Electric fields and valence band offsets at strained [111] heterojunctions

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Abstract

[111] ordered common atom strained layer superlattices (in particular the common anion GaSb/InSb system and the common cation InAs/InSb system) are investigated using the \textit{ab initio} full potential linearized augmented plane wave (FLAPW) method. We have focused our attention on the potential line-up at the two sides of the homopolar isovalent heterojunctions considered, and in particular on its dependence on the strain conditions and on the strain induced electric fields. We propose a procedure to locate the interface plane where the band alignment could be evaluated; furthermore, we suggest that the polarization charges, due to piezoelectric effects, are approximately confined to a narrow region close to the interface and do not affect the potential discontinuity. We find that the interface contribution to the valence band offset is substantially unaffected by strain conditions, whereas the total band line-up is highly tunable, as a function of the strain conditions. Finally,
we compare our results with those obtained for [001] heterojunctions, 73.20.D, 77.84, 73.20.A
I. INTRODUCTION

As is well known, the opportunity of tuning the potential line-up as a function of the strain has a relevant technological importance and thus has been the subject of many recent experimental and theoretical works. However, most of them focused on CuAu-like strained interfaces (i.e. oriented along the [001] direction). In this work we have performed \textit{ab initio} full-potential augmented plane waves (FLAPW)\textsuperscript{7} calculations (within density functional theory\textsuperscript{8}) for GaSb/InSb and InAs/InSb systems, in order to examine the valence band offset (VBO) at strained [111] heterojunctions. To our knowledge, only recently have CuPt-like (i.e. [111] ordered) systems begun to be investigated\textsuperscript{9,10} and the way the charge readjustment occurs at the interface is still far from being clear, mostly due to the non-trivial electrostatics involved.

Although both the [001] and [111] directions are polar (the [110] is non-polar), there are important differences between interfaces oriented along these two crystallographic axes. First of all, the particular geometry for the [111] superlattice leads to two inequivalent interfaces\textsuperscript{11} consider the structure for the (GaSb)\textsubscript{3}/(InSb)\textsubscript{3} superlattice shown in Fig. 1 (note that the common cation case has the same structure, except for the atomic species involved). According to convention, we have placed the interface planes \(\pi_c\) (\(\pi_s\)) at the center (sides) of the interface InSb (GaSb) axial bond (as shown in Fig. 1). Observe that the interface Sb is coordinated with three Ga atoms and one In atom in one interface (\(\pi_c\) in Fig. 1), and with three In atoms and one Ga atom in the other (\(\pi_s\) in Fig. 1). Thus, we could have, in principle, two different valence band offsets and charge accumulations (\(\sigma\)) at the interface planes \(\pi_c\) and \(\pi_s\), namely \(\sigma_c = -\sigma_s\), because of charge neutrality requirements\textsuperscript{11} Incidentally, we note that this is not the case for the [001] ordered systems, where the bond directions and the atomic coordinations result in exactly equivalent interfaces at the center and at the sides of the unit cell.

Furthermore, since the semiconductor constituents (with zincblende structure) are piezoelectric materials\textsuperscript{12,13} a uniaxial strain along the [111] direction leads to a strain induced
piezoelectric polarization $P_s$. Following the notation of Ref. [15], we obtain:

$$|P_s| = P_s = -\sqrt{3} \gamma_{14} \epsilon_4$$  \hspace{1cm} (1)

where $\gamma_{14}$ is the piezoelectric constant and $\epsilon_4$ is the off-diagonal strain tensor element. As a function of the in-plane strain ($\epsilon_\perp = \frac{a_{\text{sub}} - a_{\text{eq}}}{a_{\text{eq}}}$, with $a_{\text{sub}}$ and $a_{\text{eq}}$ denoting the substrate and equilibrium bulk lattice constants, respectively) and within the linear regime, the strain tensor component can be expressed as:

$$\epsilon_4 = -\frac{2c_{11} + 2c_{12}}{c_{11} + 2c_{12} + 4c_{44}} \epsilon_\perp$$  \hspace{1cm} (2)

The piezoelectric effect can generate electric fields so that:

$$P = P_s + \varepsilon_0 \chi E$$  \hspace{1cm} (3)

where $P$ is the dielectric polarization and $\chi$ is the dielectric susceptibility. Note that for strained layer superlattices (SLs) with [001] growth axis, the strain tensor is diagonal, so that $P_s$ vanishes.

In this paper, we discuss results obtained for common–cation and common–anion strained layer superlattices grown along the [111] direction and discuss the effects of the strain induced polarization on the properties of the superlattices. In Sect. II we give some calculational details; in Sect. III and IV we briefly review the electrostatics involved; in Sect. V we discuss how charge redistributes at the interface and how the VBO can be evaluated. Finally, in Sect. VI we summarize our conclusions.

II. STRUCTURAL AND TECHNICAL DETAILS

We have studied the SL systems (GaSb)$_3$/(InSb)$_3$ and (InAs)$_3$/(InSb)$_3$ with unit cells containing 12 atoms (as shown in Fig. [1]). For this we have considered an AC/BC type heterojunction (the case of the common anion AB/CB type heterojunction is exactly equivalent) grown on different substrates: (i) on a bulk AC semiconductor (i.e. $a_{\text{sub}} = a_{\text{AC}}$; where
$a_{AC}$ denotes the AC semiconductor equilibrium lattice constant); (ii) on a bulk BC semiconductor \((i.e. \ a_{sub} = a_{BC})\); (iii) on a substrate having an average lattice parameter \((i.e. \ a_{sub} = \frac{1}{2}(a_{AC} + a_{BC}))\). The structural parameters for the different systems considered were determined according to the macroscopic theory of elasticity (MTE) and are equal to those for the ultrathin 1x1 [111] ordered SLs of Ref. 17. With this choice, we are not considering any internal strain\(^{18}\) which would produce different bond lengths\(^{19}\) for bonds parallel to the [111] and the other directions.\(^{20}\) Of course, we expect that variations in the bond lengths may greatly affect the magnitude of the electric fields; very large deviations may even cause a sign change. However, all this will not change the basic electrostatics involved and, as we will show, the physical quantities we are interested in, such as the VBO.

We performed all-electron full-potential linearized augmented plane wave (FLAPW) calculations within the local density approximation (LDA)\(^{8}\) to density functional theory with the exchange and correlation potentials as parametrized by Hedin and Lundqvist.\(^{21}\) Technical details (such as wave function cutoff, special k-points mesh etc.) are equal to those used in a previous study and reported elsewhere.\(^{5,17}\) In order to check the convergence of the valence band offset as a function of the cell dimension, we also performed calculations for \((\text{GaSb})_4/(\text{InSb})_4\) and \((\text{InAs})_4/(\text{InSb})_4\) SLs grown on the same substrates.

### III. STRAIN INDUCED ELECTRIC FIELDS

Since they are important quantities for determining valence band offsets, we report in Fig. 2 (Fig. 3) the common atom Sb (In) core level binding energies $E_{CL}^b$ for the GaSb/InSb (InAs/InSb) [111] ordered SLs grown on an average substrate. In the upper part of Fig. 3 (a), we also report the core level binding energies for 3x3 [001] ordered InAs/InSb grown on an average substrate.

First of all, we point out that while in the 4x4 structures the $E_{CL}^b$ are perfectly aligned on a straight line in the bulk region, the same behaviour is not so obvious to extrapolate in the 3x3 structures, due to the smaller bulk region. However, in what follows, we will assume
the linear behaviour also for these structures and verify the validity of this assumption afterwards, when comparing the VBOs obtained.

From Figs. 2 and 3, we observe that the structures considered show electric fields with opposite signs at the two sides of the interface. The slopes of the linear trends of Figs. 2 and 3 give a rough estimate of the absolute values of the electric fields (\( |E| = E = \frac{\Delta E_{CL}}{\Delta z} \)). Our calculations give about 3x10^7 V/m (12x10^7 V/m) in both the GaSb (InAs) and InSb sides of the common anion (cation) heterojunction, with an error bar \( \simeq 2x10^7 \) V/m. Note that this large error bar is due to the very small variations (in particular for the common anion case) of \( E_{CL} \) in the bulk region, which are of the same order of magnitude of our numerical uncertainty upon the core level binding energies themselves.

Furthermore, we observe that the plot of the core level binding energies for [001] strained layer SLs leads to a constant trend (implying a constant value of \( E_{CL} \)), as the \( z \) coordinate (perpendicular to the interface) is varied within each semiconductor bulk region; this confirms the absence of electric fields in the [001] ordered structures.

**IV. PIEZOELECTRICITY AND POLARIZATION CHARGES**

As already pointed out, \( [111] \) ordered strained SLs show electric fields, due to piezoelectricity. Thus, elementary electrostatics of dielectric media leads to the following relation between the macroscopic quantities in each semiconductor constituent \( (i) \):

\[
D^{(i)} = \varepsilon_0 E^{(i)} + P^{(i)} = \varepsilon_0 E^{(i)} + \varepsilon_0 \chi^{(i)} E^{(i)} + P_s^{(i)}
\]  

(4)

Due to symmetry properties, the transverse (i.e. parallel to the interface) component of the piezoelectric polarization vector vanishes; thus, in the following, we will only consider the longitudinal (i.e. perpendicular to the interface) component of the electrostatic quantities involved.

The net charge accumulation at an ideal abrupt interface is related to the macroscopic polarizations in the two semiconductor constituents, through the following relation.
\[
\sigma = - (P^{(2)} - P^{(1)}) \cdot \hat{n} \tag{5}
\]

Since the perpendicular component \(D_n\) is continuous across the interface, Eq. (4) gives:

\[
\varepsilon_0 E^{(1)} + P^{(1)} = \varepsilon_0 E^{(2)} + P^{(2)} \tag{6}
\]

so that Eq. (5) can be rewritten as:

\[
\sigma = +\varepsilon_0 (E^{(2)} - E^{(1)}) \cdot \hat{n} \tag{7}
\]

In addition, from Eq. (4) and using Eq. (3), we obtain an equivalent expression for \(\sigma\):

\[
\sigma = [ +\varepsilon_0 (\chi^{(2)} E^{(2)} - \chi^{(1)} E^{(1)}) + P_s^{(2)} - P_s^{(1)} ] \cdot \hat{n} \tag{8}
\]

Note that, in the case of growth on a substrate equal to one of the constituent materials, only one side of the interface is strained and gives rise to a non-vanishing strain polarization \(P_s\). On the other hand, in the case of growth on an average substrate, \(P_s\) is non-zero and will have opposite signs in the two different materials. In fact, the piezoelectric constants \(e^{13}\) have the same sign for all the materials involved, while the two constituents are in biaxial tension and compression, respectively, leading to in-plane strains \(\varepsilon_{\perp}^{(1)}\) and \(\varepsilon_{\perp}^{(2)}\), with opposite signs.

In order to test the validity of the above description, we have performed the double macroscopic average \((\overline{\rho}^T)_{\Box}\) of the self consistent total (electrons + ions) charge density \((\rho^T = \rho^e + \rho^i)\) for some of the cases considered. We have estimated the net interface charge accumulation from the following relation:

\[
\sigma_{SCF} = \int_{b_1}^{b_2} \overline{\rho}^T(z) dz \tag{9}
\]

where the integration is performed between the two bulk regions (referring to Fig. 4 for the 3x3 case, between \(b_1\) and \(b_2\)).

We must point out that the use of the symbol \(\sigma\) for the charge accumulation does not necessarily imply that this charge must have a surface-like distribution. In fact, the electrostatics used so far, holds for any volume distributed charge density. However, as will
be discussed later, the charge distribution at the interface can be reasonably approximated as a planar charge.

Using Eq. (9) and Eq. (7), we can check the consistency of our results. In the (GaSb)_{4}/(InSb)_{4} SL grown on an average substrate, for example, we obtain $\sigma_{SCF} \approx 2 \times 10^{-4} \text{ C/m}^2$ from Eq. (9). Using Eq. (7) and the electric fields as evaluated by the core level binding energies ($E^{(1)} \approx 2.6 \times 10^7 \text{ V/m}$ in the GaSb side of the heterojunction and $E^{(2)} \approx 3.3 \times 10^7 \text{ V/m}$ in the InSb side of the heterojunction), we find $\sigma \approx 5 \times 10^{-4} \text{ C/m}^2$. The agreement between this value and $\sigma_{SCF}$ is within our numerical accuracy, which is estimated to be $1.8 \cdot 10^{-4} \text{ C/m}^2$ (considering the error bar on the electric fields) and shows the consistency of our calculations.

However, if one tries to estimate $P^{(1)}_s$ and $P^{(2)}_s$ from Eq. (1) and then substitutes the results in Eq. (8), a value for $\sigma \approx 49 \times 10^{-4} \text{ C/m}^2$ ($\sigma \approx 18 \times 10^{-4} \text{ C/m}^2$) is found, using the available calculated (experimental, elastic, dielectric and piezoelectric constants for each material. These values seem to be at variance with the integrated value $\sigma_{SCF}$. The disagreement can be attributed to the use of bulk lattice constants for a region whose thickness is as small as a few monolayers and to the fact that the theoretical and experimental constants used in Eq. (8) are not consistent with the present calculation, since the MTE structures considered do not properly take into account internal strain effects. Let us remark that the inconsistency between these values of $\sigma$ and the one obtained ab-initio will not affect the evaluation of the VBO, as will be shown (see discussion below).

Furthermore, from the steeper slopes in Fig. 3 with respect to those in Fig. 2, we observe that the magnitudes of the electric fields in the common cation systems are stronger than those in the common anion ones. Since Eq. (7) leads to a net charge accumulation proportional to the discontinuity of the electric fields, it is reasonable to expect a systematically smaller charge, $\sigma$, in the GaSb/InSb than in the InAs/InSb systems, as confirmed by our self-consistent results obtained from Eq. (3).
V. VALENCE BAND OFFSET

We recall that the potential line-up can be estimated following the procedure used in XPS experiments and widely adopted in all-electron calculations, which takes core level binding energies as reference levels. According to this method, the VBO is obtained as follows:

\[
\Delta E_v = \Delta b + \Delta E_b
\]

(10)

Here \(\Delta b\) is an “interface” term (which denotes the core level energy difference between atoms in the two bulk regions, \(i.e.\) those denoted by “b1” and “b2” in Fig. [1]) and \(\Delta E_b\) is the so called “bulk” term and indicates the binding energy difference - with respect to the topmost valence level - between the same core levels in each semiconductor strained as in the heterojunction. This last term takes into account the effects of strain on the electronic band structure of each bulk material.

We must now note that the evaluation of the \(\Delta b\) term is usually done assuming that the bulk regions of the SL are thick enough so that the atoms taken as reference can be, by all means, considered as “bulk” atoms. This procedure implicitly requires that the \(\Delta b\) term must be evaluated in the limit of infinite distances from the interface, where the reference atoms are no longer influenced by the charge rearrangement at the interface.

It is now obvious that this same procedure cannot be used for the [111] oriented heterojunctions. The presence of electric fields, in fact, makes the \(\Delta b\) term vary with the distance from the interface, so that its evaluation in the limit of “bulk region” \(i.e.\) infinitely far away from the interface) would result in an ill-defined \(\Delta b\). Let us observe, by the way, that the same conceptual problem is present for procedures that use the electrostatic potential, rather than core levels, as reference energies for the evaluation of the VBO. This problem has been usually overcome by extrapolating graphically the linear behaviour of the potential (or the core level binding energy) in the two bulk regions to an “interface plane”, \(\pi\), arbitrarily taken half-way along the interface bond, and evaluating the difference between their intercepts.
In the following, we illustrate a more rigorous procedure which will also be able to give
a reasonable estimate of the related error bar.

A. Interface charge and evaluation of the VBO

Let us first discuss how the charge is modified at the interface. We can split up this
charge distribution as the sum of two different effects: (i) a charge accumulation \( \sigma \), due
to the piezoelectric effect combined with the boundary conditions, which is basically a
monopole-like distribution and (ii) a charge depletion and accumulation at the two sides
of the heterojunction, which is the usual dipole charge of the interface and is due to the
different chemical nature and electronegativity of the constituents. The charge profile can
thus be schematically represented as a symmetric monopole centered on some ideal interface
plane \( \pi \) plus a dipole which is anti-symmetric with respect to \( \pi \).

According to this scheme and following basic electrostatic arguments, we can now say
that the monopole charge \( \sigma \) leads to a continuous potential across the interface plane. The
limits for \( z \to \infty \) and \( z \to -\infty \) of this potential must be the same, since the monopole
contribution is symmetric with respect to the plane \( \pi \). On the other hand, the dipole-like
charge leads, in these same limits, to a potential discontinuity. Thus, we expect that the
valence band offset (i.e. the potential discontinuity at the interface) is only determined by
the usual dipole term and is not affected by the presence of the strain induced electric fields.

Note that the real total charge density macroscopic average profile \( (\overline{\rho}^T) \) usually has a
very complex shape, often changing its sign. Therefore, it is not possible to clearly establish
where \( \pi \) really is. However, as a rough approximation, we can calculate the center of gravity
of the positive \( (\overline{\rho}^T_+ (z)) \) and negative \( (\overline{\rho}^T_- (z)) \) charges:

\[
\bar{z}_+ = \frac{\int z \overline{\rho}^T_+ (z) dz}{\int \overline{\rho}^T_+ (z) dz} \quad (11)
\]

\[
\bar{z}_- = \frac{\int z \overline{\rho}^T_- (z) dz}{\int \overline{\rho}^T_- (z) dz} \quad (12)
\]
where \( \overline{\rho}^T(z) = \overline{\rho}^T_+(z) + \overline{\rho}^T_-(z) \) and the integrals are performed between the two bulk regions \( b_1 \) and \( b_2 \) as in Fig. 1. (9). We may now assume that the interface region is confined between the two extremes \( z^+ \) and \( z^- \). We are now able to calculate the \( \Delta b \) term appearing in Eq. (10) and therefore the VBO.

A reasonable estimate for the \( \Delta b \) term could then be obtained from the intercepts at \( z^+ \) and \( z^- \) of the two straight lines which interpolate the core level energies. The difference of these two values can be taken as the error bar. We find, for the systems considered, that the values of \( z^+ \) and \( z^- \) are, as expected, not symmetric with respect to the half-bond position (which is, in any case, within the \( (z^+, z^-) \) interval), due to two different effects: (i) the strain, which modifies the bond lengths at the interface and (ii) the distribution and sign of the monopole term \( \sigma \). In all the cases considered, \( z^+ \) and \( z^- \) differ by as much as 2 a.u., which is to be compared with bond lengths along the \( z \) direction that are usually of the order of 5 a.u.. This estimate of the charge centers of gravity confines, with some precision, the “interface” to a quite localized region, which is even smaller than a bond length. Within this error, we may also say that the interface charge has a surface-like distribution. The numerical uncertainty on the \( \Delta b \) term can thus be related to the extrapolation procedure on the two extremes of the interface region, \( z^+ \) and \( z^- \), leading to a numerical uncertainty of about 0.03 eV.

We may now recall, as already pointed out, that in a [111] ordered SL, we have two inequivalent interfaces with, in principle, different \( \Delta b \)’s. For each of the structures examined, we find that the \( \Delta b \) values obtained following this procedure at the two inequivalent interfaces differ by as much as 0.02 eV, so that we can consider, as a first approximation, \( \Delta b_c = \Delta b_s \).

Furthermore, we also obtained equal \( \Delta b \) values for the 3x3 and 4x4 SLs (within 0.02 eV), thus confirming the validity of the extrapolation procedure; this also suggests that bulk conditions between the two interfaces are recovered even in the smaller unit cell and that good convergence for the \( \Delta b \) term is reached, as a function of the cell dimensions. Note that
the value (0.17 eV) obtained in Ref. 5 for InAs/Insb [111] grown on an average substrate is in good agreement with the one derived from Fig. 3 (a) (0.19 eV). The small discrepancy (about 0.02 eV) is due to the electric fields which modify the core level binding energies and which were not taken properly into account in Ref. 5.

As a last comment, we would like to come back to the structural choices considered. In order to ascertain the dependence of the VBO on the internal strain (not considered within MTE), we calculated the VBO for superlattices having the experimental internal strain displacement: we found a change in the band line-up of less than 0.02 eV (which is well within our numerical accuracy).

**B. Results and discussion**

In Table I we report our results for the interface contribution $\Delta b$, the bulk contribution $\Delta E_b$ and the resulting band offset value $\Delta E_v$. The superscripts ($nr$) and ($r$) indicate a semirelativistic and fully relativistic (i.e. spin-orbit coupling included with a perturbative approach) treatment of the valence levels, respectively. The final results for $\Delta E_v^{fin}$ include a correction for quasi-particle effects that were omitted in our self-consistent calculations. Thus, starting from the results of Ref. 27, we can include self-energy corrections (considered uninfluenced by different strain conditions) to the DFT-LDA energy levels by adding the quantities $\Delta QP(GaSb/InSb) = -0.03$ eV and $\Delta QP(InAs/InSb) = +0.08$ eV to our calculated values.

In order to examine the effects of the ordering direction on these quantities of interest, we plot our Table I results in Figs. 4 and 5 for GaSb/InSb and InAs/InSb interfaces, respectively, and also report the calculated values for [001] systems with equal pseudomorphic growth conditions. An inspection of Fig. 4 (a) and Fig. 5 (a) shows that, as a function of the substrate lattice parameter, the $\Delta b$ term is almost constant in the GaSb/InSb [111] systems (as in all the [001] structures - see the dashed lines), whereas in the InAs/InSb [111] systems the range in which $\Delta b$ varies is slightly larger (about 0.06 eV). This indicates
that the charge rearrangement at the interface is quite unaffected by strain conditions, while it is much more influenced by the growth direction. In fact, we point out that the $\Delta b$ absolute value is systematically higher (by as much as 0.15 eV) in the [111] structures than in those oriented along the [001] axis; furthermore, we observe that the trend relative to the small variations of the $\Delta b$ term as a function of the substrate lattice parameter seems to be opposite in the two different orientations of the heterojunctions; in particular, as the substrate lattice constant is increased, the $\Delta b$ increases (decreases) in the [111] ([001]) case. However, the variations of the $\Delta b$ term are of the same magnitude as the error bar and it is therefore impossible to define a clear $\Delta b$ trend as a function of strain conditions.

Let us now discuss the $\Delta E_b$ contribution to the band line-up. As previously noticed in Ref. 5, the MTE predicts different bond lengths (by as much as 2 %) perpendicular to the interface plane, whether we consider the [001] or the [111] ordered heterojunctions. This structural difference is probably responsible for the different $\Delta E_b$ term in SLs grown on the same substrate (and therefore with the same in-plane strain conditions) but having different crystallographic orientation, [001] or [111] (see Fig. 4 (b) and Fig. 5 (b)).

Finally, we compare the valence band offsets for the CuAu and CuPt-like heterojunctions. The perfectly decreasing trend of the VBO as $a_{sub}$ is increased, already evidenced for the [001] heterojunctions, is still valid for those oriented along the [111] axis (see Fig. 4 (c) and Fig. 5 (c)). Furthermore, we observe that the opportunity of tuning the band offset as a function of the strain conditions is greater in [111] than in [001] heterojunctions; in fact the range in which $\Delta E_v$ varies in going from the smallest to the largest $a_s$ is about 0.8 eV for GaSb/InSb and 0.9 eV InAs/InSb [111] interfaces.

VI. CONCLUSIONS

We have presented results obtained from FLAPW calculations performed for [111] interfaces, in particular for GaSb/InSb and InAs/InSb heterojunctions. In order to examine the effects of the strain induced electric fields on the charge redistribution (and hence on the
potential profile) near the heterojunction, we have proposed a simple scheme to locate the interface region. To a first approximation, we find that piezoelectric effects lead to a planar distribution of polarization charges, which doesn’t affect the potential discontinuity. We have followed an extrapolation procedure to obtain the interface contribution to the VBO which is found to be almost independent of the strain conditions, but is strongly affected by the ordering direction. The total potential discontinuity is found to vary by as much as 0.8 eV for the GaSb/InSb and 0.9 eV for the InAs/InSb [111] interfaces, thus confirming strain as an additional degree of freedom to obtain “ad hoc” band offsets.

VII. ACKNOWLEDGEMENTS

We thank S. Massidda, R. Resta and B.W. Wessels for stimulating discussions and/or a careful reading of the manuscript. Work at Northwestern University supported by the MRL Program of the National Science Foundation, at the Materials Research Center of Northwestern University, under Award No. DMR-9120521, and by a grant of computer time at the NSF supported Pittsburgh Supercomputing Center. Partial support by a supercomputing grant at Cineca (Bologna, Italy) through the Consiglio Nazionale delle Ricerche (CNR) is also acknowledged.
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From FLAPW total energy and atomic force calculations of full atomic relaxations in some of the strained binary systems, we found relaxed bond lengths differing among themselves at most by 0.6 % and with only a 0.4 % disagreement with the MTE predictions. This is probably due to the great sensitivity of the internal strain parameter $\zeta$ on the lattice constant (see for example Refs. 13,18).

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TABLE I. Interface term ($\Delta b$), strained bulk term ($\Delta E_b$) and valence band offset ($\Delta E_v$) for (GaSb)$_3$/(InSb)$_3$ and (InAs)$_3$/(InSb)$_3$ [111] superlattices as a function of the substrate lattice parameter neglecting ($\Delta E_b^{(nr)}$ and $\Delta E_v^{(nr)}$) and including ($\Delta E_b^{(r)}$ and $\Delta E_v^{(r)}$) spin-orbit effects). $\Delta E_v^{(fin)}$ is the final result ($\Delta E_v^{(r)} + \Delta QP$), to be compared with experimental values (to the best of our knowledge, not available at present). Energy differences are considered positive if the level relative to the InSb layer is higher in energy with respect to the GaSb (InAs) layer in the common-anion (common-cation) system.

| System               | $\Delta b$ | $\Delta E_b^{(nr)}$ | $\Delta E_b^{(r)}$ | $\Delta E_v^{(nr)}$ | $\Delta E_v^{(r)}$ | $\Delta E_v^{(fin)}$ |
|----------------------|------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| (GaSb)$_3$/(InSb)$_3$| +0.28      | +0.26               | +0.28               | +0.54               | +0.56               | +0.53               |
| GaSb-subs.           | +0.29      | -0.25               | -0.13               | +0.04               | +0.16               | 0.13                |
| InSb-subs.           | +0.30      | -0.70               | -0.54               | -0.40               | -0.24               | -0.27               |
| (InAs)$_3$/(InSb)$_3$| +0.16      | +0.85               | +0.99               | +1.01               | +1.15               | +1.23               |
| InAs-subs.           | +0.19      | +0.30               | +0.51               | +0.49               | +0.70               | +0.78               |
| InSb-subs.           | +0.22      | -0.20               | +0.01               | +0.02               | +0.23               | +0.31               |
FIGURES

FIG. 1. Structure for the [111] GaSb/InSb 3x3 superlattice. The atoms denoted by “b1”, “b2” and “i” indicate the atoms in the two bulk and interface regions, respectively. The dotted lines $\pi_c$ and $\pi_s$ denote the conventional positions of the interface planes at the center and at the sides of the unit cell, respectively.

FIG. 2. Sb 1s core levels binding energies ($E_{b_{CL}}^b$) (empty circles) in the (a) 3x3 and (b) 4x4 GaSb/InSb systems (grown on an average substrate) as a function of the $z$ coordinate perpendicular to the interface. The energy scale is referred to an arbitrary zero. The dashed lines indicate the linear interpolation of the bulk core levels energies; their intercepts with the conventional interface planes (full diamonds) define the interface contribution ($\Delta b$) to the VBO.

FIG. 3. In 1s core levels binding energies ($E_{b_{CL}}^b$) in the (a) 3x3 and (b) 4x4 InAs/InSb systems (grown on an average substrate) as a function of the $z$ coordinate for [111] (empty circles) and [001] (empty squares) ordered SLs. Labels and energy scale as in Fig. 2.

FIG. 4. Interface contribution $\Delta b$ (panel (a)), bulk contribution ($\Delta E_{b_{r}}^b$) (panel (b)) and total valence band offset ($\Delta E_{v}^{(r)}$) (panel (c)) for GaSb/InSb interfaces as a function of the substrate lattice constant. Filled (empty) symbols and solid (dashed) lines refer to [111] ([001]) ordered heterojunctions.

FIG. 5. Interface contribution ($\Delta b$) (panel (a)), bulk contribution ($\Delta E_{b_{r}}^b$) (panel (b)) and total valence band offset ($\Delta E_{v}^{(r)}$) (panel (c)) for InAs/InSb interfaces as a function of the substrate lattice constant. Filled (empty) symbols and solid (dashed) lines refer to [111] ([001]) ordered heterojunctions.
GaSb/InSb 3x3

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FIG. 2

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GaSb/InSb 3x3 (average substrate)

GaSb/InSb 4x4 (average substrate)
InAs/InSb $3\times 3$ (average substrate)

InAs/InSb $4\times 4$ (average substrate)

$E_b^\text{CL}(\text{eV})$ vs. $z$ (a.u.)

(a)

(b)

FIG. 3
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FIG. 4
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FIG. 5
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