

Electronic Structure and Optical Properties of Si-Ge Superlattices

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We report pseudopotential calculations of the electronic structure of a $\text{Si}_4\text{Ge}_4(001)$ superlattice grown on a Si substrate. Our results show that it is possible to account for the observed optical spectra, without invoking indirect transitions, in terms of a model in which the microscopic potential and the bond lengths in the Ge layer are bulklike.

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Recently, Pearsall *et al.*¹ have observed optical transitions in strained-layer $\text{Si}_4\text{Ge}_4(001)$ superlattices consisting of alternating layers of Si and Ge, each four atomic monolayers thick, grown on a Si substrate. In particular, they identified three new optical transitions centered at 0.76, 1.25, and 2.31 eV. Although the theoretical results presented in subsequent publications²⁻⁵ have gone a long way towards accounting for the origin of these transitions, their predictions can only be reconciled with experiment if it is assumed that the optical spectra are dominated by indirect transitions as a result of disorder effects. In this Letter, we present a new model calculation which accounts for the observed spectra without invoking the breakdown of the ordered character of this structure.

If we ignore minor differences reflecting the choice of computational procedure and the level of approximations in question, the key features of the electronic structure of the ideal Si_4Ge_4 superlattice reported in the literature are very much the same. These features can be understood in terms of a simple band-offset diagram presented in Fig. 1. In the free-standing configuration used in all theoretical models, the Si atoms retain their bulk coordi-

nates. The Ge lattice constant in the interface plane is that of bulk Si, and in the direction perpendicular to the interface it is equal to 5.83 Å (i.e., it is larger than the bulk Ge lattice constant 5.66 Å). The separation at the Si-Ge interfaces is taken to be the average of the $\langle 001 \rangle$ separation in the Si and Ge layers.

First-principles calculations⁶ show that the valence-band offset ΔE_v is 0.84 eV. The magnitude of the conduction-band offset ΔE_c depends on the difference in the bulk band gaps of Si and Ge in the $\langle 001 \rangle$ direction, and on the magnitude of the splitting of the conduction-band minima of strained Ge. In the direction of the interface plane (x, y) there is no confinement. The conduction-band minimum lies away from the zone center and its position is given by the Δ minimum point of bulk Si. In the $\langle 001 \rangle$ direction, the confinement effect pushes the electron states away from the bottom of the corresponding "well" and the band gap at the zone center (Γ) increases. This increase is substantial since both the conduction- and valence-band offsets are large. As a result the principal gap of the superlattice is the indirect gap between the Si Δ point and the top of the valence band at Γ derived from the Ge layer. The magnitude of this gap is predicted to be about 0.8 eV which happens to be close to the lowest-energy transition at 0.76 eV reported by Pearsall *et al.* The first direct transition at Γ is predicted to lie much higher at around 1.2–1.3 eV.

In the light of these results, two different interpretations of the experimental data have been proposed. Brey and Tejedor⁴ argued that the transition at 0.76 eV is a direct transition at Γ . This leaves a difference of about 0.4 eV between the theoretical and experimental gaps unaccounted for. The majority view^{2,3,5} is that the 0.76-eV transition is indeed indirect. It is argued that the electron-phonon coupling or lattice imperfections (e.g., defects, random displacements of atoms, well-width fluctuations) make this transition probability large. We find this interpretation unsatisfactory. For example, the amplitude of the reflectivity signal reported in Ref. 1 is only an order of magnitude smaller than the first $\Gamma \rightarrow \Gamma$ transition ($V1+C5$) at 2.3 eV. Furthermore, it is well known that electroreflectance spectra are insensitive to phonon-assisted transitions as numerous

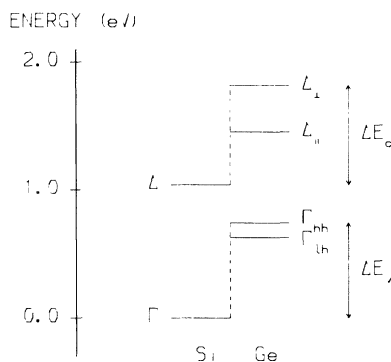


FIG. 1. The valence-band (ΔE_v) and conduction-band (ΔE_c) offsets for the Si-Ge(001) heterojunction structure lattice matched to Si considered in the text. Γ and Δ are the bulk symmetry points at the zone center and along the $\langle 001 \rangle$ axes, respectively. The values corresponding to directions parallel and perpendicular to the interfaces are shown. hh and lh indicate the heavy and light hole, respectively.

studies of bulk semiconductors have demonstrated. As for the role of imperfections, it is true that there is ample evidence about the fluctuation of the layer widths and lattice disorder in ultrathin layers, and in the samples studied in Ref. 1 in particular. However, in order to achieve the required enhancement of this indirect transition probability, a large number of atoms must be displaced over a large distance. Furthermore, if this were to be the dominant effect in the electronic structure, the link between the observed transition energy at 0.76 eV and the superlattice structure could only be described as coincidental. The same applies to transitions at higher energies. The reproducibility of the 0.76-eV peak from sample to sample would also have to be coincidental.

In an effort to provide an alternative explanation of the results of Ref. 1, we performed fresh calculations of the electronic structure and optical properties of the Si-Ge superlattice studied in Refs. 1-5. Our method of calculation is a natural extension of the empirical pseudopotential approach⁷ which has been used to model Si-SiGe strained-layer superlattices grown on an alloy buffer.⁸ We begin by choosing a suitable bulk crystal Hamiltonian H_0 (e.g., an empirical pseudopotential for silicon) such that the band-structure energies $E(n,k)$ and wave functions $\phi(n,k)$ can be generated in good agreement with experiment. Here n,k represent the band index and reduced wave vector, respectively. We then expand the superlattice wave function in terms of the complete set of $\phi(n,k)$. The Schrödinger equation for the superlattice problem is

$$\{H_0 - E + V\} \sum_{n,k} A(n,k) \phi(n,k) = 0, \quad (1)$$

where V is the potential representing the differences between the microscopic potentials of the atoms forming the superlattice layer and those of the starting material corresponding to H_0 . In our previous formulation, the starting Hamiltonian had the cubic symmetry. In the present calculation H_0 has tetragonal symmetry. This enables us to model Si-Ge superlattice grown on a Si substrate. We have also included the spin-orbit coupling to improve the accuracy of our method.

When we fit the Si and Ge pseudopotentials so as to reproduce the bulk band structure along the $\langle 001 \rangle$ direction of perfect bulk Si and tetragonally strained Ge, we obtain the electronic structure of a free-standing superlattice in good agreement with the state-of-the-art quasiparticle calculations. In particular, the lowest transition at Γ reported in Ref. 5 occurs at 1.34 eV and the optical matrix element in atomic units is 0.025. We find 1.2 eV and 0.024 a.u., respectively. (Our ΔE_v , shown in Fig. 1, is 0.75 eV, i.e., smaller than 0.82 and 0.84 eV reported in Refs. 5 and 6, respectively. The ΔE_c used in our calculation is also shown in Fig. 1.) The wave function of the conduction-band state participating in this transition is highly confined in the silicon layer, while the uppermost valence state has a significant amplitude in both Si and

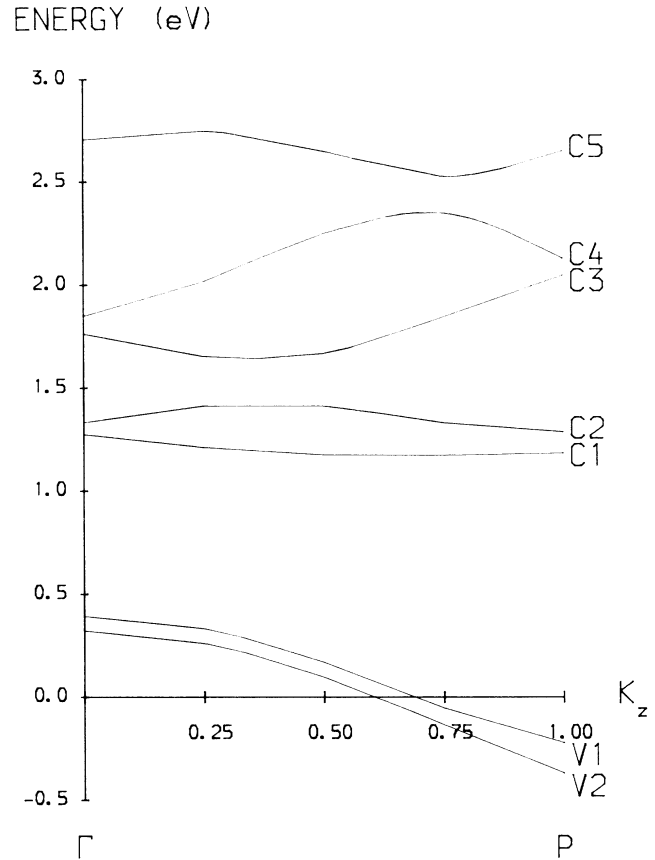


FIG. 2. The band structure of the Si₄Ge₄ superlattice along the $\langle 001 \rangle$ direction in the superlattice Brillouin zone.

Ge layers, in general agreement with all existing calculations reported in the literature.

In the course of this work, we noticed that if the form factors at finite wavelengths representing Ge atoms are chosen to be those required to compute the band structure along the $\langle 001 \rangle$ direction of a bulk cubic Ge, the superlattice band gap at Γ is significantly reduced. This also leads to an increase in the leakage of the conduction-band wave function into the Ge layer. The valence-band wave functions remain largely unchanged. The superlattice band structure near the band edges, obtained in this calculation, along the $\langle 001 \rangle$ direction in the superlattice Brillouin zone, is shown in Fig. 2. The corresponding charge densities generated at Γ are presented in Fig. 3. States V1 and V2 are the uppermost valence-band states. States C1 and C2 are the lowest conduction-band states. These states, which are nearly degenerate at Γ , originate from the degenerate bulk conduction-band minima at the bulk X point. States C3 and C4 are the excited states of bulk Δ character. C5 is the lowest Γ -type state. To facilitate a better comparison between our results and those in the literature, we present a contour plot of these states in Fig. 4.

In Table I we present the oscillator strengths and the

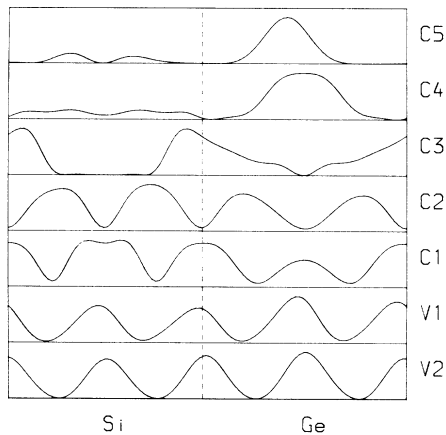


FIG. 3. A plot of the charge densities, generated at the Γ point, along the superlattice axis (z), of the states reported in Fig. 2. The broken line indicates the position of the interface.

transition energies of the lowest three transitions at the Γ point predicted in our calculations, and compare them with those observed by Pearsall *et al.* It is worth pointing out that the ratio of the reflectivity amplitudes for the transitions at 2.3 and 0.76 eV is only about ten times larger than that predicted in our calculation.

The momentum mixing is a familiar feature in thin-strained-layer superlattices. In our method, the origin of the enhancement of what is a forbidden optical transition in bulk Si and Ge can be well understood by inspecting the distribution of the expansion coefficients $A(n, k)$ of (1). In fact, the coupling between the bulk zone-edge and zone-center states in the first conduction band normally associated with the enhancement of optical matrix elements is quite small. The large enhancement of the matrix element takes place because the conduction-band valence states near the band edges are wave packets of quite novel making consisting of a large number of different bulk momentum contributions spread over many higher bands.

In the sense of the level diagram in Fig. 1, the reduction in the band gap at Γ (accompanied by a leakage of the conduction-band wave function into Ge) reported in Figs. 2–4 can be understood simply as a reduction of the effective conduction-band barrier height in the $\langle 001 \rangle$ direction (ΔE_c). As can be seen in Fig. 2, the dispersion relation remains similar to that reported in the literature. The change in the ratio of the oscillator strength of the first allowed transition to that of the lowest one lies within the error of this calculation.

An analogous change in the band structure (i.e., reduction of the superlattice band gap at Γ) is also achieved when the calculation is performed with the coordinates of the Ge atoms altered so as to make the Ge–Ge bond length more bulklike. (The nearest-neighbor distance in strained Ge is only 1.8% smaller than that in cubic Ge.) In this calculation we again assume that the lattice constant in the interface plane is

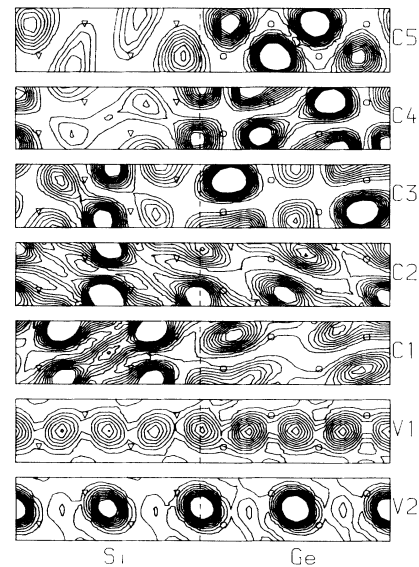


FIG. 4. A contour plot of the charge densities reported above. Ge atoms are at the open circles and Si atoms are at the inverted triangles.

fixed by the Si substrate but increase the Ge–Ge separation along the superlattice axis (z). The Ge–Si separation is reduced so that the total length of the superlattice period is unchanged.

A full-scale quantitative assessment of the equilibrium nuclear configuration of an imperfect five-well structure such as that studied by Pearsall *et al.* lies outside the scope of current computational techniques. In the idealized free-standing (infinite and defect free) Si–Ge superlattice, the lattice constant of Ge along the $\langle 001 \rangle$ axis reported in first-principles calculations⁶ in fact differs by 1% from the value obtained by minimizing the macroscopic elastic energy and used in all existing models. This is also the degree of coordinate change invoked in our model. In particular, we can appreciate the tendency towards bulklike Ge–Ge bond lengths in this structure in a simple intuitive way. It is well known from the work of Van de Walle and Martin⁶ that interfacial features in the microscopic potential are very small and are confined to the two monolayers forming the interface. However, in a defect-free infinite superlattice, the Ge atoms do not fully recover their bulk Ge–Ge bond length. The lattice

TABLE I. The theoretical and experimental transition energies E in electronvolts, from Ref. 1 and the present calculation reported in Figs. 2–4, respectively. F is the oscillator strength obtained in the present calculation.

Transition	E (theory)	E (expt)	F
V1-C1,C2	0.9	0.76 ± 0.14	0.002
V1-C3	1.4	1.25 ± 0.13	0.03
V1-C5	2.3	2.31 ± 0.12	0.3

constant of Ge in the interface plane is fixed by the Si substrate so that the bulk bond length can only be achieved by increasing the Ge-Ge separation along $\langle 001 \rangle$, at the expense of increasing the bond bending angle. In the idealized system, coherent interference effects maintain the strength of the angular (bond bending) forces and the Ge atoms sit (1–2)% away from the bulk equilibrium separation. However, it has been shown^{1,9} that there are defects at Si-Ge interfaces introduced during growth. Breaking some bonds at the interface can only weaken the coherence in the bond network and consequently reduce the angular forces preventing the Ge atoms from acquiring their bulk bond length. Since the displacements in question are of order 1% of the bulk bond length, a small number of interface defects may be sufficient to enable most Ge–Ge bonds to relax.

The Ge–Ge bond is the dominant feature in the superlattice band-structure changes in question. As for the Si–Ge bonds, there are fewer of them, and it has been shown in self-consistent calculations⁶ that a small change in their length does not alter significantly either the band offset or the energy dispersion.

We think that the results presented in this Letter strongly suggest that our model, in which the microscopic potentials representing the Ge–Ge bonds are allowed to be closer to their bulk values, can account for the key features of the observed optical spectra. This is achieved without invoking a major breakdown of the periodic order in this structure (i.e., indirect transitions). Hence our results lend fresh support to the original interpretation offered by Pearsall *et al.* and foster the prospect of

band-structure engineering in Si-Ge microstructures. The deviation from the free-standing superlattice configuration assumed here is small and can be appreciated intuitively in terms of the stability of the covalent bond. The consequences for the electronic structure and optical spectra can also be understood very simply in terms of the lowering of the effective confining barrier shown in Fig. 1.

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