InAs/GaSb(001) valence-band offset: Independence of interface composition and strain

Barbara Montanari[a)]
Istituto Nazionale di Fisica della Materia (INFM), and Scuola Internazionale Superiore di Studi Avanzati (SISSA), via Beirut 2/4, I-34014 Trieste, Italy

Maria Peressi[b)]
INFM-Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

Stefano Baroni[c)]
INFM-Scuola Internazionale Superiore di Studi Avanzati (SISSA), via Beirut 2/4, I-34014 Trieste, Italy, and Centre Européen de Calcul Atomique et Moléculaire (CECAM), ENSL, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France

Elisa Molinari[d)]
INFM-Dipartimento di Fisica, Università di Modena, via Campi 213/A, I-41100 Modena, Italy

(Received 8 July 1996; accepted for publication 7 September 1996)

The InAs/GaSb(001) valence-band offset is calculated for the two inequivalent GaAs-like and InSb-like interfaces and found to coincide to within ≈ 30 meV. This result is rationalized and generalized to arbitrary composition profiles and induced strain by using a simple model, based on the linear response theory, which is validated by a number of accurate first-principles calculations for intermixed interfaces. © *1996 American Institute of Physics.* [S0003-6951(96)02147-X]

An accurate determination of the valence-band offset (VBO) at InAs/GaSb(001) heterojunctions[1] is very important for understanding their optical and transport properties, also in view of possible applications to devices such as infrared detectors and lasers[2] and tunnel structures[3]. Such a determination is complicated by the fact that—even for ideally abrupt interfaces—two different terminations (InSb-like or GaAs-like) are possible.

Very recently, the improved quality and characterization of the samples has allowed detailed investigations of the dependence of the VBO on interface composition[4–6]. The experimental data consistently indicate that the VBO is similar for the two interfaces: the measured values for Δ VBO$=$ VBO(InSb)$-$ VBO(GaAs) are 0.014 ± 0.005eV[4], 0.00 ± 0.02 eV[5], and ≈ 0.03 eV[6]. Conversely, a clear dependence on the growth order has been reported by Wang *et al.*[5] who found the average core level separation $\Delta E_{\mathrm{CL}}=E_{\mathrm{CL}}^{\mathrm{InAs}}-E_{\mathrm{CL}}^{\mathrm{GaSb}}$ to be 90 meV larger for InAs grown on GaSb than for the opposite growth order.

The existing theoretical investigations, on the other hand, lead to contrasting results for Δ VBO, ranging from small values [0.031 eV (Ref. 7) and 0.044 eV (Ref. 8)] up to 0.15 eV[9]. Moreover, even the results which agree with the experimentally found weak dependence of the VBO upon termination are not supported by any rationale.

This letter readdresses this problem from a theoretical point of view by combining very accurate first-principles calculations performed for a number of interface configurations (both ideally abrupt and atomically intermixed) with an analysis of these results in terms of the linear response theory (LRT) of the VBO[10].

Given the similarity between the bulk lattice parameters, a_0, of InAs and GaSb (which are calculated to be 11.35 a.u. within 0.1%, in accord with experimental findings), the two materials in the heterojunction are macroscopically unstrained. Nevertheless, the strong difference between the InSb and GaAs bond lengths ($\approx 14\%$) can induce an interfacial strain whose amount depends on the composition profile at the interface and, hence, on termination and atomic interdiffusion.

We employ self-consistent field (SCF) density-functional theory, within the local-density approximation, and use norm-conserving pseudopotentials with plane-wave (PW) basis sets. The technical ingredients of our calculations (such as the size of PW basis sets and special-point sets for Brillouin-zone sampling) have been carefully checked and estimated to yield a numerical accuracy better than 20 meV in the *differences* of VBOs calculated for different interfacial configurations. The isolated interfaces are simulated by periodically repeated supercells. In all cases, interfacial strain is accounted for by accurately optimizing the supercell energy with respect to atomic positions, while keeping the same supercell c/a ratio as in the ideal zinc-blende structure. This is correct provided the composition profiles at the two interfaces are complementary, so that the resulting interfacial strains compensate.

Interface morphology can only affect the value of the VBO through its influence on the potential lineup, ΔV, defined as the drop of the average electrostatic potential (ionic plus electronic) across the interface[10]. In Fig. 1 we display the macroscopic average[10] of the electrostatic potential throughout a 16-atom supercell containing a GaAs- and an InSb-like interface. The small nonvanishing macroscopic electric field in the InAs and GaSb bulk regions indicates that the potential lineups at the two interfaces are only

[a)]On leave from: Dipartimento di Fisica, Università di Modena, via Campi 213/A, I-41100 Modena, Italy. Present address: Institut für Festkörperforschung, Forschungzentrum Jülich, D-52425 Jülich, Germany; Electronic mail: bmontana@iff312.iff.kfa-juelich.de
[b)]Electronic mail: peressi@trieste.infn.it
[c)]Electronic mail: baroni@sissa.it
[d)]Electronic mail: molinari@unimo.it

 0003-6951/96/69(21)/3218/3/$10.00 © 1996 American Institute of Physics

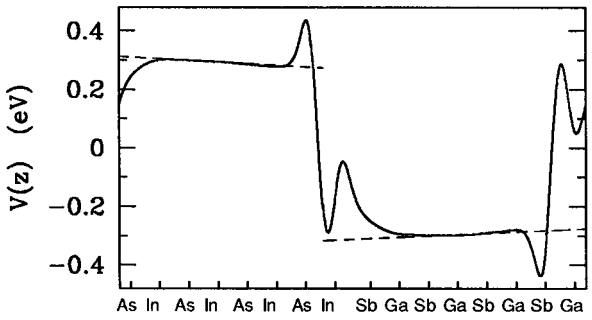

FIG. 1. Macroscopic average (Ref. 10) of the electrostatic potential (in eV) at the InAs/GaSb(001) heterostructure, with two inequivalent GaAs- and InSb-like abrupt interfaces. Dashed lines are a guide to eye which evidence the nonvanishing electric field due to the slightly different lineups at the two interfaces.

slightly different and coincide within 30 meV. By adding the potential lineup resulting from Fig. 1 to the band-structure contribution to the VBO[10], we obtain $\mathrm{VBO} \approx 0.54 \pm 0.01_5$ eV (GaSb higher), for both interfaces, in good agreement with the experimental data[1,4–6].

To understand the small dependence of the VBO on interface composition and strain, we identify two independent contributions to the VBO, i.e., a *structural* and a *chemical* one[10]. In the spirit of the LRT approach to the problem of heterojunctions[10,11], the interface is considered as a small disturbance with respect to a reference periodic system (the virtual crystal, VC), and its effects treated by self-consistent perturbation theory. In a pseudopotential scheme, the virtual ions are described by pseudopotentials which are the average of the corresponding real-ion potentials. At equilibrium, the VC is in the undistorted zinc-blende structure. The real interface is recovered from the VC in two steps: in the first, *chemical* step the virtual-ion potentials are transformed into the real ones, while keeping the atomic positions fixed at the ideal sites; in the second, *structural* step the ions are allowed to relax off their ideal positions, as a consequence of the nonvanishing forces acting on them because of the chemical substitutions. In a linear-response regime the chemical and structural contributions to the VBO are simply additive: $\mathrm{VBO} = \mathrm{VBO}_{\mathrm{chem}} + \Delta V_{\mathrm{str}}$, where this notation stresses that the VBO can only depend on structural effects through the potential lineup contribution.

The LRT approach predicts that for isovalent, lattice matched, unstrained, heterojunctions, the VBO is independent on interface details such as orientation, composition and abruptness[10]. By definition, this result also holds in the present case for $\mathrm{VBO}_{\mathrm{chem}}$. Test SCF calculations done for the two abrupt and two selected mixed unrelaxed interfaces (with one mixed anionic and one mixed cationic plane, respectively) fully confirm the LRT predictions, giving $\mathrm{VBO}_{\mathrm{chem}} = 0.38$ eV in all cases.

Remarkably, the SCF calculations performed for the fully relaxed abrupt interfaces indicate that $\Delta \mathrm{V}_{\mathrm{str}} \approx 0.16 \pm 0.01_5$ eV, almost independent of composition, although the In–Sb (Ga–As) interface interplanar distance d is elongated (contracted) by about 14% with respect to the unrelaxed value $d_0 = a_0/4$. This result can be understood by a simple generalization of the arguments which occur in the unstrained case[10]. Within LRT, the effect of interfacial strain is naturally accounted for in terms of the ionic Born effective charges[12]. The displacement of a single ionic plane along (001) in an otherwise perfectly periodic VC determines a net potential drop $\Delta V_{\mathrm{str}} = 4\pi e^2 Z_T^*(d - d_0)/(a_0^2 \epsilon_\infty)$, where Z_T^* is the *transverse effective charge*[13] and ϵ_∞ the dielectric constant. Our calculated values of Z_T^* for bulk InAs, GaSb, and for the VC, are 0.20, 0.11, and 0.16, respectively. The first two values are in good agreement with the experimental data[14], while the latter—which is the one to be used in the above formula—confirms the adequacy of the LRT in the present case. The value of the ΔV_{str} found in SCF calculations for the two inequivalent abrupt interfaces is in excellent agreement with the prediction of the above linear formula.

This reasoning can be easily extended to predict the dependence of the VBO upon composition/strain for arbitrary composition profiles. This is achieved in two steps. In the first, the interfacial strain is obtained from the corresponding composition profile along the lines previously used for Si/Ge heterostructures[11]. To linear order in the *chemical* perturbation, the force acting on each atomic plane perpendicular to the growth direction z is the sum of the *Kanzaki* planar forces[15], $F(z - z')$, due to the chemical perturbations, plus the longitudinal harmonic forces due to the displacement off equilibrium of all the planes, which are related to the VC dynamical matrix $\Phi(z - z')$. The equilibrium interplanar spacings are determined by the requirement that the force acting on each plane vanishes. SCF calculations indicate that in the present case both the interplanar force constants and the Kanzaki forces are rapidly decaying with distance and already negligible beyond nearest-neighbor planes. In this hypothesis, the distance d between two adjacent cationic, $\mathrm{In}_x\mathrm{Ga}_{1-x}$, and anionic, $\mathrm{As}_y\mathrm{Sb}_{1-y}$, planes is simply: $d(x,y) = d_0 + (x - y)\Delta d$, where $\Delta d = 2F(1)/\Phi(1)$, and the argument of the Kanzaki force and of the interplanar force constant indicate that they refer to nearest-neighbor planes. We find that: $F(1) = 0.023$ a.u. and $\Phi(1) = 0.10$ a.u. A detailed general derivation of this method is presented elsewhere[16].

In the second step we obtain the strain contribution to the VBO by a simple generalization of the formula previously used for inequivalent abrupt interfaces. For the sake of clarity we consider an interface with one mixed plane only, so that the composition profile is $\cdots$–In–As–$\mathrm{In}_x\mathrm{Ga}_{1-x}$–Sb–Ga–$\cdots$, or $\cdots$–Sb–Ga–$\mathrm{Sb}_x\mathrm{As}_{1-x}$–In–As–$\cdots$, and the corresponding interplanar distances are: $\cdots - d_1 - d_2(x) - d_3(x) - d_4 - \cdots$, where–within the above nearest-neighbor linear model–$d_1 = d_4 = d_0$, $d_2(x) = d_0 + (x - 1)\Delta d$, and $d_3(x) = d_0 + x\Delta d$. From the previous effective-charge formula, the effect on the electrostatic potential lineup is $\Delta V_{\mathrm{str}} = 4\pi e^2 Z_T^*[d_3(x) - d_2(x)]/(a_0^2 \epsilon_\infty)$. The difference $d_3(x) - d_2(x) = \Delta d$ is independent of x and, consequently, ΔV_{str} is independent on interface composition. By linearity, this results holds *for any composition profile*. Similar results were previously found for the InP/$\mathrm{Ga}_{0.5}\mathrm{In}_{0.5}$As heterojunction[12,17], but, to our knowledge, no consistent rationale for this behavior has been given since.

The adequacy of this picture is demonstrated in Fig. 2 which displays the dependence of various interplanar dis-

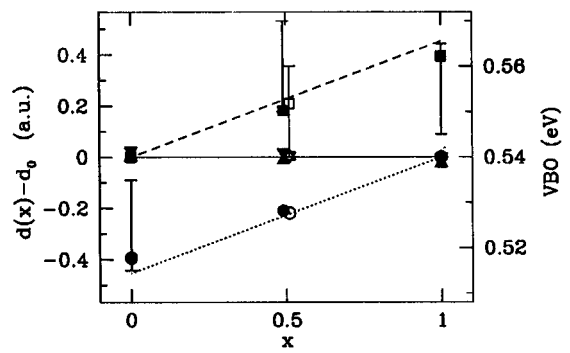

FIG. 2. Dependence of various interatomic distances upon the composition of an interfacial plane at InAs/GaSb(001). Symbols refer to SCF results (open and closed for a mixed anionic and cationic plane, respectively, slightly displaced with respect to one another at $x=0.5$ to enhance the readability of the figure). Circles and the dotted line refer to d_2, squares and the dashed line to d_3, up and down triangles up and solid line to d_4 and d_1, respectively, where d_i are the interplanar distances as indicated. The vertical bars indicate the resulting VBO (right scale) with the estimated numerical accuracy. The right (left) bar at $x=0.5$ corresponds to an anionic (cationic) mixed plane.

tances upon composition of the (cationic or anionic) interface plane, along with the resulting VBO. The dependence of the VBO upon interface composition is comparable with the difference of the VBOs in the two extreme abrupt cases, which we estimate to be ≈ 30 meV, slightly larger than the accuracy of our calculations (≈ 20 meV). We conclude that this difference reflects a physical effect which is due to small quadratic corrections to our LRT, whose sign and order of magnitude are in agreement with experimental findings[4–6] and with the theoretical works of Refs. 7,8.

A final comment is in order about the observed dependence of the VBO on the growth order[5], which was attributed to the extended nature of InAs-on-GaSb interface. According to our theory, neither the composition nor the extension of the interface can modify the interface dipole more than the estimated 30 meV. Nevertheless, if the atomic interdiffusion extends so far from the interface that the nominal bulk composition of the epilayer is never reached in the real sample, the observed interface dipole would correspond to the one between the substrate and an alloy of composition different from the nominally pure epilayer. This could indeed occur in the measurements reported in Ref. 5 for InAs-on-GaSb. In this case in fact—at variance with the GaSb-on-InAs case—a significant anion intermixing is expected, especially due to Sb riding up from the substrate. Sb incorporation can occur all over the epilayer [only $\approx$20 Å thick, while the riding up of Sb was observed through InAs layers up 1500 Å (Ref. 18)]. We therefore suggest that the measured core level separation ΔE_{CL} corresponds to a GaSb/$\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ interface rather than to the pure GaSb/InAs one, where x is the average concentration of Sb in the overlayer. Note that if $x\neq 0$, the observed variation of the separation between core levels would no longer correspond to the variation of the VBO since the position of the valence-band edge in $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ with respect to the average electrostatic potential would depend on x because of alloying effects. The variation of the core-level separation can instead be directly related to the corresponding variation of the potential lineup which—according to the above consideration—is only one of the contributions to the VBO. We estimate that—based on the observed difference between the InAs-on-GaSb and GaSb-on-InAs VBOs of 90 meV and on the assumption that the nominally pure epilayer is attained in the latter case—the average Sb concentration of the epilayer in the former case can be as large as $x\approx 0.35$.

Two authors (M.P. and S.B.) acknowledge the Italian Consiglio Nazionale delle Ricerche for partial support on ''Progetto Coordinato Calcolo Parallelo in Materia Condensata.''

[1] E. T. Yu, J. O. McCaldin, and T. C. McGill, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, Boston, 1992), Vol. 46, p. 53, and references therein.
[2] R. H. Miles, D. H. Chow, J. N. Schulman, and T. C. McGill, Appl. Phys. Lett. **57**, 801 (1990); H. Lee, P. K. York, R. J. Menna, R. U. Martinelli, D. Z. Garbuzov, S. Y. Narayan, and J. C. Connolly, Appl. Phys. Lett. **66**, 1942 (1995); H. K. Choi and G. W. Turner, Appl. Phys. Lett. **67**, 332 (1995).
[3] D. A. Collins, E. T. Yu, Y. Rajakarunanayake, J. R. Söderström, D. Z.-Y. Ting, D. H. Chow and T. C. McGill, Appl. Phys. Lett. **57**, 683 (1990).
[4] J. R. Meyer, C. A. Hoffman, B.V. Shanabrook, B. R. Bennet, R. J. Wagner, J. R. Waterman, and E. R. Youngdale, *Proceedings of the 22nd International Conference on the Physics of Semiconductors*, edited by D. J. Lockwood (World Scientific, Singapore, 1994), p. 783.
[5] M. W. Wang, D. A. Collins, T. C. McGill, R. W. Grant, and R. M. Feenstra, Appl. Phys. Lett. **66**, 2981 (1995).
[6] M. S. Daly, D. M. Symons, M. Lakrimi, R. Nicholas, N. J. Mason, and P. J. Walker, Semicond. Sci. Technol. **11**, 823 (1996).
[7] Y. Foulon and C. Priester, Phys. Rev. B **45**, 6259 (1992).
[8] R. G. Dandrea, C. B. Duke, and A. Zunger, J. Vac. Sci. Technol. B **10**, 1744 (1992).
[9] L. A. Hemstreet, C. Y. Fong, and J. S. Nelson, J. Vac. Sci. Technol. B **11**, 1693 (1992).
[10] S. Baroni, M. Peressi, R. Resta, and A. Baldereschi, *Proceedings of the 21st International Conference on the Physics of Semiconductors*, edited by P. Jiang and H. -Z. Zheng (World Scientific, Singapore, 1992), p. 689.
[11] M. Peressi and S. Baroni, Phys. Rev. B **49**, 7490 (1994).
[12] M. Peressi, S. Baroni, A. Baldereschi, and R. Resta, Phys. Rev. B **41**, 12106 (1990).
[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
[14] *Numerical Data and Functional Relationships in Science and Technology*, Group III, Vol. 17 a-b, edited by Landolt–Börnstein (Springer, New York, 1982).
[15] J. W. Flocken and J. R. Hardy, Phys. Rev. B **1**, 2447 (1970).
[16] M. Peressi, B. Montanari, S. Baroni, and E. Molinari, *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, edited by M. Scheffler and R. Zimmerman (World Scientific, Singapore, 1996), p. 943.
[17] M. S. Hybertsen, Phys. Rev. Lett. **64**, 555 (1990); J. Vac. Sci. Technol. B **8**, 773 (1990).
[18] M. W. Wang, D. A. Collins, T. C. McGill, R. W. Grant, and R. M. Feenstra, J. Vac. Sci. Technol. B **13**, 1689 (1995).