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Valence-band offsets at strained Si/Ge interfaces

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We perform a thorough theoretical analysis of the band-offset problem at strained Si/Ge interfaces. The difference between the two materials is small enough to warrant a linear-response treatment: Owing to this feature, chemical and elastic effects can be studied independently. Our main finding is that the band offset is a bulk property, depending only upon the macroscopic strain present in the two materials far from the interface, and independent of any interface feature, such as abruptness, interface strain, or buckling. In agreement with previous work, our results also indicate that the strain variations affect only weakly the valence-band offset, when it is measured between the *averages* of the split manifolds in the two materials. Starting from these reference levels, simple band-structure effects are responsible for a rather large strain-induced tunability of the offset between the *topmost* valence states.

I. INTRODUCTION

The Si/Ge superlattices are quite interesting systems either from a fundamental point of view or for technological applications.[1] In fact, they are the paradigmatic case of isovalent, nonpolar, lattice-mismatched superlattices and, on the other hand, they may offer the opportunity of direct integration on Si-fabricated devices (optoelectronics) and of band-gap engineering.

In the present paper we report on a thorough investigation of the band-offset problem at Si/Ge heterojunctions. From an experimental viewpoint, Si/Ge superlattices can be grown pseudomorphically without misfits up to a certain critical thickness. In the present theoretical study, we only consider those superlattices which are thick enough to warrant well-separated interfaces; our main issue is then whether the valence-band offset (VBO) can be tuned by means of either chemistry (i.e., altering the abruptness of the interface) or strain. The latter is due to the lattice mismatch between Si and Ge, and can be experimentally varied by choosing the direction of growth and by varying the composition of the substrate, which is usually a $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy.

The rationale for the behavior of the VBO is achieved in this work through a decoupling of the chemical and elastic effects, allowed by linear-response theory (LRT). We explicitly show that both the chemical difference between Si and Ge, and their lattice mismatch, are small enough to be treated by LRT starting from an average virtual crystal. The present theoretical study has been performed using density-functional theory (DFT), within the local-density approximation (LDA). Other calculations[2-5] have been performed—within this same framework— for Si/Ge heterostructures; these calculations, however, were mainly aimed at different issues. Wherever comparable, previous results are discussed in relationship with the present work, and found in good agreement.

In Sec. II we summarize our theoretical framework. In Sec. III we discuss the concept of macroscopic average,[6] generalized for lattice-mismatched heterojunctions. In Sec. IV we isolate the pure effect due to the chemical difference between Si and Ge on the band offset. In Sec. V we discuss the possible relevance of interface-specific features, such as alloying in the interface plane, interface strain, or buckling. In Sec. VI we investigate the dependence of the offset upon bulk strain, and we provide our final results for realistic superlattices. Finally in Sec. VII we draw our main conclusions.

II. THEORETICAL FRAMEWORK

Let us consider the valence-band offset, which is split as usual in two terms:

$$\Delta E_{\mathrm{VBO}} = \Delta E_v + \Delta V \; . \tag{1}$$

Here ΔE_v, which is referred to as the band-structure term, is the difference between the two bands edges, when the single-particle eigenvalues are measured with respect to the (arbitrary) average of the electrostatic potential in each bulk material. In the presence of homogeneous strain (generally nonhydrostatic), the threefold degenerate valence-band edges split: the *relative* deformation potentials governing such splittings are well known[2] and they will not be further considered in this work, unless otherwise explicitly stated. By ΔE_{VBO} we indicate here the offset between the *averages* of the split manifolds on the two sides of the junction. Possible many-body effects on the quasiparticle spectra—which are beyond DFT—as well as spin-orbit effects, may only affect the ΔE_v term in Eq. (1). This term is however characteristic of the two individual bulks, and can be evaluated from two separate (lattice-periodical) calculations for the two materials, although in uniformly strained geometries.

The second term ΔV in Eq. (1) is the lineup of the electrostatic potential generated by the electronic pseudocharge distribution and by the charge of the bare ion cores: it is a macroscopic quantity containing all of the genuine interface effects.[6] This term is evaluated here from either the LRT approach or from supercell calcula-

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tions. In both cases we are not interested in the thin superlattice case (which is studied, e.g., in Ref. 4) and we focus instead on the isolated-interface limit.

Some of the calculations presented in this work are used to extract the basic building blocks which are the main ingredients of LRT, in complete analogy with the work previously performed on different systems.[6] Some other supercell calculations which are needed here are more standard, similar to those performed by different authors for this same system.[2–5]

For a given Si/Ge interface, the potential lineup results from two interwoven physical effects: (i) the chemical difference between Si and Ge; (ii) the macroscopic strain due to the pseudomorphic growth. Using LRT, the two effects can be easily disentangled by studying hypothetical structures where only one of the effects is present: by linearity, the total result is simply the sum of the two separate effects. The effect of chemistry is studied here along the same lines as in our previous work for lattice-matched systems;[6] strain is investigated studying the difference in the "absolute" deformation potentials[7,8] (ADP) of the two materials. Of course, only the combined effect of strain and chemistry is experimentally observable upon varying—for a given growth direction— a single parameter: the concentration of the $Si_{1-x}Ge_x$ alloy used as a substrate, which controls the in-plane lattice constant $a_{\parallel}$ of the pseudomorphic growth. We have also investigated the relevance of interface-specific features—which can possibly be controlled during the growth—such as abruptness, interface (microscopic) strain, or buckling.

In our DFT-LDA calculations we use plane-wave basis sets up to a kinetic energy of 16 Ry and Ceperley-Alder exchange-correlation data.[9] Most of the periodic supercells used in this work contain either 12 or 16 atoms; some study of disorder at the (001) interface required up to 32 atoms per supercell. The **k**-space integration has been performed with the special-point technique; wherever possible, commensurate meshes have been used to deal with supercells of different size and shape. For instance, a supercell of 12 atoms has been dealt with using a mesh obtained by folding of the (666) Monkhorst-Pack cubic mesh[10] for the bulk crystal. We use the norm-conserving pseudopotentials of Ref. 11; with these pseudopotentials the (very-well-converged) values of the equilibrium lattice constants are $a_{\mathrm{Si}} = 10.20$ a.u. and $a_{\mathrm{Ge}} = 10.60$ a.u. Such theoretical bulk lattice constants reproduce the experimental lattice mismatch which amounts to 4%: this allows us to study the effect of the strain induced by the mismatch on a realistic ground.

III. THE MACROSCOPIC AVERAGE

DFT-LDA supercell calculations provide the *microscopic* electronic density and electrostatic potential which are the basic ingredients for obtaining the potential lineup ΔV: however the evaluation of the macroscopic quantity ΔV from these data is not an easy task. A major advance has been achieved by introducing the technique of the *macroscopic average,* proposed a few years ago by some of us,[12] and widely applied since then. This technique allows us to filter our, via a suitable convolution, the uninteresting microscopic periodic oscillations of the original data, and to blow up the very weak macroscopic features we are interested in. The way such a macroscopic average works has been illustrated in detail[6] only for lattice-matched cases. Since qualitative new features are important for lattice-mismatched systems we outline here the basic features of the macroscopic average, generalized for these systems.

Let us consider the specific example of the $(\mathrm{Si})_7/(\mathrm{Ge})_9$ superlattice grown on Si substrate along [001], whose electronic (pseudo)density is shown in Figs. 1(a) and 1(b). In such contour plots, the presence of the two interfaces is barely visible. Because of pseudomorphism, the system is periodic in the (x,y) planes: the first obvious simplification is to consider planar averages as functions of the z coordinate only: $\bar{f}(z)=1/S\int_S f(x,y,z)dx\,dy$. From the three-dimensional electronic density we thus obtain the one-dimensional density $\bar{n}(z)$ shown in Fig. 1(c); the ionic charge—not shown in Fig. 1(c)—has δ-like spikes and contributes as well to electrostatics: the planar average of the *total* charge density is related to the one of the electrostatic potential by a one-dimensional Poisson equation. This feature is conserved when further performing the macroscopic average, defined below.

The electron density, shown in Fig. 1(c), behaves as two different—though closely similar—periodic functions apart from the interfaces, which join smoothly across them; in the periodic bulklike regions, the two linear periods l_1 and l_2 are slightly different. We now just convolute twice, with two different filter functions, in a similar way as for the standard macroscopic average.[6] To be more explicit, we define

$$w_l(z)=\frac{1}{l}\Theta\left[\frac{l}{2}-|z|\right], \tag{2}$$

where Θ is the unit-step function, and we perform the double macroscopic average as

$$\bar{\bar{f}}(z)=\int dz'\int dz''\, w_{l_1}(z-z')w_{l_2}(z'-z'')\bar{f}(z'')\;; \tag{3}$$

convolutions appearing in Eq. (3) are most easily performed in reciprocal space, using Fourier techniques. Starting from the plot of Fig. 1(c), we get the averaged density $\bar{\bar{n}}(z)$ shown in Fig. 1(d): it displays indeed flat plateaus in the bulk Si and Ge regions, demonstrating the effectiveness of this double macroscopic average in washing out periodic oscillations. We also observe that the plateau values are different for the two regions, due to lattice mismatch.

We now come to the contribution of the bare ion cores. In the lattice-matched case, their macroscopically averaged charge simply provides a uniform neutralizing background; in the present case, their averaged density is nonuniform, although constant in each of the bulklike regions. Needless to say, the *total* (electronic plus ionic) charge density averages to zero in the bulklike regions. We first perform the macroscopic average, and then we solve the one-dimensional Poisson equation, taking advantage of the commutativity of the two processes. The

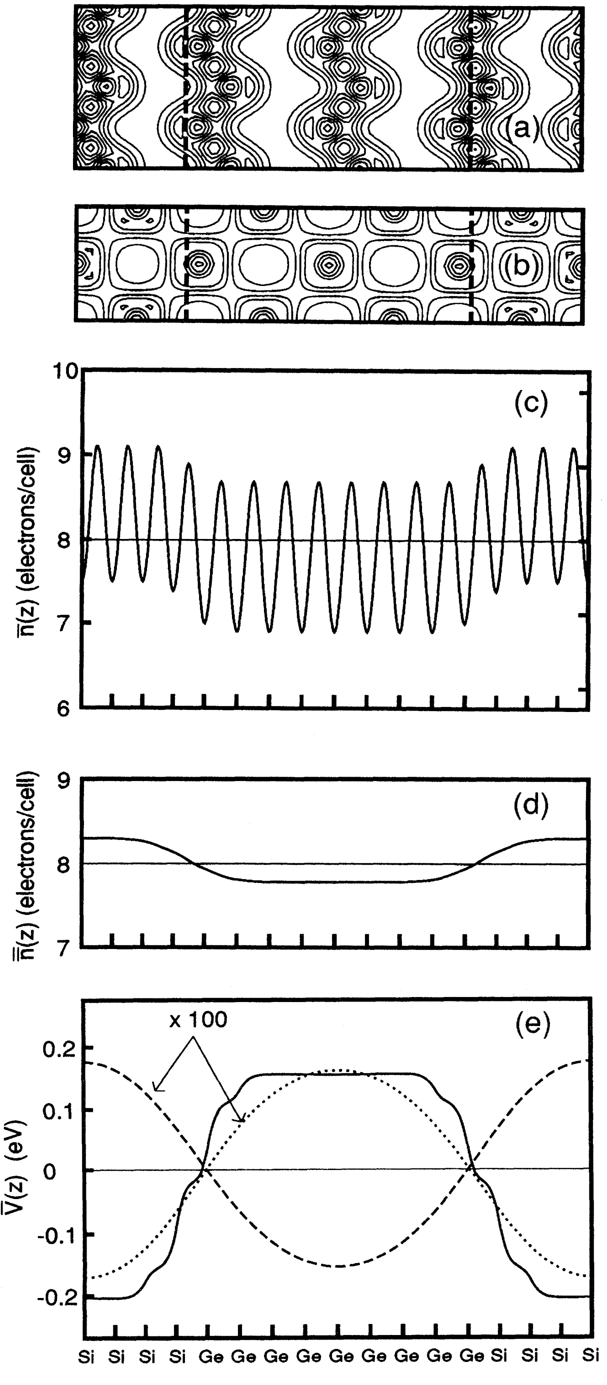

FIG. 1. Results of a calculation for a $(Si)_7/(Ge)_9$ superlattice, grown upon Si along the [001] direction. (a) Contour plot of the electronic density in the $(\bar{1}10)$ plane. Vertical dashed lines indicate the interface positions; the Ge region is at the figure center, and the Si region at the borders. (b) Same as in (a), for the (100) plane. (c) Average of the electronic density over the planes perpendicular to the [001] axis. (d) Macroscopic average performed over the planar average shown in (c). (e) Macroscopic average of the total Coulomb potential (solid line). The two contributions due to the electrons (dashed line) and to the ions (dotted line) are also shown separately, using a scale factor of 100.

result, for the same superlattice considered so far, is shown in Fig. 1(e), where the ionic and electronic terms are shown, together with their sum. The two terms undergo a large cancellation, and a scale factor of 100 has been used in Fig. 1(d) for the purpose of display. The kinks which can be detected in the total electrostatic potential are the vestiges of the δ-like nature of ionic charges, which shows up in this way after macroscopically averaging and integrating Poisson equation. Despite their cumbersome shape, such plots correctly describe macroscopic electrostatic, and are in fact completely flat in the bulk regions.

IV. EFFECT OF CHEMISTRY

In this section we isolate the pure effect due to the chemical difference between Si and Ge on $\Delta E_{\rm VBO}$. Of course in real Si/Ge heterojunctions chemical and strain effects cannot be disentangled; therefore we study *artificial* lattice-matched structures where the lattice constant of both materials has been chosen as the average of the two. Incidentally, this value is very close to the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy lattice constant at $x=0.5$.[13,14]

In order to apply LRT,[6] we define a reference system, which we choose as the *virtual crystal*. Its ionic pseudopotentials v are averages between the Si and Ge ones ($v_{\rm Si}$ and $v_{\rm Ge}$, respectively):

$$V_{\rm virt}(\mathbf{r})=\sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R}) , \tag{4}$$

where $\mathbf{R}$ are the diamond lattice sites and $v=\frac{1}{2}(v_{\rm Si}+v_{\rm Ge})$. The bare perturbation leading from the virtual crystal to the real interface is

$$\Delta V_{\sigma}(\mathbf{r})=\sum_{\mathbf{R}} \Delta v(\mathbf{r}-\mathbf{R})\sigma_{\mathbf{R}} , \tag{5}$$

where $\Delta v=\frac{1}{2}(v_{\rm Si}-v_{\rm Ge})$ and $\sigma_{\mathbf{R}}$ is an Ising-like variable whose value is $+1$ if the $\mathbf{R}$ site is occupied by Si, or -1 if it is occupied by Ge.

The basic building block of LRT is the density response $\Delta n(\mathbf{r})$ to a single isovalent substitution; in practical work, planar substitutions are more convenient. Typical results for the present system, obtained along the same lines as explained in Ref. 6, are reported in Fig. 2. According to the general theory for lattice-matched systems, the charge density of the isolated interface is obtained from the suitable superposition of such building blocks.

The accuracy of the LRT results has been checked against standard self-consistent-field supercell calculations, and found to be $\simeq 0.01$ eV (i.e., of the same order as found,[6,15] e.g., for GaAs/AlAs). In other words, the chemical difference between Si and Ge is small enough to allow the neglect of quadratic response in the valence electron system.

The only new relevant feature for this system is the rather wide spatial extent of the charge induced by a substitutional plane, clearly evident in Fig. 2. This fact has some consequences particularly for the (110) geometry, where a $(Si)_6/(Ge)_6$ superlattice is not thick enough to warrant well-separated interfaces and to recover bulklike character midway between the two interfaces: 16-atom supercells—such as in the middle panel of Fig. 2—are mandatory. This same fact also affects $(\mathrm{Si})_n/(\mathrm{Ge})_m$ superlattices grown along [001]: whenever either n or m are smaller than (say) 6, effects of interaction between interfaces are expected. Such a feature is indeed in qualitative agreement with the findings of Ref. 4, where it is shown that for ultrathin superlattices a sizable interface contribution to the total energy affects structural equilibrium.

The applicability of LRT to lattice-matched Si/Ge interfaces has a very important implication: the chemical term in ΔE_{VBO} arising from the difference between Si and Ge is a bulk effect, independent of the growth direction and of the abruptness of the interface.

V. INTERFACE-SPECIFIC FEATURES

For (001)-oriented heterojunctions, we have directly verified the insensitivity of ΔE_{VBO} to interface-specific features, such as alloying in the interface plane, or allowing the atoms close to the interface plane to relax. Such studies have been performed over a realistic, lattice-mismatched, structure, such as a Si/Ge interface grown at the $a_{\parallel}$ of Si. To this aim, we have repeated the same calculation as used for Fig. 1, but where two Ge planes—nearest neighbors to the interface—are replaced with alloyed planes: the structure is therefore of the kind $(\mathrm{Si})_7/X/(\mathrm{Ge})_7/X$, where we indicate with X the $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ alloy. This calculation has been repeated twice, using two different models for the alloy: one using virtual atoms and one using a more realistic structure where Si and Ge atoms occupy alternate lattice sites in the alloyed planes; the latter calculation requires a 32-atom supercell. In Fig. 3 we show the macroscopically averaged potentials for these two cases: despite the different behavior in the neighborhood of the interfaces, the lineup between the midbulk regions is equal—within our accuracy—in the two cases, and it is also equal to the lineup for the abrupt case, indicated in Fig. 1(e) by a solid line.

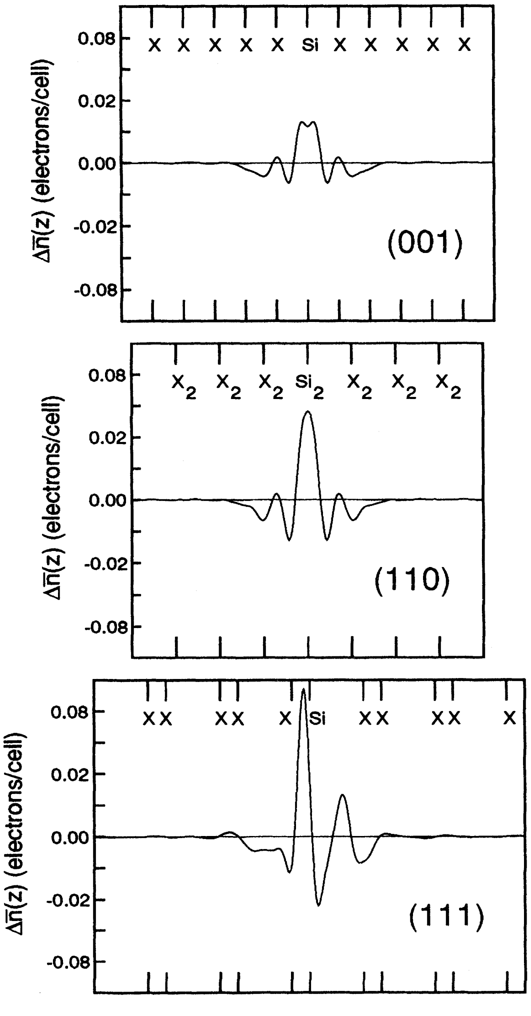

FIG. 2. Density response of a virtual crystal $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ to a single planar substitution, in three different directions. Calculations performed for the artificially lattice-matched case, at the virtual-crystal lattice constant. The supercell contains 12 atoms (for [001] and [111] directions) or 16 atoms (for [110] direction).

We investigate then the issue of whether atomic relaxations close to the interface may significantly affect the band offset: the rigid displacement of a whole atomic plane has been called "interface strain" in the band-offset context.[16,17] We have performed calculations upon structures where atomic planes close to the interface have been artificially displaced: we find that for any reasonable value of the displacement (i.e., for displacements of the same order as the difference between bulk lattice constants of Si and Ge) and for the three orientations (001), (111), and (110), the variation of the electrostatic potential lineup is smaller than our accuracy. The reasons for such behavior are easy to understand. In general the displacement of a whole ionic plane in a crystal induces a dipole which is proportional to the Born effective charge Z^* of the ions in the plane. For instance, the displacement of a plane in the [001] direction by an amount u generates a potential lineup equal to $\Delta V_u = (8\pi e^2 Z^* / a\epsilon_\infty)(u/a)$,[18] where ϵ_∞ is the electronic static dielectric

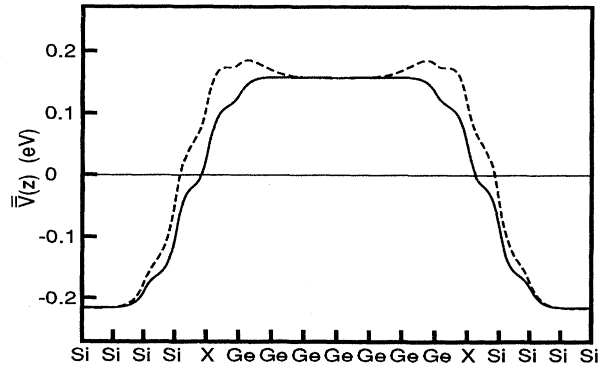

FIG. 3. Macroscopic average of the Coulomb potential for a $(\mathrm{Si})_7/X/(\mathrm{Ge})_7/X$ (001) superlattice, where X indicates planes of Si-Ge alloy. Solid line: the alloy atoms are approximated as virtual atoms. Dashed line: the alloy planes are built of Si and Ge atoms occupying alternate lattice site.

constant. The effective charges of the bulk Si and Ge atoms vanish by symmetry; this is no longer true for atoms at low-symmetry sites close to the interface. However, the actual values of such charges are expected to be fairly small, as it is in fact indicated by our calculations. We also quote that for the artificial SiGe zinc-blende structure the effective charges are found to be of the order of 0.1:[19] this is a very conservative upper bound for our interface Z^*, leading to a contribution to a potential lineup of some hundredths of eV. The possible relevance of interface buckling in affecting ΔE_{VBO} is obviously ruled out on the same ground.

To reformulate these findings in a LRT framework, let us again consider the Si/Ge system as a perturbation on the virtual crystal. Then the interface effective charges Z^* are first order in the perturbation (i.e., in the chemical difference between Si and Ge): any possible interface strain is first order as well. The dipole is therefore a second-order quantity, when expanded in such chemical difference: for this reason, interface strain or buckling come out to affect E_{VBO} in an irrelevant way for this system. Matters are different when considering heterojunctions between polar materials.[16,17]

VI. EFFECT OF BULK STRAIN

Due to the pseudomorphism of the structure, macroscopic strain is in general present in both materials. Given the alloy concentration of the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ substrate, i.e., given the in-plane lattice constants $a_{\parallel}$, we can easily determine the macroscopic lattice constants $a_{\perp}$ in the two materials by means of elasticity theory.[2]

For thin superlattices grown on Si substrate, it has been shown[3] that the lattice constant along the growth axis in the Ge slab is slightly smaller than predicted by elasticity. This feature can be accounted for by the existence of an interface energy term in the expression for the total elastic energy of the superlattice.[4] However, the effect of this contribution decreases upon increasing the number of Ge layers and vanishes in the thick superlattice limit considered here. For a $(\mathrm{Si})_6/(\mathrm{Ge})_6$ (001) superlattice the interface energy term determines a correction for the interplanar Ge distance smaller than 10^{-2} a.u.; i.e., smaller than the accuracy by which we actually determined the equilibrium lattice constants of bulk elements.

The explicit check of macroscopic elasticity theory—within the present theoretical framework—is shown in Fig. 4, where the microscopic relaxations are plotted versus the predictions of elasticity theory, for three different choices of $a_{\parallel}$. Deviations from the elasticity theory appear to be negligibly small; furthermore, the interplanar distance across the interface is very close to the average between the ones of the Si and Ge slabs. The latter finding is not surprising in view of previous theoretical work[13,14] about the bondlengths in Si-Ge alloys. Very recently, accurate measurements of the bond lengths in Si/Ge superlattices have confirmed such features.[20] As a consequence, from now on we assume that the superlattice equilibrium structure is determined by the theory of elasticity in order to obtain our final results for the realistic strained interfaces.

The results of Fig. 4 show that interface strain, i.e., the microscopic relaxation in the interface region, is small in Si/Ge. Furthermore, the results of the previous section indicate that interface strain or buckling does not affect ΔE_{VBO} at Si/Ge interfaces, because of the nonpolarity of both materials. Therefore the offset depends only on the macroscopic strain which is present in the two materials far from the interface and not on any structural details of the interface.

Having assessed the bulk nature of the strain effect on ΔE_{VBO} at Si/Ge heterojunctions, we notice that such effect coincides indeed with the difference between the ADP's of the two materials. Since the nontrivial orientation dependence of the ADP's has been recently demonstrated in a paper by us,[8] a nontrivial dependence of ΔE_{VBO} upon the bulk strain tensors in the two materials is expected as well.

In practice, the quantitative evaluation of the dependence of ΔE_{VBO} upon strain as a difference of the ADP's of elemental Si and Ge is affected at present by severe cancellation errors, which however touch only the potential lineup term in Eq. (1). A further major difficulty is the fact that the theory of the ADP's in its present formulation,[8] is in good shape *only* for the case of variable $a_{\perp}$ at constant $a_{\parallel}$.

In the following, we deal separately with the two terms in Eq. (1). The band-structure term ΔE_v is evaluated essentially as the difference of suitably defined "relative" deformation potentials of the two materials, while the po-

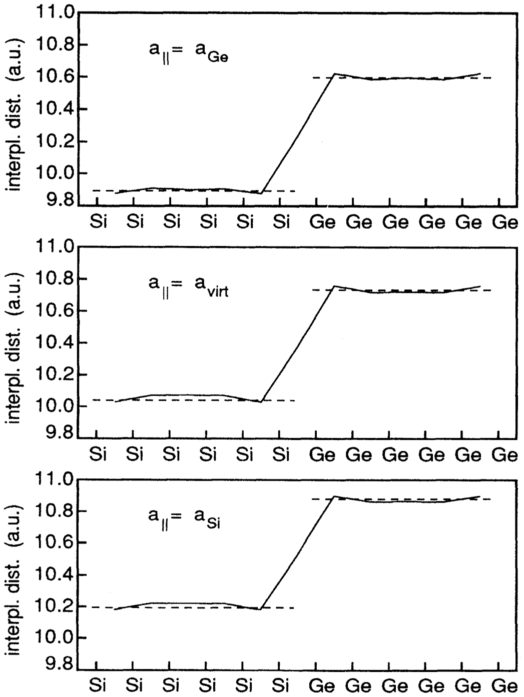

FIG. 4. Interplanar distances for a $(\mathrm{Si})_6/(\mathrm{Ge})_6$ superlattice, normalized as $a_{\perp}$. Solid line: computed from fully relaxed total energy minimization. Dashed line: predictions from macroscopic elasticity theory.

tential lineup term ΔV is directly studied, via the supercell method, for Si/Ge interfaces within selected geometries.

A. The band-structure term

It is trivial to prove that, up to linear order in the macroscopic strain, the variation of ΔE_v can only depend upon the *volume* variations in the two regions, i.e., upon the traces of the macroscopic strain tensors. We recall at this point that we always refer to ΔE_v as the average of the (possibly split) valence-band-edge manifold.

Exploiting the above fact, the term ΔE_v has been evaluated from a series of bulk DFT-LDA self-consistent calculations in the two materials, all of them performed within the diamond structure, at several values of the cubic lattice constant a in the neighborhood of the virtual-crystal value $a_{\text{virt}}=\frac{1}{2}(a_{\text{Si}}+a_{\text{Ge}})=10.40$ a.u. The two functions $E_v^{(i)}(a)$, where $(i)=\text{Si},\text{Ge}$, have been interpolated quadratically:

$$E_v^{(i)}(a)=E_v^{(i)}(a_{\text{virt}})+B^{(i)}(a-a_{\text{virt}})+C^{(i)}(a-a_{\text{virt}})^2 \; ; \quad (6)$$

the relevant parameters are reported in Table I. The deviations from linearity turn out to be fairly small over the physically interesting range $a_{\text{Si}}<a<a_{\text{Ge}}$, being smaller than 0.02 eV.

Given a Si/Ge interface, the bulk strains on the two sides are uniquely defined by the (common) value of $a_{\parallel}$ and by the two values of $a_{\perp}$ in each material. We define an effective cubic lattice constants $\tilde{a}_{\text{Si}}=(a_{\parallel}^2 a_{\perp})^{1/3}$, where $a_{\perp}$ refers to the Si region, and analogously for $\tilde{a}_{\text{Ge}}$. Then the band-structure term is easily obtained from Eq. (6), in the linear approximation, as

$$\begin{aligned}\Delta E_v &= E_v^{\text{Ge}}(\tilde{a}_{\text{Ge}})-E_v^{\text{Si}}(\tilde{a}_{\text{Si}})\\ &\simeq E_v^{\text{Ge}}(a_{\text{virt}})-E_v^{\text{Si}}(a_{\text{virt}})\\ &\quad +B^{\text{Ge}}(\tilde{a}_{\text{Ge}}-a_{\text{virt}})-B^{\text{Si}}(\tilde{a}_{\text{Si}}-a_{\text{virt}}) \; . \quad (7)\end{aligned}$$

B. The potential lineup term

The lineup term ΔV in Eq. (1) is much less trivial; we have directly evaluated it for a series of selected cases, all of them within the (001) geometry.

We begin studying the effect of macroscopic strain on the same artificial, lattice-matched structure introduced above in the context of chemical effects. Starting from the reference structure, where atoms sit at the perfect diamond sites and the lattice constant is the virtual-crystal one, we vary independently the in-plane lattice constant $a_{\parallel}$ and the interplanar one $a_{\perp}$, using however the same values on both sides of the junction. In other words, in this series of calculations the macroscopic strain is the same in the two materials, when measured starting from the *virtual* configurations.

A typical result is shown in Fig. 5, which shows the potential lineups for three values of $a_{\parallel}$ at constant $a_{\perp}$. Very good linearity is found via numerical differentiation throughout the range of interest, i.e., $a_{\perp}$ and $a_{\parallel}$ both contained in the interval $[a_{\text{Si}},a_{\text{Ge}}]$. Numerical differentiation yields

$$\frac{\partial \Delta V}{\partial \epsilon_{zz}}=0.50 \text{ eV}, \quad \frac{\partial \Delta V}{\partial(\epsilon_{xx}+\epsilon_{yy})}=-0.75 \text{ eV} \; . \quad (8)$$

Using now Eq. (7) we get, for this lattice-matched case,

$$\frac{\partial \Delta E_v}{\partial \epsilon_{zz}}=\frac{\partial \Delta E_v}{\partial(\epsilon_{xx}+\epsilon_{yy})}=B^{\text{Ge}}-B^{\text{Si}}=-0.35 \text{ eV} \; . \quad (9)$$

For the longitudinal case we thus get $(\partial \Delta E_{\text{VBO}})/\partial \epsilon_{zz}=0.15$ eV; the smallness of this figure is in agreement with the fact that the *longitudinal* ADP's of Si and Ge have very close values.[8] The transverse value is larger; nonetheless the maximum variation of ΔE_{VBO} for the relevant range of parameters is fairly small, of the order of a few hundredths of an eV, as is also evident from Fig. 5.

Last but not least, we have studied realistic interfaces, where a single parameter (the in-plane lattice constant $a_{\parallel}$) is the only independent variable, the other structural parameters being chosen such as to minimize the total energy. We have already observed above (see Fig. 4) that—in the thick superlattice limit considered in this work—straightforward elasticity theory[2] is adequate for energy minimization: we have thus used such structural information in the present calculations. A typical calculation of this kind has been already presented above in Sec. III (Fig. 1), where we aimed at illustrating the macroscopic average for the lattice-mismatched case.

Starting from double macroscopic averages such as shown in Fig. 1(d), we have calculated the potential lineup for three different values of $a_{\parallel}$, equal to a_{Si}, a_{virt}, and a_{Ge}. We obtain $\Delta V(a_{\text{Si}})=0.37$, $\Delta V(a_{\text{virt}})=0.40$, and $\Delta V(a_{\text{Ge}})=0.43$. These figures demonstrate excellent linearity; when the band structure term is added, after Eq. (7), we get the band offsets 0.47, 0.44, and 0.41, respectively. The offsets between the (averages of) valence-band-edge levels in the two materials can therefore be tuned only by 0.06 eV upon varying the substrate.

VII. CONCLUSIONS

We have performed in this work a thorough study of valence-band offsets at strained Si/Ge interfaces, in the thick superlattice limit.

First, we have studied several artificial structures, in

TABLE I. Relevant parameters for the expansion of Eq. (6).

	$E_v(a_{\text{Si}})$ (eV)	$E_v(a_{\text{virt}})$ (eV)	$E_v(a_{\text{Ge}})$ (eV)	B (eV/a.u.)	C [eV/(a.u.)^2]
Si	6.24	5.65	5.09	−2.875	0.500
Ge	7.06	6.38	5.76	−3.221	0.643

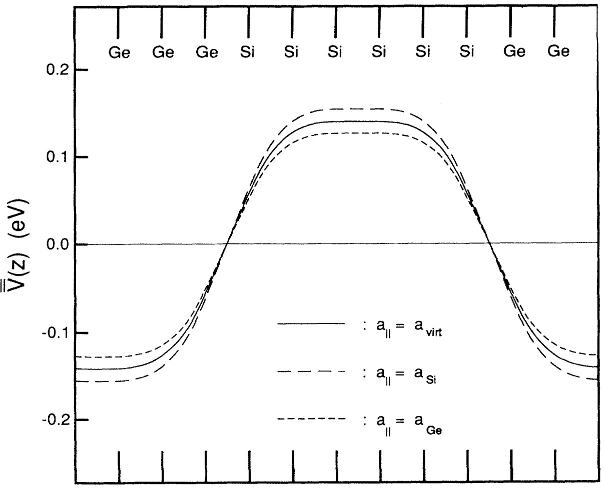

FIG. 5. Variation of the potential lineup for an artificial (001) $(Si)_6/(Ge)_6$ lattice-matched superlattice when different biaxial strains are applied (see text for more details).

order to isolate the different physical effects contributing to ΔE_{VBO}, and in particular allowing its tunability. We have thus demonstrated, for this isovalent heterojunction, that chemical effects are responsible for a term having pure bulk character. The band offset cannot be tuned by varying anyhow the composition in the interfacial region, via, e.g., interdiffusion. Further, interface strain or buckling have been shown to be irrelevant because of the nonpolarity of both materials. Hence, no interface-specific phenomenon allows tunability of ΔE_{VBO} at Si/Ge interfaces.

We have also demonstrated that ΔE_{VBO} can only depend on the macroscopic strain tensors in the two bulk regions, although such linear dependence is far from being trivial. This issue is closely related to the ADP problem, for which we have recently provided an important theorem and some calculations.[8]

Finally, we have performed calculations upon realistic structures grown along the [001] direction, where the strain is controlled via a single parameter: the concentration of the $Si_{1-x}Ge_x$ alloy used as a substrate, governing the pseudomorphic growth. Our main result is recast in Fig. 6, solid line, which displays the band offset between the *averages* of the band-edge states in Si and Ge, as a function of the concentration of the substrate. The plot shows a very weak x dependence of this quantity, which varies by only 0.06 eV over the whole range; a similar behavior was previously found in Ref. 2. We observe that such a feature may be traced back to the very close values of the absolute deformation potentials in the two materials.[8]

At this very final point, we briefly discuss the offset between the *topmost* valence states on the two sides of the junction as a function of x: this is the quantity most directly related to the experiment. We add therefore to the previously shown data the *relative* splittings due uniaxial strain and to spin-orbit effects, evaluated for the two bulk materials separately. The former splittings are straightforwardly calculated in a way consistent with the rest of this work; the latter are taken from experimental data. Our final result for the x dependence of the band offset between the topmost valence states is shown in Fig. 6, dashed line, where the tunability over the whole range is now one order of magnitude larger, i.e., 0.53 eV. This result compares well with the tabulation of Ref. 2, shown in Fig. 6 as a dotted line, which appeared some years ago and is therefore less converged in a supercell size and energy cutoff: despite a small systematic deviation, the trend and the tunability range are the same as found in this work; similar results are also reported in Ref. 5.

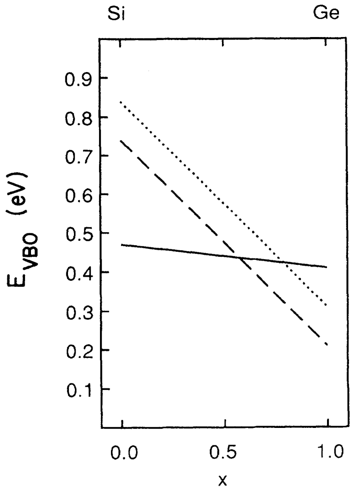

FIG. 6. Dependence of the valence-band offset at a Si/Ge interface upon the concentration of the $Si_{1-x}Ge_x$ alloy used as a substrate. Solid line: offset between the average of the valence-band-edge states, as calculated in this work. Dashed line: offset between the topmost valence-band-edge states; results from the present calculations, with the inclusion of strain splittings and spin-orbit splittings. Dotted line: drawn after Ref. 2.

The conclusion of this work is that the offset between the topmost valence-band states at a strained heterojunction between pure Si and pure Ge can be tuned by some tenths of eV by varying the substrate which governs the pseudomorphic growth, while it cannot be tuned by altering anyhow the conditions at which the interface is formed. Furthermore, most of the effect is purely band structure in nature, i.e., it depends on one-electron features of the two bulk materials separately.

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