Tight-binding calculations of ZnSe/Si wurtzite superlattices: Electronic structure and optical properties

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Our study is devoted to the theoretical investigation of the electronic and optical properties of (ZnSe)$_n$/(Si)$_m$ (0001) wurtzite (WZ) superlattices (SLs) with the range $n=m=1$–18, giving special attention to the role of interface states at the Zn–Si and Se–Si polar interfaces. The calculations are performed by means of a semiempirical tight-binding model with an $sp^3s^*$ basis. The procedure involves the construction of a tight-binding Hamiltonian model of WZ SLs from the WZ bulk in the (0001) direction with different $n$ and $m$ layers. For $(ZnSe)_{16}/(Si)_{16}$ SL, we found that the energy band gap is close to 1.665 eV, with the conduction-band minimum located at the $\Gamma$ point. The states at the conduction- and valence-band edges are confined two dimensionally in the Si layers. For a valence-band discontinuity $\Delta E_v=1.09$ eV given by Harrison theory, the band gap between the confined band edges states increases $(2.37$ eV at the $\Gamma$ point for $n=m=2)$ by decreasing the superlattice period. It is shown that the heterointerface bond relaxation strongly affects interface band in the band gap. In the $(ZnSe)_{10}/(Si)_{10}$ SL, the relaxed Si bonds at the heterointerface induce a vacant interface band and a filled interface band in the band gap. The band structures of $(ZnSe)_n/(Si)_{m}$ (0001) (WZ) (SLs) with different layer thickness are used to determine the electron and hole effective masses. Furthermore, the calculated absorption spectra of the superlattices are found to be quite different from those of bulk ZnSe and Si but fairly close to their average. The electronic structure of the superlattice turns out to be quite sensitive to the combination of the well and barrier layer thickness. This sensitivity suggests the possibility of designing suitable band structures for device application. © 2008 American Institute of Physics. [DOI: 10.1063/1.2961311]

I. INTRODUCTION

Recent progress in high-vacuum deposition technology has allowed the growth of heteroepitaxial layered II-VI compounds on IV semiconductors. As a consequence of the expanding demand for semiconductors which are relevant and useful for various electronic and optical devices, group II-VI compounds and their quantum wells have assumed tremendous importance in the past few years. The high quality of the interface with chemical and structural stability offers great potential in device applications for these systems as strong nonlinearities in semiconductor superlattices (SLs) based on II-VI compounds. Since the suitability of a material for a particular device is revealed by its overall electronic structure, the theoretical calculation of these materials has become a necessity from a basic of research and practical applications. There has been great interest in the multilayer growth of II-VI compounds for optoelectronic device applications in the visible-to-ultraviolet range in optoelectronic device applications (e.g., blue lasers on ZnSe heterostructures). For a basic understanding of the related phenomena and an optimization of materials for relevant processes (band-structure engineering), a quantitative knowledge of the electronic properties of these compounds and their interfaces is needed. Semiconductor SLs consisting of alternate layers of different materials provide extra dimensions for tailoring material properties. The combination of controlled variations in the composition, strain, and thickness of the layers provides electronic and optical properties unlike those of any ordinary bulk material, which might lead to important applications in optoelectronics. To integrate the superior properties of II-VI wide band gap compounds with the mature technology of IV semiconductors, it is of crucial importance to fully explore the knowledge of the electronic and optical properties of these layered systems. A better approach, therefore, will be to integrate the superior properties of ZnSe semiconductor with the mature technology of Si. Of particular note for the present work is the successful fabrication of II-VI/IV SLs using molecular beam epitaxy, with each layer consisting of a few monolayers of the constituent materials. Since a detailed picture of the electronic structure and stability will provide guidance for device applications, the systematic study of the II-VI/IV SL systems has become a necessity from a practical point of view.

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In this article, we report the results of a tight-binding (TB) study of ZnSe/Si (0001) wurtzite (WZ) SLs, a system involving a II–VI compound on a IV semiconductor that is fundamentally interesting and technologically important. An important feature of the ZnSe/Si WZ SLs is that the (0001) interface is polar in this system. With suitable barrier width, an interesting quantum size effect is expected due to spacial confinement. To our knowledge, our results present the first research that shed light on the underlying physics of WZ SLs and analyzed in the same section. We conclude the main points of the results in Sec. IV.

II. TIGHT-BINDING MODEL FOR WURTZITE SUPERLATTICES

We have constructed a TB Hamiltonian for the (ca)_n/(c’a’)_m (0001) WZ SL from the TB model of the WZ bulk in the (0001) direction.25 The labels n and m are the hexagonality for different layers. Here, we have used an orthogonalized extended set sp3s* with a basis of five orbitals (s, p_x, p_y, p_z, and s*) per atom. Our TB model provides good electronic structure with only nearest neighbor interactions.26

Consider a TB Hamiltonian of two different alternating WZ crystals labeled ca (c’a’) in the (0001) direction, where c (c’) and a (a’) are labeled cation and anion atoms. The WZ SL contains 2[2(n+m)] atoms in a unit cell at 

\[ R_i \] with five orbitals each; \( |\alpha\rangle \), where \( \alpha \) denotes the s, x(=p_x), y(=p_y), z(=p_z), and s*(excited s) orbitals and \( j \) represents the site index in a unit cell which runs from 1 to 2[2(n+m)]

For each wave vector \( \mathbf{k} \) in the BZ, the Bloch functions can be constructed by the linear combination of atomic orbitals:27

\[ |\xi, r_\alpha, R_i \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \mathbf{R} + i e_{\mathbf{k}} |\xi, r_\alpha, R_i \rangle}. \]

Here \( \xi \) is a quantum number that runs over the basis orbitals s', s, p_x, p_y, and p_z on the different types of sites \( \alpha \) in a unit cell. The \( \mathbf{N} \) wave vectors \( \mathbf{k} \) lie in the first BZ with the origin of the \( \beta \)th unit cell at \( R_\beta \), and \( r_\alpha \) represents the positions of the atoms in this unit cell.

The electronic eigenstates of the SL are expanded as

\[ |k, \lambda \rangle = \sum_{\xi, \alpha} \langle \xi, r_\alpha | k, \lambda \rangle \]

\[ = \sum_{\xi, \alpha} C_{\xi \alpha}(k, \lambda) |\xi, r_\alpha, k \rangle. \]

\( \lambda \) denotes the band index and \( C_{\xi \alpha}(k, \lambda) \) is the eigenwave function, which can be obtained by solving the Schrödinger equation.

\[ \sum_{\xi, \alpha'} \langle \xi, r_\alpha, k | H | \xi', r_{\alpha'}, k \rangle - E_k(k) \delta_{\xi \xi'} \delta_{\alpha \alpha'} |\xi, r_\alpha, k \rangle = 0. \]

Therefore, we obtain the Hamiltonian matrix for (ca)_n/(c’a’)_m (0001) WZ SL.
Here, the blocks $H_{c(a)}$, $H_{c(a')}$, $H_{ac(a',c')}$, and $H_{bac(a',c')}$ denote intramaterial interactions for $(ca)_n/(c'a')_m$ (0001) WZ SL, and every element represents a $5 \times 5$ matrix. The blocks $H_{ca(c',a')}$ and $H_{bac(c',a')}$ are expressed as

$$H_{ac(a',c')} = \begin{bmatrix} a(a) & ac(a'c') \\ ac^*(a'c')^* & c(c') \end{bmatrix},$$

$$H_{bac(a',c')} = \begin{bmatrix} aa(a'a') & ac(a'c') \\ ca(c'a') & cc(c'c') \end{bmatrix}.$$

The diagonal elements $H_{[j=a(a')}$ and $c(c')]$ correspond to intrasite energies, and the others contain the nearest atomic interactions in the same layer ($H_{ij}$) or between two neighbor layers ($H_{0ij}$) perpendicular to the (0001) direction. The terms $a(a')$ and $c(c')$ are regarded as the anion and cation atoms of the ZnSe and Si semiconductors. In a SETB method, one works within the one-electron approximation made to the exact many-body Hamiltonian operator (e.g., density functional theory) which includes the electron-electron, electron-ion, and ion-ion interactions and the exchange and correlation potentials. In the TB Hamiltonian for the electronic structure, the on-site (intrasite) terms are diagonal parts and correspond to the Hartree–Fock term values of the isolated atoms. The intersite terms (hopping parameters) take explicitly into account the equal importance of hybridization effects and electron-electron interactions by including interatomic electronic hopping and electron-electron and electron-core interactions. The electron-electron Coulomb interactions and the exchange-correlation potential are approximated in the interatomic TB Hamiltonian matrix. In the TB context there are no double-counting errors; the Coulomb corrections in the system are canceled by those in the free atoms. The TB parameters include the on-site and intersite elements which depend on bond angles through angular momentum expansion. Only the nearest neighbor interactions are included. The intramaterial elements in the Hamiltonian can be formed uniquely by using the corresponding bulk parameters. While for the intermaterial elements at the ideal interface, a simple average of the bulk parameters is fitted to first-principles band structure including the quasi-particle self-consistent GW approximation. These parameters are tested against some well established bulk results.9,10 For reference, we give the parameters used in our calculations for the bulk ZnSe and Si in Table I. Our parameters give the correct indirect ($M$ point) and direct gaps for Si (1.05 eV) and ZnSe (2.87 eV), respectively, and a correct order of conduction-band minima (CBMs) $\Gamma$-K-M for WZ bulk ZnSe and Si materials. We neglect the effect of the lattice distortions, except in Sec. III A 5 of our results where we study the effect of the ZnSi and SeSi bond-length distortions. The valence-band discontinuity between ZnSe and Si, $\Delta E_v$

<table>
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<tr>
<th>ZnSe</th>
<th>Si</th>
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<td>$E(s,a)$</td>
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</tr>
<tr>
<td>$E(p,a)$</td>
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</tr>
<tr>
<td>$E(s,c)$</td>
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<tr>
<td>$E(p,c)$</td>
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<tr>
<td>$E'(s,a)$</td>
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<td>$E'(s,c)$</td>
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<tr>
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<td>3.1839</td>
</tr>
<tr>
<td>$V_{p_x,s}$</td>
<td>5.6350</td>
</tr>
</tbody>
</table>
$= [E_a(Si) - E_a(ZnSe)]$, is assumed to be 1.09 eV, which is the theoretical value of Harrison.\textsuperscript{14} For Si and ZnSe in the WZ structure, the previous calculations\textsuperscript{8,9} showed the bulk structural properties to be insensitive to spin-orbit interactions. Spin-orbit coupling is not included and will not affect the SLs ZnSe/Si. This method reduces the size of the Hamiltonian matrix considerably compared with methods based on plane-wave basis and allows us to treat localized states. So, our TB model is efficient to investigate the electronic properties of WZ SLs.

If heterointerface bonds with length $d$ are selected by an amount of $\Delta$, the intermaterial interaction energies decrease, approximately obeying Harrison’s $d^{-2}$ scaling rule.\textsuperscript{14} Stretched bonds also change the bond angle for the (0001) interface. Accordingly, in the system with a uniformly relaxed interface, the intermaterial blocks $H_i(i=0,1)$ are expressed as

$$H_i = (1 + \Delta/d)^{-2} H_i (\Delta).$$

Here $\Delta_0$ and $\Delta_1$, respectively, represent the heterointerface bond relaxation of $a$ to $c'$ and of $a'$ to $c$ for $(ca)_n$ and $(c'a')_n$ (0001) SLs, with $a$ ($a'$) and $c$ ($c'$) label anion and cation of ZnSe and Si compounds, respectively. In the above replacement, the $\Delta$ dependence of $H_i(\Delta)$ results from the nearest neighbor interaction change due to the bond angle change. Its explicit form is given by

$$(0001)\text{interface}: \quad \begin{align*}
    u'_{xx} &= u_{xx} - (1 - \delta) u_{xy}, \\
    u'_{zz} &= u_{xx} + 2(1 - \delta) u_{xy}, \\
    u'_{xy} &= \delta u_{xy}, \\
    u'_{xz} &= \delta^2 (3\delta - 2) u_{xy}, \\
    u'_{sx} &= \sqrt{\delta} u_{sp}, \\
    u'_{sz} &= \sqrt{\delta} u_{sp}.
\end{align*}$$

Here $\delta = 1 + \Delta/d)^{-2}$ and $u_{ab}$ and $u'_{ab}$ are intermaterial elements at the interface.

This method is quite simple but is sufficiently reasonable to investigate the qualitative effects of heterointerface bond relaxation on electronic structure properties.\textsuperscript{28-31} Thus, the electronic structure can be obtained by diagonalizing the Hamiltonian.

### III. RESULTS

#### A. Electronic properties of (ZnSe)$_n$/Si$_2$)$_m$ (0001) wurtzite superlattices

##### 1. Band structures of (ZnSe)$_n$/Si$_2$)$_m$ (0001) wurtzite superlattices

As stated in Sec. II, we have constructed a TB Hamiltonian for the WZ SL (0001) case in order to investigate the electronic structure of (ZnSe)$_n$/Si$_2$)$_m$ (0001) SLs. To calculate the band structures of ZnSe/Si WZ SLs grown in the (0001) direction, the high-symmetry $k$ points $\Gamma$, $M$, $H$, $K$, and $A$ are used. Figure 1 displays the obtained band structure of (ZnSe)$_{16}$/Si$_{16}$ (0001) WZ SL with unrelaxed interface. In this study, the (ZnSe)$_{16}$/Si$_{16}$ (0001) WZ SL is found to have a direct band gap of 1.665 eV at the $\Gamma$ point (see Fig. 1), whereas a transition from direct to indirect is found for (ZnSe)$_{16}$/Si$_{16}$ (111) zinc-blende (ZB) SL.\textsuperscript{32} In the case of direct-band-gap WZ SL, the CBM is found at the ZB $\Gamma$-folded state; it exhibits mainly Si layers and is therefore highly isotropic. This can be seen from the dispersion curve of Fig. 1. The small (4.25%) lattice mismatch between ZnSe and Si could cause some relaxations of the atoms, but this is not expected to affect the band structure significantly. The ZnSe/Si (0001) WZ is of type I SL, i.e., the band gap at the $\Gamma$ point occurs entirely within the CBM. The valence-band holes and conduction-band electrons tend to be confined in the Si layers.

Note that the ZnSe/Si(111) ZB SL has the half number of atoms and very similar neighbor map as the WZ structure, but the symmetry is quite different. We have chosen this growth direction because of the similarities between the ZB structure in this direction and the hexagonal WZ structure (they differ only in the second nearest neighbors). Also, experimentally the [0001] direction could be a natural growth direction for SLs. Therefore, to make a direct comparison between WZ SL and the corresponding WZ pure material, we have folded the full WZ BZ onto the corresponding SL zone [1001]. Then, $\Gamma$ folds onto $\Gamma$ and $M$ points. We can understand the minimum of the band gap at the $\Gamma$ point by mapping symmetry points of the full WZ zone onto the SL zone. $M$ and $L$ points of the bulk WZ zone map onto the SL $M$ point. However, the $L$ point in the SL comes from a point halfway from $M$ to $L$ in the bulk WZ zone. Because the first $M$ conduction level in the WZ bulk Si is lower in energy than the $\Gamma$ level, the gap at the $\Gamma$ level of SL will be lowered. This situation can be explained by the folding of the bulk WZ zone onto the WZ SL zone. When comparing to the band structure of the (ZnSe)$_{16}$/Si$_{16}$ (111) ZB SL,\textsuperscript{32} we observe a breaking of degeneracy except for the $\Delta$ ($\Gamma \rightarrow A$) direction due to the lower symmetry (hcp versus hexagonal) a nearly constant value of the top of the valence band along the $\Delta$ direction. One difference in the band structures is that the
Therefore, we will derive the components of the effective-conduction-electron mass along the growth direction principal curvature of the energy bands. This should also be true direction in the cubic. The transverse constant as the SL thickness varies increases, while the heavy-hole mass \( m_{hh} \) increases with increasing number of layers. Near the VBM, in Table II, the light-hole effective mass \( m_{lh} \) along the directions ([1000] and [1100]) and perpendicular ([0001]) to the layers.

### 2. Effective masses

The effective masses of electrons and holes in SLs are important parameters, which are required for many analyses. The investigation of the energy band structure and determination of effective masses are therefore of vital importance. The effective-mass tensor \( m(k) \) is defined as

\[
\frac{1}{m(k)_{ij}} = \frac{\partial^2 E(k)}{(\hbar^2 \partial k_i \partial k_j)},
\]

where \(+(-)\) stands for electrons (holes). When the effective masses in the three principal directions were determined, we studied the band curvature around the band extrema in the parabolic region. In this work the longitudinal (||) direction is along the \( c \) direction in the hexagonal and along the [100] direction in the cubic. The transverse (\( \perp \)) direction is in the plane perpendicular to the longitudinal direction.

In general, we expect that the TB method gives the principal curvature of the energy bands. This should also be true near the extreme \( k \) of the band structure within the BZ. Therefore, we will derive the components of the effective-mass tensors \( m_{ij}(k) \) from our calculations using the second derivatives of the bands.

For the effective masses, fine dispersion curves in the vicinity of the valence-band maximum (VBM) and CBM were calculated using up to 40 \( k \) points. The effective masses of \((\text{ZnSe})_n/(\text{Si})_m\) (0001) SLs with \( n=m=2-10 \) are gathered in Table II. In the \( xy \) plane ([1000] and [1100] directions), which is perpendicular to the growth direction [0001]), the conduction-electron masses \( m_c \) are highly isotropic and remain constant as the SL thickness varies (therefore only results along [1100] are given in Table II). At the VBM (the \( \Gamma \) point), there are two degenerate dispersion curves corresponding to the heavy-hole and light-hole bands. The light-hole effective mass \( m_{lh} \) increases as the thickness of the SL increases, while the heavy-hole mass \( m_{hh} \) decreases. The conduction-electron mass along the growth direction [0001] increases with increasing number of layers. Near the VBM, the twofold degenerate heavy-hole band rapidly becomes flat (i.e., nondispersive) as the number of layers increases, leading to large effective masses. The light-hole effective masses depend on layer thickness in the [1000] and [1100] directions.

### 3. Charge density

The corresponding charge densities of the vacant band states (fourth lowest to lowest) and highest valence-band states at the \( \Gamma \) point are shown as a function of layer index \( j \) in Fig. 2. As displayed in Fig. 1, the band structure consists of crowded bands and solitary bands. All the band-edge states in Fig. 2 are confined in two dimensions in the Si well layers. These states are clearly localized on the interface. Therefore, it is reasonable to believe that those crowded sub-bands, having \((\text{ZnSe})_{16}/(\text{Si})_{16}\) (0001) SL band structure, originate from those of Si by zone-folding effects. The crowded bands coincide with the joint projected band structure for bulk ZnSe and Si and exhibit extended states. There are two kinds of interface states in the (0001)-grown ZnSe/Si SL, one is located at the Zn–Si interface (upper valence band) and the other one is lying at the Se–Si (lower conduction band) interface. On the other hand, the solitary bands give eigenstates localized around the interface. Therefore, these can be called interface bands. From Fig. 2, we notice that the corresponding eigenstates are localized within 16 layers from the Zn–Si interface. It is also shown that the lowest vacant band gives an interface band. Note that the eigenstates of the conduction bands near the interface states are resonant with the interface band. One can also find that these interface states extend over quite a different region of \( k \) space.

### 4. Energy gap

To illustrate the quantum confinement, we calculate the energy gap for \((\text{ZnSe})_n/(\text{Si})_m\) (0001) SLs, with the range \( n=m=2-18 \). The calculated energy gap of the \((\text{ZnSe})_n/(\text{Si})_m\) (0001) SLs as a function of \( n=m \), as shown as curve joining the solid lines at even integer values of \( n \) and \( m \), is given in Fig. 3. In the same figure, the interface bands \( E^j \) at the \( \Gamma \) point are also plotted. The theory shows that the transition is the direct \( A \) to \( \Gamma \) for all cases. The fundamental band gap of the SL, corresponding to the gap between the Si VBM and the Si folded CBM, decreases as the Si layer thickness increases (see Fig. 3). This transition is quite sensitive to the band discontinuity. It shows that the thickness of Si layers plays an important role in the formation of the fundamental band gap of the SL.

<table>
<thead>
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<th>Period</th>
<th>[1000]</th>
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<tr>
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<td>(m_{hh})</td>
<td>(m_{hh})</td>
<td>(m_{lh})</td>
</tr>
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</tr>
<tr>
<td>(8, 8)</td>
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</tr>
<tr>
<td>(10, 10)</td>
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<td>−0.86</td>
<td>−0.30</td>
</tr>
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</table>
Origin of the band-gap shrinkage in (ZnSe)$_1$/Si$_2$/ (0001) superlattice SL. Figure 4 illustrates the band structure of (ZnSe)$_1$/Si$_2$/ (0001) SL. The band gap shrinks at $\Gamma$ and $L$ points due to the lowering of the conduction-band edges, as already shown in Fig. 4. The band gap does not shrink at the $H$ point. This corresponds to the absence of the interface bands at the same point in the system under study. The band-gap shrinkage is related to the presence of the interface bands. The origin of the band-gap shrinkage is related to the fact that the overlap of the interface states becomes so large. So, these states can combine as the band states. Indeed, our $sp^3s^*$ TB model proves to be very useful for predicting the band-gap shrinkage.

5. Heterointerface bond relaxation

The electronic structures of (ZnSe)$_n$/Si$_m$/ (0001) with $n$ and $m$ up to 10 are then straightforwardly calculated based on the $sp^3s^*$ TB formalism. Our purpose is to apply our TB model for ZnSe/Si WZ semiconductor interfaces and also to demonstrate that the heterointerface bond relaxation induces interface states. In Fig. 5, the calculated interface-band structures are shown for two values of heterointerface bond stretch $\Delta$ in (0001) ZnSe–Si systems. As shown in this figure, with a $\Delta$ equal to 0.2, both vacant and filled interface bands appear in the band gap in the interfaces with relaxed Si bonds. However, the situation is different in the case of ZnSe/Si(111) ZB SL where the vacant interface band lies below the conduction-band edge.

Furthermore, for the (0001) interface case with relaxed Si bonds where $\Delta=0.5$, the lowest conduction-band states are lowered in the band gap. Consequently, the interface band gives a large density of states (DOS) in the band gap. It is clearly seen in Fig. 5 that the interface bands extend deeply in the band gap with an increase in $\Delta$ for the (0001) interface orientation. Specifically, in the (0001) interfaces with relaxed Si bonds, the vacant interface band is lowered

FIG. 2. (Color online) Calculated planar average of the charge densities of the interface and confined band-edge states at the $\Gamma$ point for (ZnSe)$_1$/Si$_2$/ (0001) SL with ideal interface.

FIG. 3. Band gap $E_g$ of (ZnSe)$_n$/Si$_m$/ (0001) SLs as a function of the number of layers $n=m$. Interface band $E_I$ at the $\Gamma$ point as a function of the number of layers $n=m$.

FIG. 4. (Color online) Band structure of the (ZnSe)$_1$/Si$_2$/ (0001) SL.
below the conduction-band edge as $\Delta$ increases and forms a valley which is located at the $\Gamma$ point. It must be noted that this symmetry point originates from the WZ $A$ point. On the other hand, in the (0001) interface with relaxed Si bonds, the lowest conduction band is lowered and forms an unoccupied interface band in the band gap with an increase in $\Delta$. The Fermi level $E_F$ is heightened as $\Delta$ increases. Specifically, at the (0001) ZnSe/Si interfaces, the interface band merges with the conduction band and exhibits metallic structures, as the heterointerface bond relaxation increases (see Fig. 5). In any case, the vacant interface states and filled interface states are, respectively, localized at cation and anion sites. We have shown that the heterointerface bond relaxation strongly affects the interface-band formation in the band gap. Furthermore, the results show that the (0001) interface is the most sensitive in the formation of these bands. In particular, the vacant interface gap states with a high density in ZnSe/Si systems are predicted to be induced by the interface Si bond relaxation.

6. Optical transition

Spectroscopy is one of the most actively pursued areas of experimental solid state physics, and techniques such as optical absorption have yielded a wealth of information about the band structure of semiconductor SLs. Theoretically, the spectra are seen to be dependent on quantities such as DOS and matrix elements coupling the initial to final state. In the case of absorption spectra for semiconductor SLs, the main structures are observed to be correlated with the interband critical points. It is very common to assume that the dipole matrix elements involved are constant throughout the BZ and to compare the spectra directly with JDOS.

We compute the matrix elements starting from a TB Hamiltonian even if the full wave functions are not known. The Slater–Koster method is computationally very economical in obtaining the full-zone band structure of semiconductors SLs, and our procedure for the optical matrix elements requires little additional computation beyond solving the eigenvalue problem for the energies.

7. Applications of optical matrix elements

Optical-absorption spectra in semiconductor SLs are normally dominated by transitions from the valence to the conduction bands. Then, we can compute the JDOS for ZnSe/Si (0001) WZ SLs which is given by the below formula. Our aim is to see how our TB model is extended to optical properties for these systems.

In the empirical TB approach, a momentum matrix element can be written as

$$P_{\lambda,\lambda'}(k, k') = \langle k, \lambda | p | k', \lambda' \rangle$$

$$= \frac{1}{N} \sum_{\xi, \alpha, \alpha'} C_{\xi \alpha}^*(k, \lambda) C_{\xi \alpha'}(k', \lambda')$$

$$\times \sum_{l,l'} e^{i(k'_{l+l'}-k_{l+l'})}$$

$$\times \langle \xi, r_{\alpha}, R_l | p | \xi', r_{\alpha'}, R_{l'} \rangle. \quad (7)$$

Because of the strongly localized atomic orbitals in the TB model, the momentum matrix elements between atoms separated by more than first-neighbor distances can be neglected.\textsuperscript{33,34} Therefore, Eq. (7) reduces to

$$P_{\lambda,\lambda'}(k, k') = \sum_{\xi, \alpha, \alpha'} C_{\xi \alpha}^*(k, \lambda) C_{\xi \alpha}(k', \lambda') P_{\xi,\xi'}(k, k'; \alpha), \quad (8)$$

$$P_{\xi,\xi'}(k, k'; \alpha) = \frac{1}{\sqrt{N}} \sum_{l} e^{i(k_{l+l'}-k_{l+l'})} \tau_{\alpha} \langle \xi, r_{\alpha}, R_l | p | \xi', r_{\alpha}, R_{l'} \rangle. \quad (9)$$

Here $\tau_{\alpha}$ is the position of the neighbor atoms. The absorption coefficient of a SL is given by\textsuperscript{34} (apart from a constant factor)

$$\alpha(h \omega) = \frac{1}{\omega} \sum_{k, \lambda, \lambda'} |e P_{\lambda,\lambda'}(k, k')|^2 \delta[E_{\lambda'}(k) - E_{\lambda}(k) - h \omega], \quad (10)$$

where $e$ is the direction of polarization. The parameters $\langle \xi, r_{\alpha}, R_l | p | \xi', r_{\alpha'}, R_{l'} \rangle$ can be determined by comparing the theoretical computed values of materials bulk (ZnSe and Si)
Detailed calculations of the electronic structures and optical transitions for the (ZnSe)$_n$/(Si)$_m$ (0001) SLs with a wide range of $n, m \pm 18$ are performed with our SETB scheme. We have developed a TB model to calculate the band structure of (ZnSe)$_n$/(Si)$_m$ (0001) SLs in the WZ structure. This SL exhibits rather interesting features which differ greatly from those original materials with respect to optical properties as well as in electronic structure. The electronic structure and optical properties of (ZnSe)$_n$/(Si)$_m$ (0001) SL are investigated theoretically to clarify the general features of the zone-folding and band-mixing effects in the SL composed of indirect-band-gap semiconductor (Si). The nature of this SL is clarified as follows.

(i) The energy gap of the SL can be adjusted by changing the layer-thickness combination in a SL period. We have found two interface bands in the lower and upper regions of the gap. The states of the lower interface band are located at the Zn–Si interface, while those of the upper interface band are located at the Se–Si interface.

(ii) Our calculations also indicate that the thick-layer ZnSe/Si (0001) WZ SL is of type I. A quantum confinement effect is found that causes the states at the conduction- and valence-band edges to be confined to two dimensions in the Si wells. It is found that the fundamental energy gap increases (up to 2.37 eV at the $\Gamma$ point for $n=m=2$) with decreasing SL period. Also, the Si layer plays an important role in determining the fundamental energy gap of the SL system due to spatial quantum confinement effects. The CBMs shift from $\Gamma$ to H while decreasing the period of SL $(n=m=1)$. A sudden shrinkage in the band gap ($E_g = 2.78$ eV at the $H$ point) is obtained for $n=m=1$. The origin of the band-gap shrinkage is related to the fact that the interface states increasingly overlap and combine as band states.

(iii) Moreover, our theoretical study within our TB model revealed that the heterointerface bond relaxation strongly affects the interface-band formation. The features of the interface bands largely depend on the ZnSe/Si semiconductors species and also on interface orientations. In a ZnSe/Si (0001) WZ SL system, relaxed Si bonds at the interface only induce a filled interface band below the conduction-band edge. An increase in the bond stretch heightens this interface band. More specifically, at (0001) ZnSe/Si interfaces with relaxed interface bonds, the interface band merges with the conduction band and exhibits metallic structures. Consequently, the extended states in the conduction bands are fairly resonant with the localized interface states. Therefore, it can be concluded that the existence of the interface state in ZnSe/Si SL systems is associated with the bond heterointerface relaxation. In particular, the vacant interface gap states with a high density in ZnSe/Si systems are predicted to be induced by the interface Si bond relaxation.

### IV. SUMMARY AND CONCLUSIONS

with their experimental results. The summations in Eq. (10) are over special points in the BZ. In our calculations, we took 32 special points in the $\frac{1}{2}$ two-dimensional BZ ($k_x, k_y$) and two special points in the $\frac{1}{2}$ one-dimensional BZ ($k_z$). The calculated JDOSs corresponding to the optical transitions from the top six valence subbands to the lowest conduction subband are given in Fig. 6, which shows the band-edge absorptions. With increasing $n$ and $m$, the absorption edge of ZnSe/Si SLs extends to lower energy (see Fig. 6). The intensity of the JDOS drops significantly as $n$ and $m$ increase. This is due to a smaller portion of the total JDOS which is being sampled with the optical transitions coming from only the top six valence subbands to the lowest conduction subband. The curves rise rather slowly with some visible structures that may be related to critical-point transitions. Two main peaks are identified around 4.8 and 6.9 eV in all plots. Compared with the absorption spectra of corresponding bulk materials (ZnSe and Si), we note that the first peak originates from Si [4.2 eV (Ref. 37)] and the second from ZnSe [6.6 eV (Ref. 38)]. This SL exhibits interesting features which differ from the original bulk materials with respect to both its optical properties and its electronic structure. Larger oscillator strengths can be obtained in shorter-period SLs, which are quite promising for applications to optical devices operating in the visible-light region.
(iv) Furthermore, the JDOSs of the ZnSe/Si SLs are obtained which correspond to the optical transitions in these systems. The calculated absorption spectra are found to be quite different from those of bulk ZnSe and Si but fairly close to their average. Our results indicate that the ZnSe/Si WZ SLs appear to be very promising for optoelectronic applications in the blue-green optical range. The possibility of designing the band structure suggested here will pave the way to applying SLs composed of indirect-band-gap semiconductor to novel functional devices.