Evolution of the band-gap and band-edge energies of the lattice-matched Ga In As Sb/Ga Sb and Ga In As Sb/In As alloys as a function of composition

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Evolution of the band-gap and band-edge energies of the lattice-matched GaInAsSb/GaSb and GaInAsSb/InAs alloys as a function of composition

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Using atomistic pseudopotential calculations we predict the evolution of the valence-band maximum energy E , and conduction-band minimum energy E , for a compositionally graded quaternary Ga$_{13}$ In As Sb$_{13}$ alloy lattice matched to GaSb or InAs as a function of , or, equivalently, as a function of distance from the substrate. We find upward-concave bowing for both E and E, in contradiction with simple interpolative models. A transition from staggered type II to broken-gap type III lineup relative to GaSb is predicted to occur at =0.81 and =0.92 on a GaSb substrate, and at =0.59 and =0.62 on an InAs substrate. In the latter case, the quaternary alloy has a minimum gap at =0.85 and =0.87. © *2005 A I P .*

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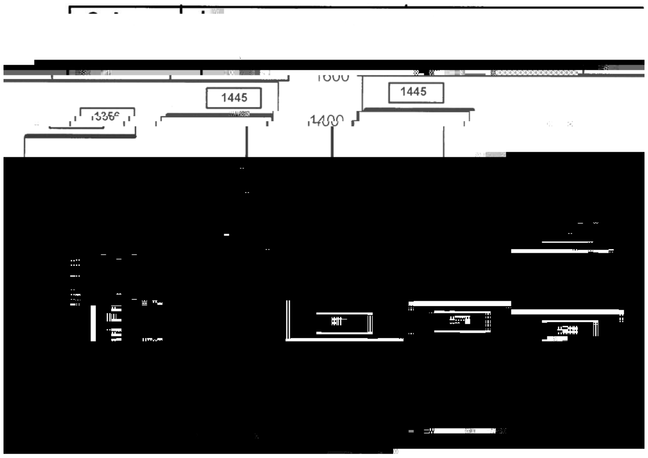
I. INTRODUCTION

The materials belonging to the 6.1 lattice-constant family of semiconductors InAs, GaSb, and AlSb are becoming increasingly important for a large variety of applications, ranging from transistors both bipolar and field-effect transistors FETs , to infrared detectors, photomixers, resonant tunnel diodes, and superlattices for quantum cascade lasers and other applications.[1] All these heterostructure devices involve at least two of the three semiconductors of the family. The two dominant properties in such heterointerfaces are the fact that: i GaAs, InAs, InSb, and GaSb have an unusual set of band alignments[2,3] Fig. 1 spanning type-I straddling arrangement in GaAs/InAs, GaSb/InSb, and GaSb/GaAs, as well as type-III broken-gap arrangement in InAs/InSb and InAs/GaSb; and ii by simultaneously adjusting the alloy composition , in a particular fashion = , it is possible to maintain a fixed lattice constant , for the entire Ga$_{13}$ In As Sb$_{13}$ composition range. For example, one can select a function = so that , ≡ $_{\mathrm{GaSb}}$, thus the alloy can be grown lattice matched on a GaSb substrate. This can be accomplished by starting with GaSb, then adding both a fraction of In and a fraction of As in a graded fashion e.g., 1% composition change per monolayer , reaching eventually the ternary InAs$_{0.89}$Sb$_{0.11}$ which is lattice matched to GaSb. Given i and ii above, it is interesting to inquire how would the alloy band gap E , and the valence as well as the conduction-band edges E , and E , depend on the composition , under lattice-matched conditions. To investigate the behavior of band lineups under compositional grading is important: for example, high-speed bipolar transistors increasingly employ designs in which the energy gap in the base regions decreases from emitter to collector to speed up the flow of minority carriers. In fact, the technology of transistors based on Si/Ge alloys[4] , yielding the fastest Si-based transistors is entirely based on this principle. But the amount of grading is limited by the severe 4% lattice mismatch between Si and Ge. In a GaSb-to-InAs graded base, strain can be avoided using the quaternary system, and much larger energy-gap gradients could be employed. In order to design such a device, however, it is essential to know how exactly the energy gap varies along the



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gradient. It is also important to determine what will be the nature of the bowing (upwards or downwards) of the conduction-band minimum (CBM) and the valence-band maximum (VBM) and at which composition (x, y) would the system $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ matched to GaSb or InAs revert from type II (staggered) to type III (broken gap). Would the band gap of the quaternary have a minimum at some intermediate (x, y)? It is of fundamental importance to answer these questions since quaternary alloys at different compositions provide the device engineer with a larger flexibility in the tuning of device characteristics such as band gaps and band offsets between the components. Unfortunately, while most of the band-structure parameters of binary and ternary III-V systems are known,[5] no analogously detailed informations about the quaternary system can be found in the literature.

The paper is organized as follows. In Sec. II we use [illegible] elasticity, to determine the lattice-matching condition $x = F(y)$ of the quaternary alloy $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ with the substrate, GaSb or InAs, and compare the results with the usually employed approximations based on Vegard's Law. In Sec. III we present our atomistic empirical pseudopotential method (EPM) used to solve the band structure of the narrow gap quaternary $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ random alloy. In Sec. IV we show our results for the valence- and conduction-band edges E_v and E_c as a function of the alloy composition $(x, y) = (F(y), y)$ for $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ grown both on GaSb and InAs, and compare the results with the interpolative models widely used by the device engineers' community.[5] In Sec. V we determine the fraction x of In and y of As (via $x = F(y)$), in the quaternary alloys grown on GaSb or InAs at which the transition from a staggered to a broken-gap lineup with the substrate takes place. Finally, in Sec. VI we compare our theoretical predictions for band alignments and band gaps with the available experimental data present in the literature.

II. FINDING VARIOUS SUBSTRATE-MATCHING $X=F(Y)$ CONDITIONS

Here we contrast Vegard-like approximations[6] with atomistic strain minimizing predictions.[7]

A. Vegard's law

The simplest Vegard-like approximation for a quaternary is

$$a(x,y) = xy\,a_{\mathrm{InAs}} + (1-x)y\,a_{\mathrm{GaAs}} + x(1-y)\,a_{\mathrm{InSb}} + (1-x)(1-y)\,a_{\mathrm{GaSb}}. \quad (1)$$

The condition $a(x,y) \equiv a_s$, with $a_s = a_{\mathrm{GaSb}}$ or with $a_s = a_{\mathrm{InAs}}$ leads to the function $x = F_{\mathrm{Vegard}}(y)$ for which $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ is lattice-matched to GaSb. Other approximations include the linear $y=0.89x$ rule obtained by considering the quaternary alloy $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}_y\mathrm{Sb}_{1-y}$ as the solid solution[5] of GaSb and the lattice-matched ternary $\mathrm{InAs}_{0.89}\mathrm{Sb}_{0.11}$ alloy, that is $(\mathrm{GaSb})_{1-x}(\mathrm{InAs}$

InSb+GaAs is the correct description since In Sb plus Ga As bonds are the majority.

To decide what atomic arrangement is thermodynamically the more appropriate one for Ga_{13} In As Sb_{13}, one can proceed as in Ref. 9 and minimize the energy functional,

$$\begin{aligned} E_{\text{tot}} \quad , \quad \mathbf{R}, = 1,\ldots,N \quad &= E_{\text{chem}} \quad , \\ &\quad \mathbf{R}, = 1,\ldots,N \quad + E_{\text{strain}} \quad , \\ &\quad \mathbf{R}, = 1,\ldots,N \quad , \end{aligned} \tag{3}$$

where indicates that E_{tot}, E_{chem}, and E_{strain} are functionals of the atomic configurations obtained by differently arranging the cations Ga, In and the anions As, Sb on the N sites of a zinc-blende lattice. In Eq. 3

$$E_{\text{chem}} = \frac{1}{2} \quad {}_{=1} \; E \quad {}_{3} \; , \tag{4}$$

where ${}_{3}$ is the number of bonds of type 3, and E is the to be adjusted in order to minimize the elastic energy. This leads to a strong dependence of the calculated bond lengths, bond angles, and a is at the minimum elastic energy on the initial distribution of atoms within the 512 unit cell. In the case of the ternary alloy one has to adjust only two kind of bonds In As and In Sb and the three different kind of bond angles, thus the final minimum energy configuration is less sensitive to the initial choice of the atomic positions.

To each fixed In fraction , there corresponds a small range □ of possible As compositions for which the quaternary alloy is lattice matched to its substrate. By averaging over a number of different atomic configurations we calculate the quaternary alloy lattice parameter , which satisfies the matching condition with the substrate. The lattice parameter , obtained using the atomistic calculations turns out to be different from the Vegard-like behavior given by Eq. 1 . This is true even in the simpler case of ternary alloys, as seen in Fig. 4 which compares the lattice constant of the ternary InAs Sb$_{13}$ alloy given by Vergard's law dashed line with that obtained by the atomistic calculation averaged over a large number of different atomic configurations, full dots . The lattice parameter predicted by the atomistic elasticity departs from the linear Vegard trend mostly around composition $=0.5$, where the In As and In Sb

, it does not have the band-gap error problem,[17] thus the band gaps are in good agreement with the experimental values. , because of the small cutoff needed in $v\;\mathbf{G}$ the method is much faster computationally, and thus can treat systems with hundreds and thousands of atoms per unit cell. This is essential for the description of random alloys where the configurational and atomic disorder effects are relevant. Such effects are often neglected by the virtual crystal approximation VCA currently employed together with self-consistent DFT-LDA calculations.[18]

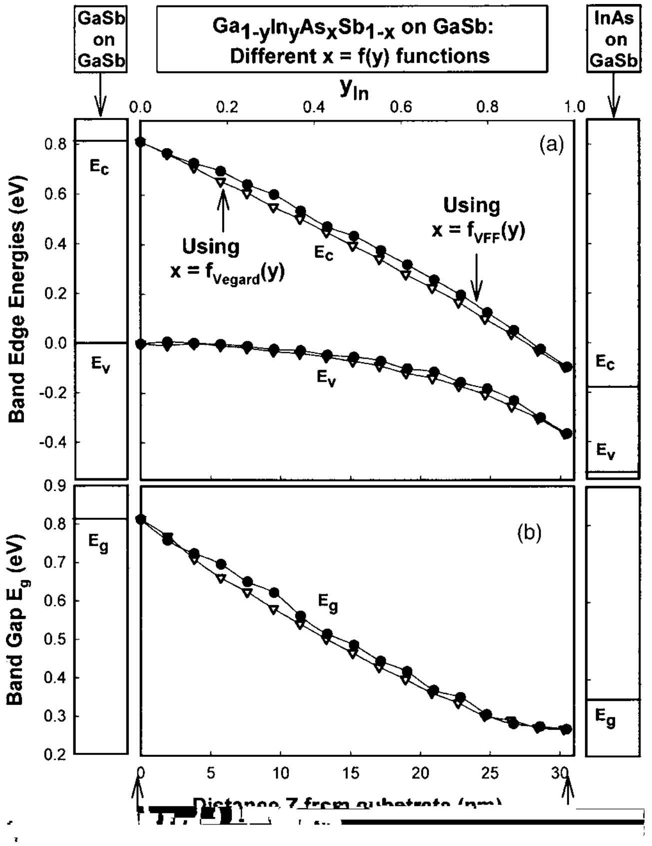

FIG. 6. Comparison of: a the valence- and conduction-band edges and b band gaps of the quaternary Ga$_{13}$ In As Sb$_{13}$ /GaSb alloy calculated using the Vegard-like lattice-matching functions = $_{\mathrm{Vegard}}$ downward empty triangles with the = $_{\mathrm{VFF}}$ extracted by the atomistic VFF calculations full circles .

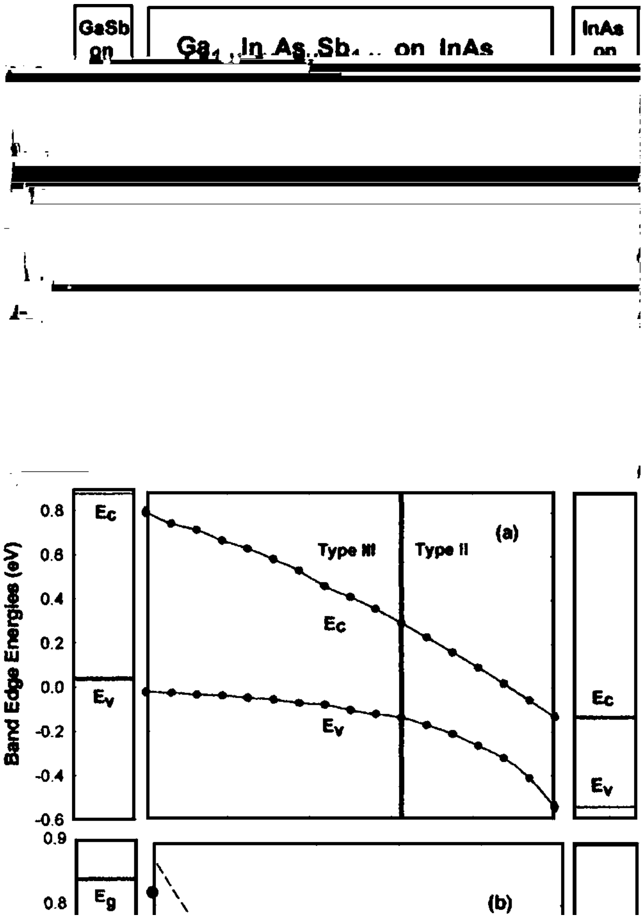

FIG. 7. a

device application, the free passage of electrons from the InAs conduction band to the GaSb valence band could be either desirable Ohmic contacts between and or it could be a nuisance. The strong positive bowing of the valence-band edge found in this work see Figs. 5 7 shows that grading should be avoided at all cost if interband transport is desirable, but would be very beneficial to the opposite objective.

To understand the unexpected negative bowings of the conduction-band edges in Figs. 5 and 7 we first note that they are displayed with respect to the standard[5] linear interpolation of band edges of GaSb and InAs$_{0.89}$Sb$_{0.11}$ for the GaSb substrate, Fig. 5 , and InAs and GaAs$_{0.08}$Sb$_{0.92}$ for the InAs substrate, Fig. 7 . These reference materials have almost exclusively Ga Sb and In As bonds with a very small percentage of In Sb bonds for the GaSb substrate or Ga As bonds for the InAs substrate . This choice of end-point reference materials is different from the usual practice in ternary alloys, such as InAs Sb$_{13}$ where the bowing is evaluated relatively to the linear interpolation InAs + 1 3 InSb of the two end-point materials InAs and InSb. The latter is a consistent choice since the ternary alloy has the same bonds In As and In Sb as the end points. But in the quaternary alloy Ga$_{13}$ In As Sb$_{13}$ four bonds Ga Sb, In As, In Sb, and Ga As are present, yet they are not considered when the quaternary is considered as the superposition of GaSb and InAs$_{0.89}$Sb$_{0.11}$ for the GaSb substrate or as the superposition of InAs and GaAs$_{0.08}$Sb$_{0.92}$ for the InAs substrate .

To illustrate how bowing depends on reference energies, we show in Fig. 8 for the quaternary alloy grown on InAs by the solid circles the energy □E = ; of the EPM-calculated conduction-band minimum E with respect to the conventional reference energy E^{TR} of ,

$$\square E^{\mathrm{TR}} \quad = \quad ; \quad = E \quad \mathrm{Ga}_{13}\ \mathrm{In}\ \mathrm{As}\ \mathrm{Sb}_{13}/\mathrm{InAs} \;\; 3\, E^{\mathrm{TR}} \quad , \tag{9}$$

where

$$E^{\mathrm{TR}} \quad = E \quad \mathrm{InAs} \; + \; 1\;3 \quad E \quad \mathrm{GaAs}_{0.08}\mathrm{Sb}_{0.92}/\mathrm{InAs} \; . \tag{10}$$

We see that □E^{TR}□0, implying negative bowing □0 as also seen by the solid circles in Fig. 7 a . To see that this □0 is merely an artifact of selecting E^{TR} of Eq. 10 as a reference, we also show in Fig. 8 the energy of the conduction-band minimum solid circles with respect to the alternative reference energy E^{BR} of constituents,

$$E^{\mathrm{BR}} \quad = \quad E^{\mathrm{InAs}} + \quad 1\,3 \quad E^{\mathrm{GaAs}} + \; 1\,3 \quad E^{\mathrm{InSb}} + \; 1\,3$$

$$\square \; 1\,3 \quad E^{\mathrm{GaSb}}. \qquad 11$$

Given

$$\square E^{\mathrm{BR}} \quad = \qquad ; \quad = E \quad \mathrm{Ga}_{1\,3} \ \mathrm{In\ As\ Sb}_{1\,3} \ /\mathrm{InAs} \;\; 3 \; E^{\mathrm{BR}} \qquad , \qquad 12$$

We see that $\square E_{\mathrm{c}}^{\mathrm{BR}} \square\, 0$, implying a bowing $\square\, 0$, as normally expected. Since the reference $E^{\mathrm{BR}} \quad \square\, E^{\mathrm{TR}}$ we see that

$$E \quad = E \quad = 0\ 3\ \frac{\square^{2}}{+\square}. \tag{13}$$

The parameters □ and □ for GaSb, InAs, GaAs, and InSb are given in Ref. 5. For the quaternary alloy with In composition and As composition we estimated the □ and □ parameters using a linear interpolation of the binary □ and □ values, using an expression of the form as in Eq. 1. We can see in Fig. 5 b that the $=0$ K translated experimental data lie between the dashed line corresponding to the relation for E at $=0$ K proposed in Ref. 5 and our calculated values, and there is a difference of the order of about 30 meV at $=0.16$ among the band-gap values measured by different groups. Our calculated values are always slightly than the experimental data for □0.1 and the deviation between experiment and theory seems to increase with increasing In and As content. Unfortunately, in the energy range 0.30 □ □0.70, where the differences between the predictions of the atomistic calculations and of the interpolative schemes are larger, the quaternary alloy presents a miscibility gap.[28] Until recently only two lattice-matched regions with indium content 0□ □0.28 and □0.70 were successfully grown and only for these compositions measurements of the band gaps have been performed. Reference 28 reports the measurement of a minimum gap $E=0.34$ eV at $=77$ K and $E=0.26$ eV at $=300$ K, smaller than the gap of InAs, for the quaternary alloy with □0.70. Our calculations predict gaps from 0.27 to 0.35 eV in the range □0.75 in reasonable agreement with the experimental values.

Experimental values of E of Ga

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