Thin [001] and [110] GaAs/AlAs superlattices: Distinction between direct and indirect semiconductors

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We have calculated oscillator strengths of across-gap transitions in $n \times n$ GaAs/AlAs superlattices ($n = 1,2$) grown along the [001] and [110] directions using the augmented spherical wave *ab initio* band-structure method. We find that the rate for radiative emission across the direct gap in the very thin [001] superlattices is at least 2 orders of magnitude smaller than the corresponding quantity in GaAs. The radiative transition rates across the direct and indirect gaps turn out to be comparable in these superlattices. The 2×2 [110] superlattice is direct and has a direct-gap oscillator strength which is 78% of that of GaAs.

Recently, Ishibashi *et al.* have been able to grow high-quality, very thin $n \times n$ GaAs/AlAs [001] superlattices with $n = 1,2,\ldots$.[1] The question has been raised whether such $n \times n$ superlattices are direct or indirect; the corresponding alloy $Al_{0.5}Ga_{0.5}As$ is indirect.[2] The work of Ishibashi *et al.*[1] provides evidence for the superlattices to be direct in terms of energy from $n = 2$ onwards. The $n = 1$ superlattice appears to be energywise indirect. The lowest Γ-point conduction-band state of the thin ($n = 1,2$) superlattices is a band-folded X state. Obviously the optical matrix element from this stage to the top of the valence-band state will be small.

In this paper we perform *ab initio* calculations of the rate for radiative emission across the direct gap in the very thin 1×1 and 2×2 [001] superlattices and show that it is at least 2 orders of magnitude smaller than the corresponding quantity in GaAs and that the radiative transition rates across the direct and indirect gap are comparable in these superlattices. We note that such calculations cannot be done using semiempirical (for example envelope-function-type[3]) approaches since for the thin superlattices considered here the superlattice crystal potential must be determined self-consistently.

For a spectroscopist the distinction between a direct and an indirect semiconductor is related to the typically much larger transition rate for emission of radiation across the direct gap than across the indirect gap: From the point of view of spectroscopy the very thin [001] superlattices are thus neither direct nor indirect. Moreover, the radiative transitions are very weak, corresponding to lifetimes of $0.1-1$ μs. These superlattices therefore may not be very useful for applications involving light emission.

Earlier theoretical calculations of Christensen *et al.*,[4] Nakayama *et al.*,[5] Bylander *et al.*,[6] Gilbert *et al.*,[7] and Nelson *et al.*[8] have focused on the superlattice band structure. Their results are more or less in line with the findings of Ishibashi *et al.*:[1] for $n = 1$ the minimum of the conduction band is found to be at R (Refs. 4–7) making the 1×1 superlattice energywise indirect. For $n = 2$ the minimum of the conduction band is found to be at Γ by Nakayama *et al.*[5] and in between Γ and Z by Gilbert *et al.*[7] Theoretically it is not clear whether the 2×2 [001] superlattice is energywise direct or indirect.[8]

This paper is focused on the transition rate aspect. We calculate oscillator strengths of Γ-point across-gap transitions in very thin ($n = 1,2$) GaAs/AlAs superlattices grown along the [001] and [110] directions using the augmented spherical wave[9] (ASW) *ab initio* band-structure method. A self-consistent potential for the $n \times n$ [001] and [110] GaAs/AlAs superlattices was generated by solving the Kohn and Sham equation[10] iteratively within the ASW basis set,[9] using the local-density approximation (LDA) for the exchange and correlation functional.[10] Scalar-relativistic effects were ignored and "empty" spheres were placed at the interstitial sites.[11] The ASW basis set consisted of s, p, and d orbitals centered at each atomic and empty sphere site. All muffin-tin sphere radii were taken to be equal. The lattice constant was set equal to 5.653 Å. The number of special k points in the irreducible wedge of the Brillouin zone was taken to be 18 (6) for the tetragonal structure and 27 (8) for the orthorhombic structure (the numbers in parentheses apply to the 2×2 superlattice). Self-consistency of the superlattice crystal potential was achieved at a level of 1 mRy. The across-gap oscillator strength between a valence-band state ϕ_v and a conduction-band state ϕ_c induced by light of polarization $\mathbf{e}$ is equal to $(2/m)\,|\langle \phi_v \,|\, \mathbf{p}\cdot\mathbf{e} \,|\, \phi_c \rangle|^2/\Delta E$; here m is the electron mass, $\mathbf{p}$ is the momentum operator, and ΔE is the energy difference between the states ϕ_v and ϕ_c. We have shown before that calculated oscillator strengths are typically accurate to within 20% (Ref. 12) despite the fact that the gap is typically calculated to be 30–50% too small.[12] Details concerning the calculation of the oscillator strengths from the self-consistently obtained wave functions can be found elsewhere.[12] We estimate the accuracy of the relative positions of the energy levels in the conduction band to be around 30–100 meV.[13]

Our results for the optical properties of the superlattices are as follows. Results for ground-state properties are summarized in Ref. 14. For the 1×1 [001] and 1×1

[110] GaAs/AlAs superlattice we find Fig. 1. The bottom of the conduction band is at $R(L)$, which is the folded L point of the underlying fcc lattice. The lowest superlattice conduction-band Γ state is X_z derived, i.e., $\Gamma(X_z)$, and is 71 meV higher in energy than $R(L)$. The Γ-derived state $\Gamma(\Gamma)$ is still 23 meV higher in energy. The heavy-hole (HH) and light-hole (LH) derived top of the valence-band states Γ(HH) and Γ(LH) are split by 23 meV, the Γ(HH) state being higher in energy. In accordance with the experimental result[1] and other band-structure calculations[4-8] the 1×1 GaAs/AlAs superlattice is thus found to be energywise indirect. We find that the direct-gap oscillator strength $[\Gamma(X_z)-\Gamma(\mathrm{HH})]$ of the 1×1 GaAs/AlAs superlattice is very small, 0.3% of that of GaAs and 0.6% of the $[\Gamma(\Gamma)-\Gamma(\mathrm{HH})]$ superlattice oscillator strength.

For the 2×2 [001] superlattice we arrive at a more complicated picture; see Fig. 2. The indirect gap $E(M(X_z))-E(\Gamma(\mathrm{HH}))$ is barely smaller (1 meV) than the direct gap $E(\Gamma(X_z))-E(\Gamma(\mathrm{HH}))$. We find the lowest Γ-derived superlattice conduction-band state $\Gamma(\Gamma)$ to be 135 meV higher in energy than the state $\Gamma(X_z)$. The $[\Gamma(X_z)-\Gamma(\mathrm{HH})]$ oscillator strength in the 2×2 [001] GaAs/AlAs superlattice is found to be 6% of that of bulk GaAs and 13% of the $[\Gamma(\Gamma)-\Gamma(\mathrm{HH})]$ superlattice oscillator strength.

The results for the 2×2 [110] superlattice are depicted in Fig. 3. The superlattice has a direct gap $E(\Gamma(\Gamma))-E(\Gamma(\mathrm{HH}))$ which is 143 meV smaller than the smallest indirect gap $E(Y(X_y))-E(\Gamma(\mathrm{HH}))$. The direct-gap oscillator strength is 78% of that of bulk GaAs. Note also that for this growth direction the twofold degeneracy of the heavy-hole bands is limited resulting in three separate valence bands at Γ instead of two folded heavy-hole bands and one folded light-hole Γ_{fcc}-derived band.

The values for the calculated oscillator strengths are related to the origin of the corresponding conduction-band state; they are large for Γ-derived conduction-band states and small for any other (e.g., X) derived conduction-band state. In Table I we present the character of the superlattice states at the Γ bottom of the conduction band in terms of the bulk GaAs and AlAs Γ and

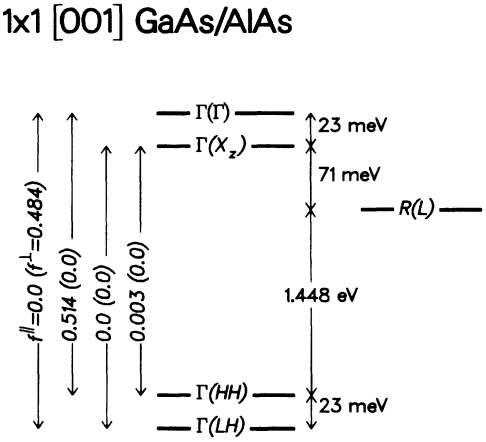

FIG. 1. Schematic representation of the energy levels at high-symmetry points of the 1×1 [001] GaAs/AlAs superlattice. Γ(HH) and Γ(LH) denote superlattice valence-band states and $\Gamma(X_z)$, $\Gamma(\Gamma)$, and $R(L)$ denote conduction-band states. The fcc origin of the superlattice symmetry points is indicated in parentheses. The calculated oscillator strengths f between a conduction-band state Γ_c and a valence-band state Γ_v for light polarization in plane ($f^{\parallel}\equiv f^{xx}+f^{yy}$) and along [001] ($f^{\perp}\equiv f^{zz}$) are in units of the calculated direct-gap oscillator strength $f^{\mathrm{GaAs}}\equiv f^{xx}+f^{yy}+f^{zz}$ [=13.8 (Ref. 12)] of bulk GaAs. For comparison, the calculated result of f^{AlAs} is 7.0 for bulk AlAs (Ref. 12).

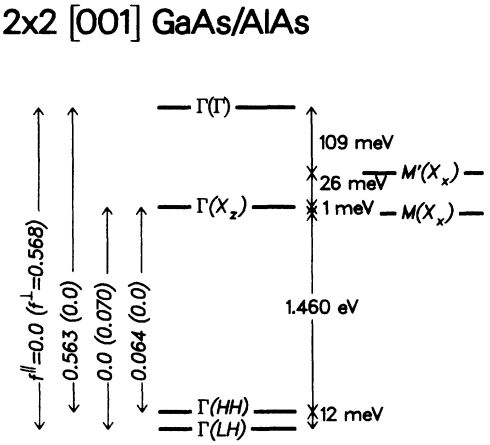

FIG. 2. Schematic representation of the energy levels at high-symmetry points of the 2×2 [001] GaAs/AlAs superlattice. Γ(HH) and Γ(LH) denote superlattice valence-band states and $\Gamma(X_z)$, $\Gamma(\Gamma)$, $M(X_x)$, and $M'(X_x)$ denote conduction-band states. Notation and units for the calculated oscillator strengths $f^{\parallel}$ and $f^{\perp}$ are the same as in Fig. 1.

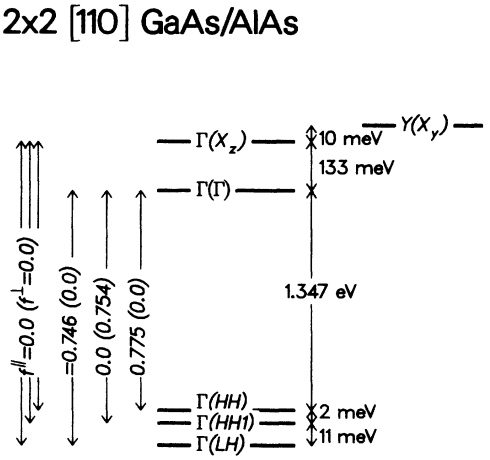

FIG. 3. Schematic representation of the energy levels at high-symmetry points of the 2×2 [001] GaAs/AlAs superlattice. Γ(HH) and Γ(HH1), and Γ(LH) denote superlattice valence-band states and $\Gamma(X_z)$, $\Gamma(\Gamma)$, and $Y(X_y)$ denote conduction-band states. Notation and units for the calculated oscillator strengths $f^{\parallel}$ and $f^{\perp}$ are the same as in Fig. 1.

TABLE I. Relative character of the superlattice states at the Γ bottom of the conduction band in terms of the bulk GaAs and AlAs Γ and X conduction-band states.

	State	Γ (GaAs)	X (GaAs)	Γ (AlAs)	X (AlAs)
1×1 [001]	$\Gamma(X_z)$	<0.01	0.47	<0.01	0.53
	$\Gamma(\Gamma)$	0.65	<0.01	0.35	<0.01
2×2 [001]	$\Gamma(X_z)$	0.13	0.39	0.08	0.40
	$\Gamma(\Gamma)$	0.58	<0.01	0.42	<0.01
2×2 [110]	$\Gamma(\Gamma)$	0.60	<0.01	0.40	<0.01
	$\Gamma(X_z)$	0.12	0.34	<0.01	0.54

X conduction-band states. This decomposition is only indicative since (i) it is based on the s and p percentage of the Ga- and Al-based ASW basis functions of the relevant wave function and (ii) it ignores other mixed-in states.

We now discuss the issue of the superlattices being energywise and spectroscopically direct or indirect. The 2×2 [110] superlattice is direct in any sense, i.e., it is energywise direct and has a large direct-gap oscillator strength. The situation for the 2×2 [001] superlattice is complicated. We find energy differences $\Delta E(\Gamma(X_z) - M(X_x)) \simeq 1$ meV and $\Delta E(\Gamma(\Gamma) - \Gamma(X_z)) \simeq 130$ meV, i.e., energywise the superlattice is barely indirect. Elementary calculation shows that the ratio r of the radiative transition rates for the direct $\Gamma(X_z)$-Γ(HH) and the indirect $M(X_z)$-Γ(HH) transition is given by $r \simeq 0.01(S/\Delta E)^2$.[17] Here S is an energy measure of the strength of the electron-phonon coupling involved in the phonon-assisted indirect rate and ΔE is the difference in energy between the direct and the indirect transitions involved in the perturbative calculation of that rate or, if the relevant phonon energy is larger, ΔE is that phonon energy [10–30 meV (Ref. 18)]. We estimate $S \simeq 10-100$ meV (Ref. 19) and therefore $r \simeq 1$. The 2×2 [001] superlattice can therefore be qualified neither direct nor indirect from a spectroscopic point of view. The 1×1 [001] superlattice is energywise indirect. However, here again one should realize that the direct [$\Gamma(X_z)$-Γ(HH)] and the indirect transition [$R(L)$-Γ(HH)] have comparable strength and are extremely weak. The oscillator strength of the direct transition [$\Gamma(X_z)$-Γ(HH)] is only 0.6% of that of the Γ(Γ)-Γ(HH) transition.

Both for the 1×1 and the 2×2 [001] superlattices the radiative rates, both on the direct and the indirect transition, are so small, corresponding with $\simeq 0.1$ μs lifetimes at low temperatures, that nonradiative processes associated with impurities may interfere with the radiative processes. Precisely this occurs in the experiments of Ishibashi *et al.*[1] This is clear from their experimental results on the quantum efficiences and their assumption that the indirect recombination is completely nonradiative. In view of our theoretical results this implies that the direct recombination would probably also have a substantial contribution due to nonradiative decay. We note that Nelson *et al.*[8] have shown that the lowest conduction-band state becomes a Γ-point GaAs derived conduction-band state for the wider $n \times n$ superlattices ($n = 10-12$) implying a large across-gap oscillator strength.

We stress that the issue of a superlattice being energywise direct or indirect cannot be fully settled by *ab initio* band-structure calculations since they are known to be able to produce relative positions of energy levels in conduction-band spectra only to an accuracy of 30–100 meV.[13] The 2×2 [001] superlattice is particularly difficult in this respect since the relevant energy difference $E(\Gamma(X_z)) - E(M(X_x))$ is so small ($\simeq 1$ meV). This is unfortunate since the ordering of the X_{xy} and X_z-derived states is subject to debate.[20] We note, however, that the accuracy of this calculated energy difference is on a considerably better level (a few meV) than the 30–100 meV mentioned before since both states originate from the equivalent bulk X states. But even the ordering of $\Gamma(X_z)$ and $\Gamma(\Gamma)$ is subject to debate. We find $\Gamma(X_z)$ to be 135 meV lower in energy than $\Gamma(\Gamma)$. Nakayama and Kamimura[5] find the opposite result: from Fig. 4 of their paper we estimate $\Gamma(\Gamma)$ to be $\simeq 100$ meV lower in energy. These authors have adjusted the α parameter of the exchange-correlation potential in order to obtain calculated band structures of bulk GaAs and AlAs which agree better with the experimental band structures. Nevertheless, differences between experimental and theoretical conduction-band structures are still on the level of 100–200 meV. This is close to the level of inaccuracy of the relative positions of conduction-band energy levels expected anyway for true *ab initio* band-structure calculations.[13]

In conclusion, we have calculated the radiative rates on direct transitions and estimated the phonon-assisted radiative rates on indirect transitions in 1×1 and 2×2 [001] and [110] GaAs/AlAs superlattices. The rates in [001] superlattices are at least 2 orders of magnitude smaller than the across-gap direct transitions in GaAs. These superlattices therefore do not hold many prospects for light emission applications. Our calculations show that the interpretation of spectroscopic experiments on the "energywise direct or indirect" issue will be hindered by the fact that radiative rates on direct and indirect transitions, and possibly also nonradiative rates, are of comparable magnitude. We therefore suggest to settle the direct or indirect issue by the use of pressure or magnetic fields to discriminate between the different anisotropy in **k** space of the various "direct" (Γ) and "indirect" valleys. We have also shown that from a spectroscopic point of view the 2×2 [001] superlattice can neither be called direct nor indirect since the corresponding transitions are equally strong. The 2×2 [110] superlattice is energywise and spectroscopically direct since band folding and mixing yields a Γ-derived lowest conduction-band state.

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[14]Our calculated results for the ground-state properties of these superlattices are in accordance with the results from other *ab initio* calculations. We define the GaAs/AlAs interface heat of formation as $\Delta H(n\times n)=\{E(n\times n$ GaAs/AlAs$)-[E(\text{GaAs})+E(\text{AlAs})]/2\}/n$; we have calculated the total energies E(GaAs) and E(AlAs) under the same conditions as the SL calculation, i.e., using the same unit cell, the same number of k points in the Brillouin zone, etc. We find $\Delta H(1\times 1)$ [001]$)\equiv\Delta H(1\times 1)$ [110]$)\simeq 30$ meV [cf. Bylander and Kleinman (15 meV) using relativistic pseudopotentials (Ref. 15) and Wood *et al.* (25 meV) using both semirelativistic pseudopotentials and the LAPW method (Ref. 16)]. We find $\Delta H(2\times 2)$ [001]$)\simeq 19$ meV and $\Delta H(2\times 2)$ [110]$)\simeq 30$ meV. By shifting the bulk GaAs and AlAs potential rigidly to fit the potential of the corresponding monolayers of the GaAs/AlAs SL optimally, we find a value of 0.6 eV for the valence-band offset $[(\Gamma(\text{HH})^{\text{GaAs}})-[(\Gamma(\text{HH})^{\text{AlAs}})$ in *both* [001] and [110] GaAs/AlAs superlattices (cf. 446 meV for [001] and 447 meV for [110] in Ref. 15).

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