Localization and band-gap pinning in semiconductor superlattices with layer-thickness fluctuations

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Abstract

We consider (AlAs)$_n$/(GaAs)$_n$ superlattices with random thickness fluctuations $\Delta n$ around the nominal period $n$. Using three-dimensional pseudopotential plane-wave band theory, we show that (i) any amount $\Delta n/n$ of thickness fluctuations leads to band-edge wavefunction localization, (ii) for small $\Delta n/n$ the SL band gap is pinned at the gap level produced by a single layer with “wrong” thickness $n + \Delta n$, (iii) the bound states due to monolayer thickness fluctuations lead to significant band-gap reductions, e.g., in $n = 2, 4, 6$, and 10 monolayer SL’s the reductions are 166, 67, 29, and 14 meV for $\langle 111 \rangle$ SL’s, and 133, 64, 36, and 27 meV for $\langle 001 \rangle$ SL’s, (iv) $\langle 001 \rangle$ AlAs/GaAs SL’s with monolayer thickness fluctuations have a direct band gap, while the ideal $\langle 001 \rangle$ SL’s are indirect for $n < 4$.

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The electronic structure and quantum-confinement effects in semiconductor superlattices are usually modeled by assuming an ideal structure, i.e., that the interfaces are atomically abrupt and that the individual layer thicknesses remain constant throughout the superlattice [1,2]. Actual heterostructures, however, often deviate from ideality in two ways: (i) lateral imperfections in the \((x, y)\) plane, such as intermixed [3], stepped [4], or islanded [5] interfaces, and (ii) vertical (\(z\) direction), discrete thickness fluctuations around its nominal value, even though the interfaces could remain reasonably flat and atomically abrupt in the \((x, y)\) plane [3]. It is likely that both types of interfacial imperfections coexist in many samples [7]. In case (i) the translational symmetry is broken in the substrate plane \((x, y)\), and the concentration profile along the growth direction is continuous (“graded” or “intermixed” interfaces), while in case (ii) a discrete, rectangular-shaped concentration profile exists, but the superlattice translational symmetry is broken along the growth direction \(z\). Case (i) has been modeled theoretically by assuming graded (rather than square) potential wells [8], or by considering supercells with atomic swaps across the interfaces [9]. In this paper we consider layer-thickness fluctuations [case (ii)], i.e., \((A)_{n} / (G)_{n}\) superlattices (SL) with nominal layer thicknesses of \(n\) monolayers (ML) of material \(A = \text{AlAs}\) and \(n\) ML of material \(G = \text{GaAs}\), but where each layer is occasionally thinner or thicker than its intended thickness \(n\). We use a three-dimensional pseudopotential band-structure description within a highly flexible plane-wave basis [10], rather than one-dimensional effective-mass models [11], or one-dimensional [12] or three-dimensional [13] tight-binding models.

Superlattices with layer-thickness fluctuations are described by supercells containing several hundreds of atoms [14]. The novel empirical pseudopotentials used here [10] have been tested extensively for AlAs/GaAs bulk materials, short-period superlattices, and random alloys. The results [10] compare well with experiment and with state-of-the-art, self-consistent pseudopotential calculations, however, without suffering from the band-gap underestimation of the local-density approximation [10]. For periods \(n \leq 20\) we consider single monolayer fluctuations, so the layer thicknesses are in the set \(\{n - 1, n, n + 1\}\), while for \(n > 20\) we consider a fixed fraction \(\Delta n / n\) of layer-thickness fluctuations \(\Delta n\).
We find that: (i) any amount $\Delta n/n$ of thickness fluctuations leads to band-edge wave-function localization, (ii) for small $\Delta n/n$ the SL band gap is pinned at the gap level produced by a single layer with “wrong” thickness $n' \neq n$ (a “chain mutation”), (iii) the bound states due to monolayer thickness fluctuations lead to band-gap reductions that monotonically decrease with increasing $n$. These fluctuation-induced bound states will photoluminesce at energies below the “intrinsic” absorption edge. (iv) $\langle 001 \rangle$ AlAs/GaAs SL’s with monolayer thickness fluctuations have a direct band gap, while the ideal $\langle 001 \rangle$ SL’s are indirect for $n < 4$.

Consider first, by way of reference, the band structure of ideal AlAs/GaAs SL’s with layers oriented along (111) or (001) (Fig. 1). In agreement with previous theoretical studies [2], we find that (i) the ideal $\langle 111 \rangle$ SL has a direct band gap for all $n$ values, since the conduction-band minimum (CBM) is the $\Gamma$-folded $\Gamma_{1c}(\Gamma_{1c})$ state. This SL has a “type-I” band arrangement with both the highest valence and the lowest conduction state localized on the GaAs layers. (ii) The second conduction band at $\bar{\Gamma}$ is folded from the zincblende $\Gamma$–$L_z$ bands; for small $n$ the pseudodirect $\Gamma_{1c}(L_{1c})$ state mixes strongly with the direct $\Gamma_{1c}(\Gamma_{1c})$ state. The mixing, and thus the level repulsion, shows odd-even oscillations for small $n$ (reflecting localization of repelling states on the same or on either sublattice [2]). Note that the one-dimensional effective-mass model (dashed lines [15] in Fig. 1) completely misses the strong non-monotonic variations of SL energy levels with layer thickness.

The situation is very different for $\langle 001 \rangle$ oriented ideal SL’s. The prominent properties apparent in Fig. 1(b) are: (i) the $n = 1$ SL has an indirect band gap at the $L$-folded point $\bar{R}$ [1,2]; (ii) for $n < 4$, the lateral $X_{x,y}$ valleys (folded to $\bar{M}$) and the $X_z$ valley (folded to $\bar{\Gamma}$) are nearly degenerate [16]; (iii) for $1 < n \leq 8$ the pseudodirect, AlAs-like $\Gamma_{1c}(X_z)$ state is below the direct, GaAs-like $\Gamma_{1c}(\Gamma_{1c})$ state, thus the SL is type II; for $n > 8$, however, $\Gamma_{1c}(\Gamma_{1c})$ is lower, so the system is type I (experimentally, the type-II/type-I crossover is found at $n \approx 11$ [16]).

We now allow the layer thicknesses in the $n \times n$ SL’s to fluctuate around the ideal value $n$ by $\pm 1$ ML. The growth sequence is now defined in terms of a distribution function $p(n')$. 
which we assume to be uncorrelated and symmetric around the nominal thickness \( n \). We define the relative frequency \( R \) of monolayer fluctuations by

\[
p(n \pm 1) = R p(n).
\]  

Because the distribution \( p(n') \) is normalized, we can write \( p(n) = 1/(1+2R) \) and \( p(n \pm 1) = R/(1+2R) \). For the \textit{ideal} \( n \times n \) superlattice \( R = 0 \), and \( p(n') = \delta(n' - n) \), whereas for \( R = 1 \) the layer thicknesses \( \{n - 1, n, n + 1\} \) occur with equal probability \( p = \frac{1}{3} \). A single chain mutation in a finite superlattice of length \( N \) monolayers corresponds to \( R \approx \frac{2n}{N} \), which will denoted here as the \( R \to 0 \) limit (to be distinguished from \( R = 0 \) with no mutations). To simulate the lack of periodicity along the growth direction, we have used supercells of a total length \( N \) between 100 and 1000 ML, and repeated these supercells periodically. A particular growth sequence was created by a random number generator, specifying \( n \), \( N \) and \( R \).

The band-edge energies of \((\text{AlAs})_n/(\text{GaAs})_n\) SL’s with \textit{one-monolayer thickness fluctuations} about \( n \) are plotted in Fig. 2 relative to the band edges of the \textit{ideal} SL’s (the energy zero). We see that: (i) thickness fluctuations create both hole (\( \Delta \varepsilon_h \)) and electron (\( \Delta \varepsilon_e \)) bound states for \textit{any degree} of thickness fluctuation (\( 0 < R \leq 1 \)), (ii) the band-gap reductions \( \Delta E_g = \Delta \varepsilon_h + \Delta \varepsilon_e \) decay with \( n \), and have a definite dependence on superlattice direction; they are 166, 67, 29, and 14 meV for \( n = 2, 4, 6, \) and 10 in the \( \langle 111 \rangle \) direction, and 133, 64, 36, and 27 meV in the \( \langle 001 \rangle \) direction, respectively, (iii) the dilute limit of a single chain mutation already produces a \textit{finite gap reduction} \( \Delta E_g(R \to 0) \), (iv) \( \Delta E_g(R \to 0) \) merges with \( \Delta E_g(R = 1) \) at \( n \gtrsim 6 \), at which point the gap reduction becomes independent ("band-gap pinning") of the number of chain mutations.

The appearance of gap levels in SL’s with one-monolayer thickness fluctuations is accompanied by \textit{wavefunction localization}. For example, inspection of the CBM wavefunction of an \( n = 6 \) \( \langle 111 \rangle \) superlattice with random \( \pm 1 \) monolayer fluctuations [Fig. 3(a)] reveals that it is localized on \( \sim 4 \) GaAs wells, with minimal amplitude in the AlAs barriers and maximal amplitude on the two neighboring mutated (7-ML) GaAs wells ("twin" fluctuation denoted...
by bold arrows). The CBM thus resembles a bound state in a coupled double quantum well. The hole wavefunction at the valence-band maximum (VBM) is likewise localized on a number of mutated, 7-ML GaAs wells [Fig. 3(a)]; in contrast to the CBM, however, the reason for the multi-well pattern of the VBM wavefunction is that these states are in fact decoupled, quantum-well confined states, which are degenerate in energy within the accuracy of our calculation (≤0.1 meV). A typical hole and electron wavefunction localized on an isolated (GaAs)$_7$ mutation in an otherwise ideal $6 \times 6 \langle 111 \rangle$ SL are shown in Fig. 3(b).

We see that the hole wavefunction of an isolated mutation ($R \rightarrow 0$) resembles that of the concentrated ($R = 1$) mutations [Fig. 3(a)], and its binding energy $\Delta \varepsilon_h (R \rightarrow 0) = 11$ meV equals the value at $R = 1$. At the CBM, the larger penetration of the wavefunction into neighboring GaAs wells can produce deeper gap states, and consequently pinning occurs at a larger $n$ ($n_p \approx 10$) than for hole states.

Experimentally, the fluctuation-induced localized bound states should be observable as photoluminescence centers whose energy is below the absorption edge of the underlying “ideal” SL structure. This photoluminescence will lack phonon lines, because the optical transitions are direct in the planar Brillouin zone (the transverse wave vector $\vec{k}_\perp$ is still a good quantum number), and because the $k_z$ selection rule is relaxed by vertical disorder. Indeed, while calculations [2] on ideal $\langle 111 \rangle$ (AlAs)$_n$/(GaAs)$_n$ SL’s predicted a direct band gap with a type-I band arrangement, Cingolani et al. [17] noted a $\sim 100$ meV red shift of the photoluminescence at 1.80 eV relative to the absorption in (AlAs)$_6$/(GaAs)$_6 \langle 111 \rangle$ SL’s, interpreting this as reflecting a type II band arrangement. However, since they noted that their SL had a ±1 ML period uncertainty, it is possible that the red shifted photoluminescence originates from thickness-fluctuation bound states. Our calculated band gap of the $n = 6$ superlattice with ±1 ML thickness fluctuations is 1.78 eV for $R = 1$, and 1.80 eV for $R \rightarrow 0$, close to their observed photoluminescence peak position (1.80 eV) [17,18].

Figure 2 shows that the bound states of isolated mutations ($R \rightarrow 0$) merge with those of concentrated layer-thickness fluctuations ($R \rightarrow 1$) at some “pinning period” $n_p$. In what follows we discuss the (i) $n < n_p$ and (ii) $n \geq n_p$ regimes. In the short-period regime
(n < n_p), the band-gap reduction depends on R. This regime coincides with the region in Fig. II where the band gaps of the ideal SL’s have a complex n-dependence, showing strong
non-effective-mass behavior. The \langle 001 \rangle (AlAs)_2/(GaAs)_2 SL with monolayer fluctuations is in fact identical to the intentionally disordered SL grown by Sasaki et al. [19]. In that
structure, A_2 and G_2 layers are randomly replaced by A_1, A_3, G_1, and G_3 layers. We find
the following changes in the band structure when the layer thicknesses fluctuate by ±1 ML:

(i) For the n = 2 \langle 001 \rangle SL we obtain \Delta \varepsilon_e(R = 1) = 22, 81, and 171 meV at \bar{M}, \bar{\Gamma}, and \bar{X} in
the planar Brillouin zone. Since the level shift \Delta \varepsilon_e at \bar{\Gamma} exceeds the one at \bar{M} by \sim 60 meV,
layer-thickness fluctuations transform the indirect 2 \times 2, ideal superlattice into a direct-gap
material [20]. The large binding energy at \bar{X} originates from the increased level repulsion
of the folded L_{1c} states when the translational and rotational symmetry of the ideal n = 2
superlattice is broken. This level repulsion is larger for odd n than for even n, and it leads
to an L-like, indirect CBM for n = 1 [Fig. IV(b)]. (ii) The n = 2 \langle 001 \rangle SL is direct even in
the R \rightarrow 0 limit of isolated chain mutations. (iii) Numerous electron and hole states are
localized on the same spatial region along z, hence the \langle 001 \rangle SL’s with thickness fluctuations
will exhibit type-I, rather than type-II characteristics as ideal n < 10 SL’s do. (iv) While for
n > n_p only mutated, wider GaAs wells bind a carrier (see below), in the short-period \langle 001 \rangle
case even an (AlAs)_{n+1} mutation binds an electron. In fact, the AlAs-like bound electron
lies deeper in the gap than the GaAs-like bound electron [see the two dotted lines near the
CBM in Fig. II(b)].

We next discuss the SL properties in the regime of band-gap pinning n \geq n_p. At this
point the band-gap reduction is pinned at the value

\[ \Delta E_g(R) = \lim_{R \rightarrow 0} \Delta E_g(R) = \Delta \varepsilon_e + \Delta \varepsilon_h, \]  

(2)

where \Delta \varepsilon_e (\Delta \varepsilon_h) is the electron (hole) binding energy of an isolated \langle R \rightarrow 0 \rangle layer mutation.

Qualitatively, Eq. (3) can be understood in terms of a one-dimensional effective-mass picture,
where the SL is modeled by a Kronig-Penney model, with the usual boundary conditions of
a continuous envelope function F(z) and current \frac{1}{m^*} F'(z), where the effective mass m^* is
different in the well and barrier material. Each of the \((n + 1)\)-ML mutations gives rise to a bound state below the band edge of the \(n \times n\) SL \([11, 21]\). The gray lines in Fig. 2 indicate that this simple picture is expected to agree quantitatively with our pseudopotential calculation for \(n \gtrsim 10\) (note, however, the large discrepancy with our three-dimensional calculation at smaller \(n\)’s). For very large \(n\), when the quantum wells are completely decoupled, the SL energy spectrum is simply that of degenerate single quantum wells. Hence the extra binding energy of an \((n + \Delta n)\)-ML mutation approaches asymptotically

\[
\Delta \varepsilon_c = \varepsilon_0(n) - \varepsilon_0(n + \Delta n) \approx \frac{2\Delta n}{n} \varepsilon_0(n),
\]

where \(\varepsilon_0(n)\) is the ground-state energy of a carrier with mass \(m^*\) in a \(n\)-ML wide quantum well, which scales like \(\frac{1}{m^* n^2}\) for large \(n\). Using a fixed \(\Delta n/n = 10\%\) we obtain from the first equality of Eq. (3) \(\Delta \varepsilon_c = 10.0, 2.4\) and \(0.7\) meV for \(n = 20, 50\) and \(100\) in the \((111)\) SL \(\text{[the last equality of Eq. (3) gives 14.3, 3.0 and 0.8 meV, respectively]}\). The band-gap reduction for a given \(\Delta n/n\) is obtained by inserting \(\Delta \varepsilon_h\) and \(\Delta \varepsilon_e\) from Eq. (3) in Eq. (2). The degeneracy of the gap level \(\Delta \varepsilon_c\) is equal to the number \(M_{n+\Delta n}\) of \((n + \Delta n)\)-ML well mutations, which, in the case of \(\Delta n = 1\) \(\text{[see Eq. (1)]},\) is given by

\[
M_{n+1} \approx \frac{R}{1 + 2R} \frac{N}{2n}.
\]

Using Eqs. (3) and (4) one can predict the band-gap reduction and number of localized states in the multiple quantum-well regime.

In summary, we have shown that discrete layer-thickness fluctuations in \((\text{AlAs})_n/(\text{GaAs})_n\) superlattices lead to (i) localization of the wavefunctions near the band edges, (ii) a reduced band gap, which is pinned at the value corresponding to an isolated layer-thickness fluctuation for \(n > n_p\), and (iii) a crossover to a direct band gap in the case of short-period \((001)\) SL’s.

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[18] We have separately studied the influence of atomic intermixing within 2 ML across the interface, and found that the direct band gap is blue shifted from 1.81 eV in the ideal SL to ~1.89 eV, close to the observed absorption edge (1.90 eV). However, we have not studied the combined influence of ML fluctuations and intermixing on the band gaps, and can only speculate that the experimental results might be compatible with the coexistence of these two types of imperfections.

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FIGURES

FIG. 1. Energy levels of ideal (AlAs)$_n$/(GaAs)$_n$ superlattices along (a) ⟨111⟩ and (b) ⟨001⟩, as a function of period $n$. The bulk levels in the middle column are reached asymptotically as $n \to \infty$. $\Gamma_{15v}(\text{AlAs})$ is 500 meV below the GaAs VBM. The SL states are denoted with an overbar, while their parent zincblende states $\Gamma$, $X$, and $L$ are given parentheses. The dashed lines are obtained from a one-band envelope-function model using the effective masses and band offset from our pseudopotential calculation [15].

FIG. 2. Gap levels in the presence of one-monolayer thickness fluctuations in (AlAs)$_n$/(GaAs)$_n$ superlattices along (a) ⟨111⟩ and (b) ⟨001⟩, as a function of period $n$. Energies are measured with respect to the band extrema of the ideal $n \times n$ SL (see Fig. 1). One-band envelope-function results for a $(n + 1)$-ML mutation embedded in the $n \times n$ SL are indicated by a dashed gray line. $R = 1$ and $R \to 0$ denote, respectively, the concentrated and dilute limit of chain mutations [Eq. (1)].

FIG. 3. Planar averages of wavefunctions squared of the CBM and VBM in the (AlAs)$_6$/(GaAs)$_6$ SL along ⟨111⟩ with ±1 layer-thickness fluctuations. Hole wavefunctions are plotted in the negative direction, with a small offset for clarity. (a) Concentrated limit ($R = 1$), (b) dilute limit ($R \to 0$), i.e., a single (GaAs)$_7$ mutation embedded in a 6 × 6 SL host. The rectangular lines show the growth sequence of the SL, with GaAs layers represented by wells, and AlAs layers represented by barriers, respectively. The vertical arrows in (a) indicate the 7 ML thick, “mutated” wells.
| Valence state (eV) | Conduction state (eV) |
|-------------------|----------------------|
| \( \Gamma_c(L) \) | \( \Gamma_c(\Gamma) \) |
| \( M_c / X_c(X) \) | \( \Gamma_{1c}(GaAs) \) |
| \( \Gamma_{15c}(GaAs) \) | \( \Gamma_{15c}(GaAs) \) |
| \( \Gamma_c(\Gamma) \) | \( \Gamma_c(\Gamma) \) |

(a) <111>

(b) <001>

Layer thickness (ML)

- EPM
- EMA
Wavefunction amplitude

Position along [111] (ML)

$\Psi_{CB}$

$\Psi_{VB}$
Band-edge shift (meV) vs. Layer thickness (ML)

(a) <111> (GaAs)

(b) <001> (GaAs)

R=1

R~0