Role of interface states in band structures of short-period $(GaAs)_n/(Ge_2)_n$ [001] superlattices under a zero-field model

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(Received 25 June 1991; revised manuscript received 4 October 1991)

We have calculated the band structures of the $(GaAs)_n/(Ge_2)_n$ [001] superlattices (SL's) with $n=1-10$ giving special attention to the role of the interface states at the Ga-Ge and As-Ge *polar* interfaces. The calculations are performed by means of a semiempirical tight-binding method with an sp^3s^* basis. The presence of the electric field in the SL is totally ignored, i.e., "the zero-field model." For the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL, the band gap is 0.85 eV, with the conduction-band minimum at the X point, into which the fcc L point is folded. The states at the conduction- and valence-band edges are confined two dimensionally in the Ge layers. Furthermore, 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 Ga-Ge interface, while those of the upper interface band are located at the As-Ge interface. The energies of the interface states depend on the parameters representing the Ga-Ge and As-Ge bond lengths and the valence-band discontinuity between GaAs and Ge, but the interface states do not disappear from the gap with reasonable choices of the parameters. By decreasing the SL period n, the energy gap between the confined band-edge states increases (1.07 eV at the X point for $n=2$) due to the quantum confinement effect. A sudden shrinkage in the band gap ($E_g=0.16$ eV at the R point) is obtained for $n=1$. The origin of the band-gap shrinkage is related to the fact that the overlap of the interface states becomes so large that they combine as band states.

I. INTRODUCTION

GaAs/Ge [001] superlattices (SL's) have been grown by molecular-beam epitaxy for the past ten years[1-7] for the purpose of studying structures based on the heterojunctions between the polar (GaAs) and nonpolar (Ge) semiconductors. In an abrupt planar GaAs/Ge [001] heterojunction, two kinds of interfaces are possible: the As-Ge interface in (···GaAsGaAs/GeGeGeGe···) case and the Ga-Ge interface in (···AsGaAsGa/GeGeGeGe···) case. For both kinds of interfaces, two significant features were predicted by theorists. One is a high density of interface states localized at the Ga-Ge and As-Ge interfaces, which was studied by an empirical tight-binding method[8] and a self-consistent pseudopotential method.[9] The other is an electric field in the GaAs and Ge layers, which was studied by a simple electrostatic consideration.[10] In the $(GaAs)_n/(Ge_2)_n$ [001] SL's, both kinds of interfaces are included in one structure (···GaAsGaAs/GeGe···GeGe/GaAsGaAs···). For example, we show the atomic arrangement of a $(GaAs)_6/(Ge_2)_6$ [001] SL in Fig. 1. The above-mentioned two features of GaAs/Ge [001] interfaces are considered to affect the band structures, $E(\mathbf{k})$, of the $(GaAs)_n/(Ge_2)_n$ [001] SL's. However, these band structures have not been studied experimentally because of the imperfect crystalline qualities of the grown layers due to the formation of antiphase boundaries[5] and columnar structures.[6]

On the other hand, recently, theoretical calculations on the electronic structures of $(GaAs)_m/(Ge_2)_n$ [001] SL's with $m,n\leq 5$ have been reported by means of *ab initio* methods.[11-15] Among them, the most striking result on the band structures is the disappearance of the band gap in the $(GaAs)_1/(Ge_2)_1$ [001] SL reported by Ohno.[11] This band-gap shrinkage is unique to the GaAs/Ge system because the more common systems, $(GaAs)_1/(AlAs)_1$ and $(Si)_1/(Ge)_1$ [001] SL's, do not exhibit such a band-gap shrinkage. The other researchers[12-15] have not reported the band structures, $E(\mathbf{k})$, explicitly because they concentrated mainly on the band discontinuities and the formation enthalpies of the SL's.

Up to the present, to our knowledge there is no study which reports $E(\mathbf{k})$ of the $(GaAs)_n/(Ge_2)_n$ [001] SL with a wide range of n. It is not understood how the two features of the GaAs/Ge [001] interfaces affect the band structures of the SL's. The effects of the two features on the band-gap shrinkage in the $(GaAs)_1/(Ge_2)_1$ [001] SL are not made clear.

In this study, we calculate the band structures, $E(\mathbf{k})$, of the $(GaAs)_n/(Ge_2)_n$ [001] SL's with a wide range of n,

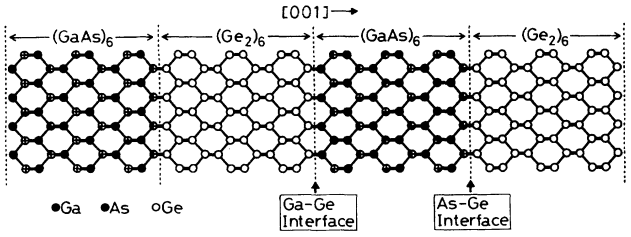


FIG. 1. Atomic arrangement of the $(GaAs)_n/(Ge_2)_n$ [001] superlattice with $n=6$ viewed along the $[\bar{1}10]$ direction.

here $n=1-10$. We give special attention to the role of the interface states, which is the first of the two features of the GaAs/Ge interfaces. The effect of the interface states on the band-gap shrinkage is explained. The calculations are performed by means of a semiempirical tight-binding method with the sp^3s^* basis without self-consistent procedures. We ignore the effect of the electric field, which is the second of the two features. The method of calculations will be discussed as "the zero-field model" in the next section. Such methods were applied for obtaining dispersions of interface bands and wave functions of interface states at polar [001] heterojunctions.[8,16,17] To study the role of the electric field, which is the second feature, a self-consistent calculation is needed.[12–15] We leave a self-consistent calculation as a final goal of our study.

II. CALCULATIONS

A. The zero-field model

The $(GaAs)_n/(Ge_2)_n$ [001] SL has two kinds of abrupt planar interface, the Ga-Ge and As-Ge interfaces, as already shown in Fig. 1. For both kinds of interface, Harrison *et al.*[10] pointed out the presence of the electric fields whose directions are opposite in the GaAs and Ge layers. In other words, the potential in both layers has different average gradients (see Fig. 2 of Ref. 10). These were basically deduced from the differences in the nuclear charges of the Ga, As, and Ge atoms.[10] By the similar

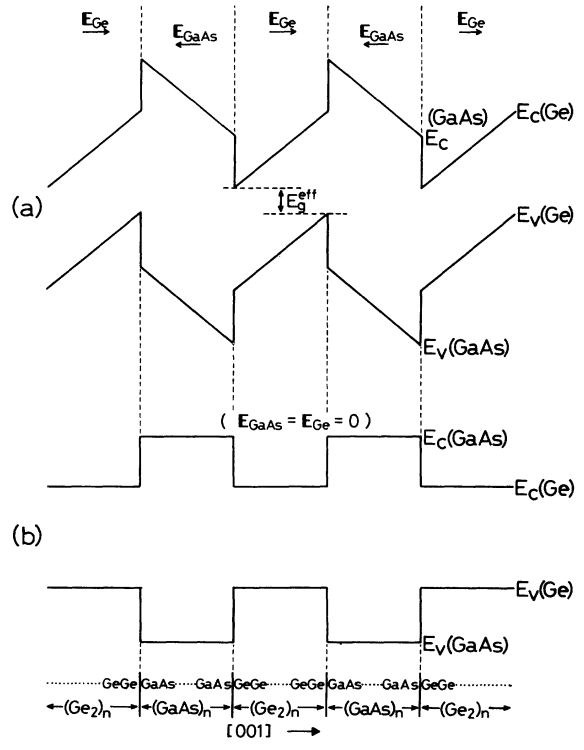


FIG. 2. Schematic energy-band diagrams of the $(GaAs)_n/(Ge_2)_n$ [001] superlattice, (a) with the electric field and (b) under the zero-field model.

electrostatic considerations, the $(GaAs)_n/(Ge_2)_n$ [001] SL is found to have the energy-band diagram as schematically shown in Fig. 2(a). The confining potentials for electrons and holes exhibit deviation from the square-well potentials.

Let us discuss the tight-binding Hamiltonian H under the presence of the electric field. Generally, the matrix element of the Hamiltonian, $H_{i\alpha,j\beta}$, is defined as[18]

$$H_{i\alpha,j\beta}=\langle\chi_\alpha^i|H|\chi_\beta^j\rangle \ . \tag{1}$$

Here, i (j) denotes the ith (jth) atom in the unit cell of the $(GaAs)_n/(Ge_2)_n$ [001] SL (the Ga or As atoms for $1\le i,j\le 2n$, and the Ge atoms for $2n+1\le i,j<4n$), α and β denote the type of basis orbitals ($\alpha,\beta=s,p_x,p_y,p_z$, and s^*), and

$$|\chi_\beta^j\rangle=N^{-1/2}\sum_L \exp(i\mathbf{k}\cdot\mathbf{r}_L)|\phi_\beta^j(\mathbf{r}-\mathbf{r}_L)\rangle \tag{2}$$

denotes the Bloch sum composed by a linear combination of $|\phi_\beta^j(\mathbf{r}-\mathbf{r}_L)\rangle$, the β-type orbitals of the jth atom at $\mathbf{r}_L$. N is the number of unit cells in a unit volume. We are interested in the diagonal elements, which affect the potential in the SL.

The diagonal element $H_{i\alpha,i\alpha}$ is expressed as a sum of two terms:

$$H_{i\alpha,i\alpha}=H^0_{i\alpha,i\alpha}+\Delta H_{i\alpha,i\alpha} \ . \tag{3}$$

The term $H^0_{i\alpha,i\alpha}$ is independent of the electric field and coincides with the corresponding element of the tight-binding Hamiltonian for semiconductor SL's, which have no electric field.[19] $H^0_{i\alpha,i\alpha}$ is equal to $E(\alpha,\text{Ga})$ or $E(\alpha,\text{As})$ for $1\le i\le 2n$, and $E(\alpha,\text{Ge})$ for $2n+1\le i\le 4n$, where $E(\alpha,\text{Ga})$, $E(\alpha,\text{As})$, and $E(\alpha,\text{Ge})$ are the notations used for the diagonal elements of the sp^3s^* Hamiltonian for the bulk GaAs and Ge.[18] On the other hand, $\Delta H_{i\alpha,i\alpha}$ changes gradually plane by plane, representing the potential gradients in the GaAs and Ge layers. Thus the term $\Delta H_{i\alpha,i\alpha}$ exhibits the effects of the electric field. We could determine $\Delta H_{i\alpha,i\alpha}$ by applying a self-consistent tight-binding scheme.[20,21]

In this study, since we focus exclusively on the role of the interface states, we ignore the effect of the electric field in the SL's in the same way as Pollmann and Pantelides for the GaAs/Ge and ZnSe/Ge [001] interfaces,[8] Yamaguchi for the $(GaAs)_{90}/(ZnSe)_{90}$ [001] SL,[16] Shen, Zhang, and Fu for the $(GaAs)_n/(ZnSe)_n$ [001] SL's with $n=2-12$,[17] and Shen, Dow, and Ren for $(GaAs)_1/(ZnSe)_{10}$ [001] SL.[22] They reported the interface bands, the wave functions of the interface states, and the density of the interface states in the gap. The electric fields are forced to vanish by setting $\Delta H_{i\alpha,i\alpha}=0$ for all the i's and α's. We call this method of calculation "the zero-field model." The energy-band diagram of the $(GaAs)_n/(Ge_2)_n$ [001] SL's under the zero-field model is schematically shown in Fig. 2(b).

As suggested by Dandrea, Froyen, and Zunger,[15] the electric field in the $(GaAs)_n/(Ge_2)_n$ [001] SL can be zero if the Ga-Ge and As-Ge bonds have a deficiency of $\frac{1}{4}$ electron and an excess of $\frac{1}{4}$ electron, respectively. In other words, the SL under the zero-field model corresponds

to what they called "the uncompensated system," where the deficiency and excess of electron are not compensated by charge transfer from the As-Ge donorlike bond to the Ga-Ge acceptorlike bond.[15]

By use of the zero-field model, we can study the role of the interface states separately from that of the electric field in a short period SL. However, we should notice that the band structures based on the zero-field model are different from the true ones in some respects. For example, the zero-field model does not take account of the deviation of the confinement potential from the square wells, and the reduction of the effective band gap E_g^{eff} [see Fig. 2(a)], caused by the effect of the electric fields.

B. Tight-binding parameters

We use a semiempirical nearest-neighbor tight-binding method with a basis of five orbitals (s, p_x, p_y, p_z, and s^*) per atom. We employ the tight-binding parameters as follows.

(i) The diagonal and interatomic matrix elements of the Hamiltonian of the bulk GaAs and Ge are taken from the values by Vogl, Hjalmarson, and Dow.[18] Their values give $E_g(\Gamma_1^c\text{-}\Gamma_{15}^v)=1.55$ eV and $E_g(X_1^c\text{-}\Gamma_{15}^v)=2.03$ eV for GaAs, and $E_g(L_1^c\text{-}\Gamma_{25}')=0.76$ eV and $E_g(\Gamma_2'\text{-}\Gamma_{25}')=0.90$ eV for Ge. They are fitted to the band gaps calculated by Chelikowsky and Cohen[23] at the Γ and X points for GaAs and the L and Γ points for Ge. Although the revised parameters are reported,[24] we show the results calculated by the original ones in the Ref. 18.

(ii) For the interatomic matrix elements of the nearest-neighbor As-Ge and Ga-Ge pairs, we adopt the arithmetic averages of the corresponding matrix elements of the bulk GaAs and Ge.[8,16]

(iii) Spin-orbit coupling is not included.

(iv) The effect of the lattice distortions is ignored except in Sec. III C where we study the effects of the Ga-Ge and As-Ge bond length distortions.

(v) The valence-band discontinuity between GaAs and Ge, $\Delta E_v[=E_v(\text{Ge})-E_v(\text{GaAs})]$, is assumed to be 0.41 eV, which is the theoretical value by Harrison.[25] The value is close to 0.49 eV, the average value of experimental ΔE_v's reported by various researchers.[26] We study the effects of choice of ΔE_v in Sec. III D.

III. BAND STRUCTURE OF $(GaAs)_{10}/(Ge_2)_{10}$ [001] SUPERLATTICE

A. Band structures

The band structure of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL under the zero-field model is shown in Fig. 3. The inset shows the Brillouin zone of the $(GaAs)_n/(Ge_2)_n$ [001] SL. The irreducible part is indicated with the labels of the eight symmetry points (R, Z, Γ, X, M, X', R', and A). The axis from the Γ point to the X point is normal to the projection of the Ga-Ge and As-Ge bonds on the (001) plane. The X_z and X_y points of the fcc Brillouin zone are folded into the Γ and M points in the SL Brillouin zone, respectively. The L point is folded into the R and X points when n is odd and even, respectively.[16]

The valence and conduction bands of the SL consist of many crowded bands formed by the zone folding effect. The notations for the band edges in Fig. 3 are Γ^v, the top of the valence band, and Γ^c, X^c, and M^c, the lowest conduction-band states at the Γ, X, and M points. The bottom of the conduction band is the X^c state at the X point which corresponds to the fcc L point. Hence, under the zero-field model, this SL has an indirect band gap of $E_g(X^c\text{-}\Gamma^v)=0.85$ eV, which is 0.09 eV larger than the band gap of the bulk Ge, $E_g(L_1^c\text{-}\Gamma_{25}')=0.76$ eV.

Additionally, we have found two interface bands, $I1$ and $I2$ (see Fig. 3), lying in the lower and upper regions of the gap, respectively. The lower band $I1$, is an occupied one, while the upper band $I2$, is an empty one. The notations for the interface states in Fig. 3 are Γ^{I1}, the interface state of the $I1$ band, and Γ^{I2}, R^{I2}, X^{I2}, and M^{I2}, the interface states of the $I2$ band.

B. Charge densities

The charge densities $|\Psi_k|^2$ of some of the band edge states and the interface states are shown in Figs. 4(a) and 4(b). All the band edge states in Fig. 4 are confined two dimensionally in the Ge "well" layers. On the other hand, the charge density of the interface state Γ^{I1} has a peak at the Ga-Ge interface while the charge densities of the X^{I2} and Γ^{I2} states have peaks at the As-Ge interface. This indicates that the $I1$ and $I2$ bands consist of the interface states at the Ga-Ge and As-Ge interfaces, respectively.

To see the degree of localization of the interface states, we calculate the interface charge of an interface state P_{if}, which we define as the sum of the charge densities on the four atomic planes at the interface; i.e., the ($\cdots$ GeGe/GaAs $\cdots$) planes at the Ga-Ge interface for

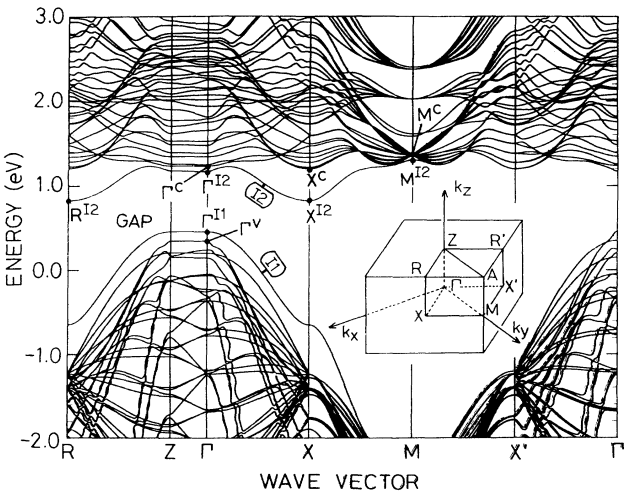
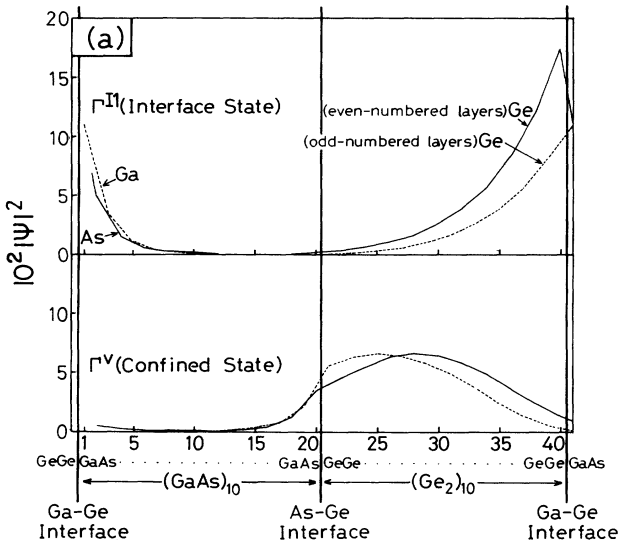


FIG. 3. Band structures of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice calculated by the first-neighbor sp^3s^* tight-binding method under the zero-field model. The zero of energy corresponds to the top of the valence band of the GaAs. The inset shows the Brillouin zone of the $(GaAs)_n/(Ge_2)_n$ [001] superlattice.

the $I1$ band, the ($\cdots$ GaAs/GeGe $\cdots$) planes at the As-Ge interface for the $I2$ band. Thus P_{if} is expressed as

$$P_{if}=\begin{cases}\sum_{(\mathrm{Ge,Ge/Ga,As})}|\Psi|^2 & \text{for a state of the } I1 \text{ band} \quad (4a)\\ \sum_{(\mathrm{Ga,As/Ge,Ge})}|\Psi|^2 & \text{for a state of the } I2 \text{ band} . \quad (4b)\end{cases}$$

P_{if} as a function of the wave vector is shown in Fig. 5. As shown in the figure, P_{if} varies in the reciprocal space. The strongly localized states ($P_{if}>90\%$) of the $I1$ and $I2$ bands appear around the R and X points. For the $I1$ band, the states around the M point are also localized strongly. The above indicates that the interface states tend to be localized in the reciprocal space. Additionally, P_{if} for the M^{I2} state is only 14.2%, indicating the delocalization of this state. We have found such delocalization of the states of the $I2$ band only in the very vicinity



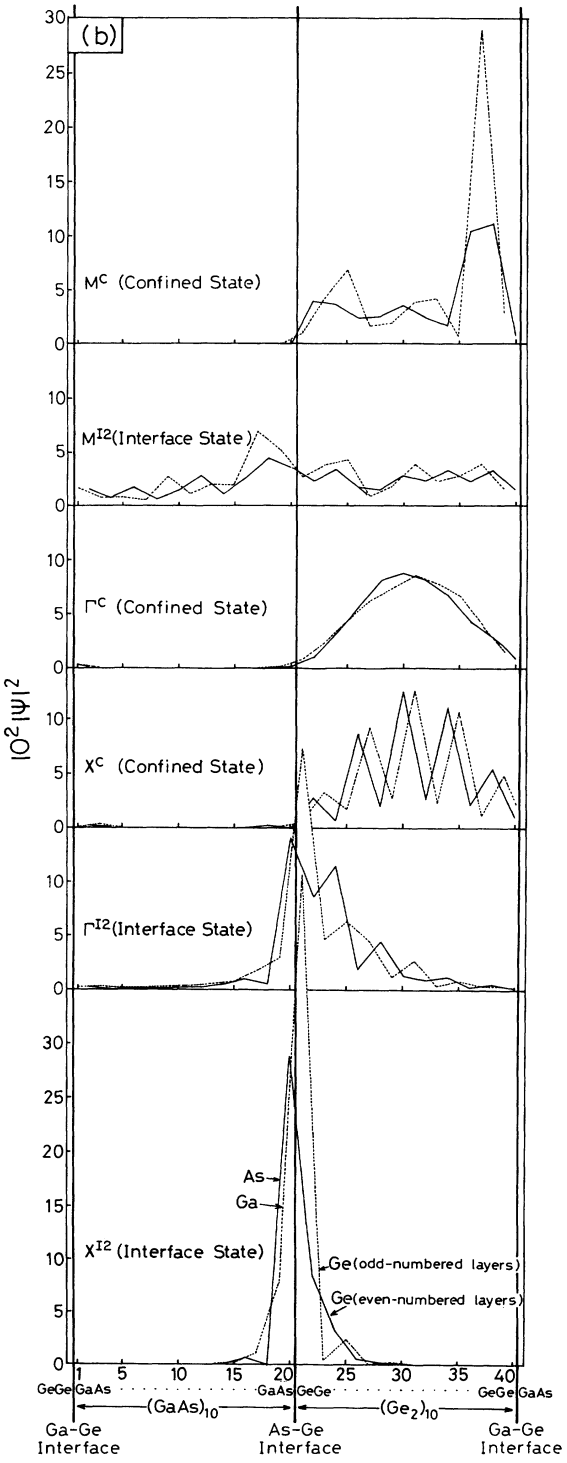


FIG. 4. Charge densities in the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice. (a) The occupied states; the interface state (Γ^{I1}) and the confined state (Γ^{v}). (b) The empty states; the interface states (X^{I2}, Γ^{I2}, and M^{I2}) and the confined states (X^{c}, Γ^{c}, and M^{c}). The panels are stacked up in order of energy. The dashed lines indicate charge densities on the Ga and odd-numbered Ge layers, the solid lines those on the As and even-numbered Ge layers.

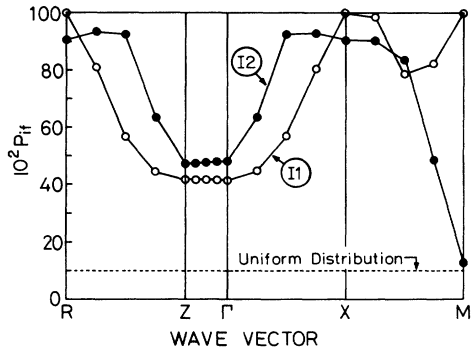


FIG. 5. Interface charge of an interface state, P_{if}, which is defined as the sum of the charge densities on the four atomic planes at the interface in the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice. P_{if}'s for the $I1$ and $I2$ bands are shown as functions of the wave vector. The dashed line indicates P_{if} of a wave function which is distributed uniformly in the superlattice (i.e., $P_{if}=100\%\times 4/40$). See the text for the definition of the P_{if}.

of the M point. The delocalization is not found for the $I1$ band.

The X^{I2} state is the typical interface state because it is localized strongly ($P_{if}=90.9\%$) at the As-Ge interface. This state consists chiefly of the s, s^*, and p_z orbitals on the first As and Ge planes ($\cdots$ GaAs/GeGe $\cdots$) and the p_x and p_y orbitals on the second Ga and Ge planes ($\cdots$ GaAs/GeGe $\cdots$) at the As-Ge interface; i.e., the s-p hybridized state.

The present result for the interface states found in the SL is qualitatively consistent with that obtained by Pollmann and Pantelides[8] in the single heterojunctions. In both results, the interface band appears just above the valence-band edge at the Ga-Ge interface and below the conduction-band edge at the As-Ge interface. However, the dispersion of the interface band at the As-Ge interface is calculated much more accurately in the present study than in the study of Pollmann and Pantelides, because they used a nearest-neighbor sp^3 method which does not produce an accurate dispersion of a lowest conduction band.[18]

The presence of the interface states at a GaAs/Ge [001] heterojunction has not been confirmed by the experiments.[1-7] However, for example, the $I2$ band, which can trap carriers at the X-point minimum with a binding energy of ≈ 0.35 eV relative to E_c(Ge), could be formed at an atomically flat As-Ge interface. Such interface is expected to be realized experimentally in a GaAs/(Ge_2)/GaAs [001] structure proposed by Muñoz, Chetty and Martin,[13] where the inserted (Ge_2) layer induces a local dipole for tuning a band discontinuity.

C. Effect of lattice distortions

The difference in the lattice constants between the bulk GaAs and Ge is negligibly small ($\cong 0.1\%$). However,

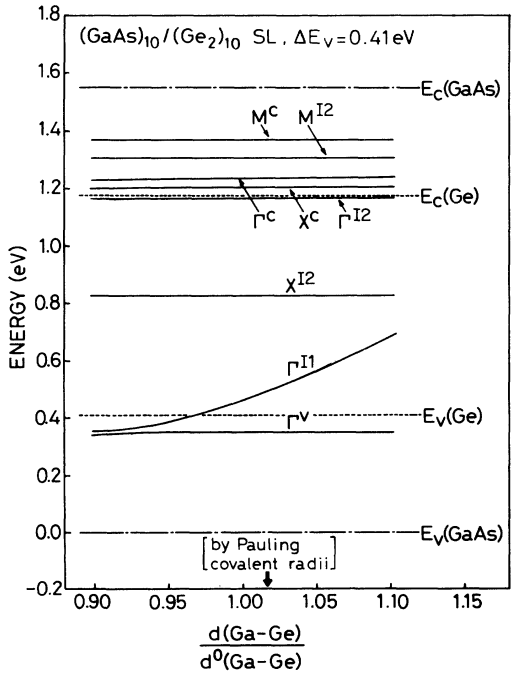


FIG. 6. Band energies of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice as functions of the Ga-Ge bond length, d(Ga-Ge), at the Ga-Ge interface. d^0(Ga-Ge) equals 2.44 Å, the distortion-free length of the Ga-Ge bond. E_c(Ge) and E_v(Ge) denote the bottom of the conduction band and the top of the valence band, respectively, for the bulk Ge. E_c(GaAs) and E_v(GaAs) denote the corresponding energies for the bulk GaAs. The notations for the states are the same as those in Fig. 3.

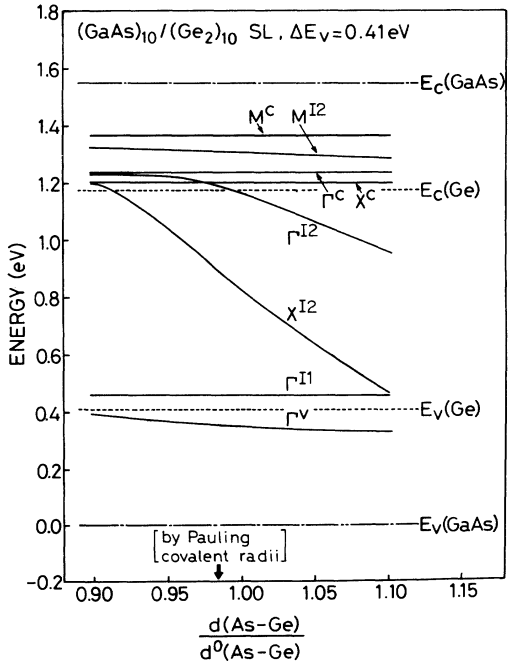


FIG. 7. Band energies of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice as functions of the As-Ge bond length, d(As-Ge), at the As-Ge interface. d^0(As-Ge) equals 2.44 Å, the distortion-free length of the As-Ge bond. The notations for the states are the same as those in Fig. 3.

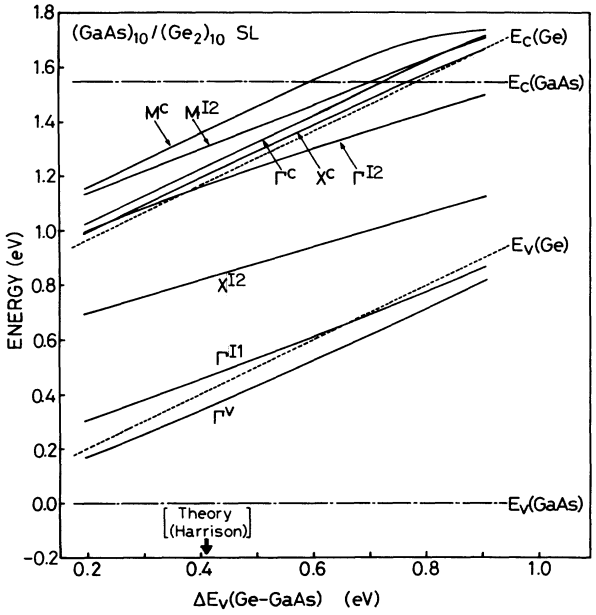


FIG. 8. Band energies of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] superlattice as functions of the valence-band discontinuity between GaAs and Ge, ΔE_v. The notations for the states are the same as those in Fig. 3.

owing to the difference in the covalent radii between the Ga, As, and Ge atoms, the Ga-Ge and As-Ge bond lengths at the interfaces [d(Ga-Ge) and d(As-Ge), respectively] are expected to be different from the Ge-Ge and Ga-As bond lengths in the bulk [d(Ge-Ge) and d(Ga-As), respectively]. For example, if we adopt the Pauling's tetrahedral covalent radii (Ga, 1.26 Å; Ge, 1.22 Å; As, 1.18 Å),[27] we obtain d(Ga-Ge)=2.48 Å and d(As-Ge)=2.40 Å which are 1.6% longer and 1.6% shorter, respectively, than the bulk value, d(Ge-Ge)=d(Ga-As)=2.44 Å.[10] In this section, we include such bond length distortions by the approximation that the interatomic matrix elements are inversely proportional to the square of bond length.[28]

In Figs. 6 and 7, we show the band energies of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL as functions of d(Ga-Ge) and d(As-Ge), respectively. d(Ga-Ge) and d(As-Ge) are varied within ±10% of their distortion-free values, d^0(Ga-Ge)=d^0(As-Ge)=2.44 Å. The energy of the Γ^{I1} state, which is the interface state at the Ga-Ge interface, shifts by varying d(Ga-Ge), and the energies of the Γ^{I2} and X^{I2} states, which are those at the As-Ge interface, shift by varying d(As-Ge). However, the interface states do not disappear from the gap as far as we estimate the extent of the lattice distortions based on the Pauling covalent radii. To obtain more accurate results on the energies of the interface states, calculations on the Ga-Ge and As-Ge bond lengths based on a total energy minimization is required.[29]

On the other hand, the shifts in the energies of the band edges (the Γ^v, Γ^c, X^c, and M^c states) are negligibly small. The distortions of the Ga-Ge and As-Ge "interface bonds" do not affect the energies of the band edges but affect only those of the interface states in the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL.

D. Effect of choice of ΔE_v

So far no reliable value for the ΔE_v between GaAs and Ge has been reported experimentally. The experimental ΔE_v's for [001], [110], and [111] heterojunctions range from 0.23 to 0.70 eV with the average value of 0.49 eV.[26] As already mentioned in Sec. II B, we adopt ΔE_v=0.41 eV, the theoretical value by Harrison based on the universal-parameter tight-binding method.[25] In this section we vary the ΔE_v as a parameter to check how the result of the band structure calculation is affected by the choice of the ΔE_v.

In Fig. 8, we show the band energies of the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL as functions of the ΔE_v. The range of the ΔE_v in Fig. 8, 0.2–0.9 eV, covers that of the experimental results. The zero of energy is taken at the top of the valence band of the bulk GaAs. The relative positions of the interface states, Γ^{I1}, Γ^{I2}, and X^{I2}, in the gap shift down with increasing ΔE_v, but they do not disappear from the gap within the examined range. It is concluded that the relative positions of the interface states in the gap depend on the choice of the ΔE_v but they are always present in the gap as far as the ΔE_v is chosen within the range of experimental ΔE_v's.

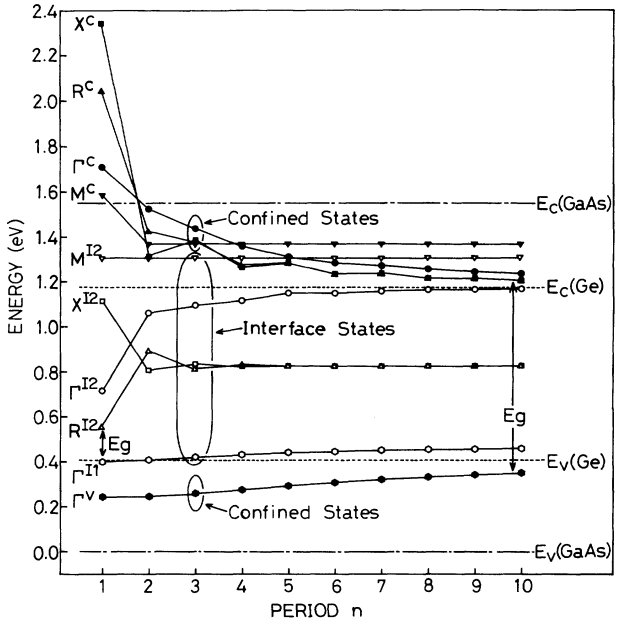


FIG. 9. Band energies of the $(GaAs)_n/(Ge_2)_n$ [001] superlattices with n=1–10. The energies of the interface and band-edge states, where the latter are the confined states in the Ge layers, are shown. The notations for the states are the same as those in Fig. 3.

IV. BAND STRUCTURE OF $(GaAs)_n/(Ge_2)_n$ [001] SUPERLATTICES WITH $n < 10$

A. Change in band structures with decreasing the superlattice period

In this section we study how the band structures change with decreasing the SL period n, from 10 to 1. We show the energies of the interface and band-edge states in the $(GaAs)_n/(Ge_2)_n$ [001] SL's with $n = 1-10$ in Fig. 9. The latter states are confined two dimensionally in the Ge layers as stated in Sec. III B. The distinction between the two kinds of states, the interface and confined states, is definite in case of $n = 10$, as shown in Fig. 4. However, with n approaching 1, it becomes difficult to distinguish the two kinds of states because the number of the Ga-Ge and As-Ge "interface bonds" approaches that of the Ge-Ge and Ga-As "bulk bonds." Nevertheless, to see the trend systematically, we formally label the highest occupied state and the lowest empty state at each symmetry point as the interface states, the next highest and next lowest states as the confined states, even in case of $n = 1$.

As shown in Fig. 9, the energies of the confined states in the conduction-band edge shift up and those in the valence-band edge shift down with decreasing the SL period n, due to the quantum confinement effect. Consequently, the energy gap between the confined states increases up to 1.07 eV at the X point with $n = 2$.

The energies of the interface states do not shift very much down to $n = 2$. However, with n changing from 2 to 1, the energies of the R^{I2} and Γ^{I2} states decrease by ~ 0.35 eV suddenly. At the same time, the energy of the X^{I2} state increases by the same amount. The states labeled "interface states" at $n = 1$ are virtually the band-edge states because the number of the interface bonds and that of the bulk bonds are the same. The energy gap should be defined as the gap between the empty and occupied "interface states" resulting in $E_g(R^{I2}\text{-}\Gamma^{I1}) = 0.16$ eV. The band gap of the $(GaAs)_n/(Ge_2)_n$ [001] SL shrinks suddenly with $n = 1$.

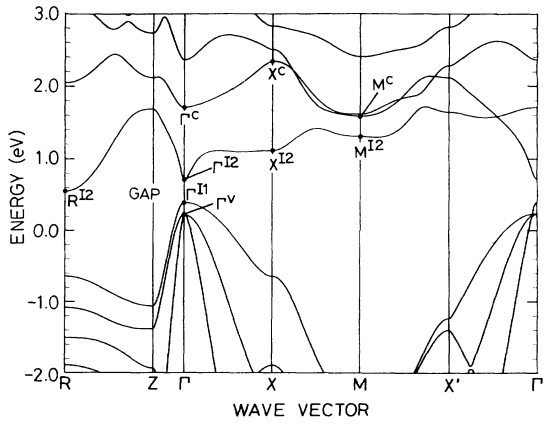


FIG. 10. Band structures of the $(GaAs)_1/(Ge_2)_1$ [001] superlattice calculated by the first-neighbor sp^3s^* tight-binding method under the zero-field model. The zero of energy corresponds to the top of the valence band of the GaAs.

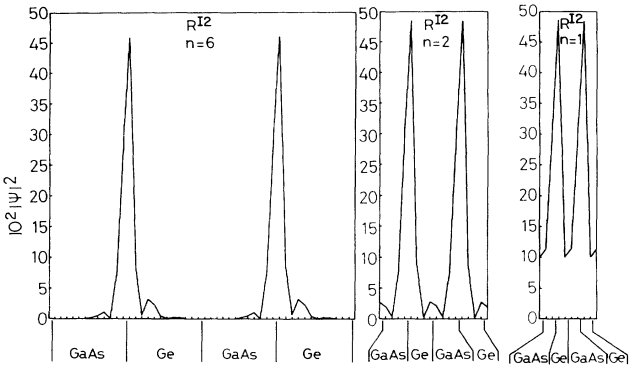


FIG. 11. Charge densities of the empty interface states at the R point, the R^{I2} states, in the $(GaAs)_n/(Ge_2)_n$ [001] superlattices with $n = 6$, 2, and 1. The charge densities on the Ga, As, and Ge layers are indicated by the solid line.

B. Origin of band-gap shrinkage in $(GaAs)_1/(Ge_2)_1$ [001] superlattice

Figure 10 shows the band structures of the $(GaAs)_1/(Ge_2)_1$ [001] SL. The band gap shrinks at the R and Γ points due to the lowering of the conduction-band edges as already shown in Fig. 9. The disagreement of the value of the band gap ($E_g = 0.16$ eV) with that reported by Ohno[11] ($E_g = 0$ eV) is ascribed to the approximations used in the tight-binding method. However, the simple sp^3s^* tight-binding method proves to be very useful for predicting the band-gap shrinkage.

The band gap does not shrink at the M and X' points. This corresponds to the absence of the interface bands at the same two points in the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL. The band-gap shrinkage has relation to the presence of the interface bands. To understand the origin of the band-gap shrinkage more clearly, we plot the charge density of the R^{I2} state with $n = 6$, 2, and 1 in Fig. 11. The R^{I2} state is the bottom of the conduction band with $n = 1$. With $n = 6$ and 2, the R^{I2} states, which are localized at the As-Ge interfaces, are still isolated from each other. They overlap and connect each other with $n = 1$. The origin of the band-gap shrinkage is related to the fact that the overlap of the interface states becomes so large that they can combine as the band states.

We have also found band-gap shrinkage in the Ga/Ge/As/Ge [001] SL (Ref. 30) and the $(GaAs)_1/(Ge_2)_{1/2}$ [001] SL (or Ga/As/Ge SL) (Ref. 31) by using the same tight-binding parameters. These results will be reported elsewhere.

V. CONCLUSIONS

We have calculated the band structures of the $(GaAs)_n/(Ge_2)_n$ [001] SL's with $n = 1-10$ by means of a semiempirical tight-binding method with the sp^3s^* basis. The presence of the electric field in the SL's is totally ignored; i.e., "the zero-field model." For the $(GaAs)_{10}/(Ge_2)_{10}$ [001] SL, the band gap is 0.85 eV. The conduction-band minimum is located at the X point of the SL Brillouin zone. The states at the conduction- and

valence-band edges are confined two dimensionally in the Ge layers. Furthermore, 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 Ga-Ge interface, those of the upper interface band located at the As-Ge interface. The energies of the interface states depend on (i) the lengths of the Ga-Ge and As-Ge bonds, and (ii) $\Delta E_v[=E_v(\text{Ge})-E_v(\text{GaAs})]$. However, the interface states do not disappear from the gap within the reasonable choice of the parameters; $[d(\text{Ga-Ge})-d^0(\text{Ga-Ge})]/d^0(\text{Ga-Ge})\approx+1.6\%$, $[d(\text{As-Ge})-d^0(\text{As-Ge})]/d^0(\text{As-Ge})\approx-1.6\%$, and $0.2\leq\Delta E_v\leq 0.9$ eV. By decreasing the SL period n, the energy gap between the confined band-edge states increases due to the quantum confinement effect. A sudden shrinkage in the band gap $[E_g(R^{I2}\text{-}\Gamma^{I1})=0.16$ eV] is obtained with $n=1$. The origin of the band-gap shrinkage is related to the fact that the overlap of the interface states becomes so large that they can combine as the band states.

ACKNOWLEDGMENTS

We are grateful to Dr. K. Hirakawa for valuable discussions. We also thank Dr. P. Vogl for sending us the revised tight-binding parameters of Ref. 18. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, and also by the Industry-University Joint Research Program "Mesoscopic Electronics."

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