akıncı, H. Ünlü, *Thin Solid Films* **516**, 7098 (2008)
25. Ö. Akıncı, H.H. Gürel, H. Ünlü, *J. Nanoscience Nanotechnology* **8**, 540 (2008)
26. Ö. Akıncı, Ö., H.H. Gürel, H.H. and H. Ünlü, *Thin Solid Films*, 517, 2431 (2009)
27. H.H. Gürel, O. Akıncı, H. Ünlü, *Superlattices Microstruct.* **51**, 725 (2012)
28. H.H. Gürel, H. Ünlü, *Mater. Sci. Semicond. Process.* **16**, 1619 (2013)
29. J.L. Martins, A. Zunger, *Physical Review B* **30**, 6217 (1984)
30. P. Hohenberg and W. Kohn, *Phys. Rev.* 136 B, 864 (1964)
31. J.C. Slater and G. F. Koster (1954), *Physical Review*, 94, 1498 (1954)
32. D.J. Chadi, M.L. Cohen, *Physica Status Solidi* **68**, 405 (1975)
33. D.J. Chadi, *Physical Review B* **16**, 790 (1977)
34. W.A. Harrison, *Electronic Structure and the Properties of Solids*, Freeman (1980)
35. D.N. Talwar, C.S. Ting, *Physical Review B* **25**, 2660 (1982)
36. J.P. Loehr, Talwar, *Phys. Rev. B* **55**, 4353 (1997)
37. T.B. Boykin, L.J. Gamble, G. Klimeck, R.C. Bowen, *Phys. Rev. B* **59**, 7301 (1999)
38. Y. Fu, K.A. Chao, *Phys. Rev. B* **43**, 4119 (1991)
39. A.D. Carlo, *Semiconductor Sci. and Tech.* **18**, R1 (2001)
40. E.P. O'Reilly, A. Lindsay, A., S. Tomic, M.K. Saadi, *Semicond. Sci. Technol.* **17**, 870 (2002)
41. P. Vogl, H.P. Hjalmarson, J.D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983)
42. M. Jancu, F. R.Scholz, F. Beltram, F. Bassani, *Phys. Rev. B* **57**, 6493 (1998)
43. J.M. Jancu, F. Bassani, F. Della Sala, R. Schols, *Appl. Phys. Lett.* **81**, 4838 (2002)
44. S. Sapra, N. Shanthi, D.D. Sarma, *Phys. Rev. B* **66**, 205202 (2002)
45. W. Kohn, J.L. Sham, *Phys. Rev.* **140A**, 1133 (1965)
46. V. Fiorentini, A. Baldereschi, *Phys. Rev. B* **51**, 17196 (1995)
47. F. Tran, P. Blaha, *Phys. Rev. Lett.* **102**, 226401 (2009)
48. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program For Calculating Crystal Properties*, Vienna University of Technology, Vienna, Austria, 2001

Low-Dimensional and Nanostructured Materials and
Devices

Properties, Synthesis, Characterization, Modelling and
Applications

Ünlü, H.; Horing, N.J.M.; Dabowski, J. (Eds.)

2016, XXVII, 674 p. 319 illus., 218 illus. in color.,

Hardcover

ISBN: 978-3-319-25338-1