Deep levels in type-II InAs/GaSb superlattices

Jun Shen
Motorola Inc., Phoenix Corporate Research Labs, Tempe, Arizona 85284

Shang Yuan Ren and John D. Dow
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287
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The theory of sp^3-bonded substitutional deep impurity levels is extended to type-II gap-misaligned InAs/GaSb superlattices. The theory predicts that some shallow impurities (donors or acceptors) in either bulk InAs or bulk GaSb can become deep traps in a thin-layer superlattice. This happens because the deep levels associated with point defects in either InAs or GaSb layers (when measured relative to the valence-band maximum of InAs) are much less sensitive to changes of the layer thicknesses of the superlattice than the superlattice band edges. Some common column-IV dopants may lose their amphoteric character [i.e., being a donor when substituting for the column-III host atom (C_{In} in InAs) and an acceptor when substituting for the column-V host atom (C_{As} in InAs)] and become deep traps for some superlattice layer thicknesses and can even become "false valence" dopants (e.g., C_{In} is predicted to be an acceptor in a 10×10 InAs/GaSb [001] superlattice) for other layer thicknesses. The deep-level splitting and shifting in the type-II superlattice is found to follow the same physics as in the type-I superlattice. A semiconductor-semimetal-semiconductor transition is predicted to occur as the InAs layer thickness increases.

I. INTRODUCTION

A type-II superlattice such as InAs/GaSb is different from a type-I superlattice such as GaAs/$Al_xGa_{1-x}As$ due to the relative positions of the band-edge energies in the two constituent semiconductors (see Fig. 1). Recall that in a type-I superlattice such as GaAs/$Al_xGa_{1-x}As$, the fundamental band gap of the small-gap material (GaAs) lies entirely within the fundamental gap of the large-gap material ($Al_xGa_{1-x}As$). There are two types of type-II alignment: misaligned and staggered. InAs/GaSb falls into the misaligned category because the lower-energy (InAs) conduction-band edge lies *below* the valence-band edge of the other constituent material, GaSb, by 0.15 eV. Thus, for superlattices composed of thick layers of InAs and GaSb, the superlattice is semimetallic and electrons from the top of the GaSb valence band transfer to the InAs conduction-band minimum, which lies at lower energy. We shall see that the band gap of the superlattice can be tailored from zero to 0.8 eV by altering the InAs and GaSb layer thicknesses, making InAs/GaSb potentially important in infrared device applications. One purpose of this paper is to explore how changing InAs and GaSb layer thicknesses affects the fundamental band gap of the superlattice and to determine the conditions under which the superlattice is a semiconductor with a positive fundamental band gap or a semimetal with a zero or apparently negative gap. We are also interested in impurities and dopants and how their doping characters are affected when the band gap vanishes as a function of layer thickness. For example, a 1×10 InAs/GaSb superlattice is a semiconductor with a band gap almost equal to that of GaSb, but for $N_{InAs}>26$, the $N_{InAs}\times10$ InAs/GaSb superlattice is theoretically semimetallic (see Fig. 2). We would like to understand the physics of impurity levels in $N_{InAs}\times N_{GaSb}$ superlattices as (for example) N_{InAs} increases from unity to 40. (Here an $N_{InAs}\times N_{GaAs}$ superlattice consists of N_{InAs} bilayers of InAs, followed by N_{GaSb} bilayers of GaSb, repeated periodically in the [001] direction.)

A central point, now well established,[1] is that every *s*- and *p*-bonded substitutional impurity in a zinc-blende semiconductor produces four "deep levels" in the vicinity of the fundamental band gap, and these levels are associated with the large (≈5 eV) central-cell potential of the impurity, which significantly alters the four nearest-neighbor bonds. The resulting deep levels are one *s* like or A_1 symmetric and one triply degenerate or *p*-like T_2 level. While the T_2 level normally lies above the A_1 level, the positions of these levels with respect to the band edges of the host semiconductor can be anywhere. (See Fig. 3.) Hence, as the band edges of the host change (e.g., in a superlattice as the layer thicknesses change), some impurities exhibit deep-shallow transitions, while others exhibit deep to false-valence transitions.[3] Deep-shallow transitions, first clarified by the experiments of Wolford *et al.*,[4] occur when an impurity that normally produces a deep level in the fundamental band gap of a semiconductor has its environment changed in such a way that the deep level passes out of the gap into a host band. When this happens, the ground electronic state of the impurity changes, and often its doping character changes as well. For example, the *N* isoelectronic anion-site trap in $GaAs_{1-x}P_x$ ceases being a trap for $x<0.24$. Similarly, cation-site Si in $Al_xGa_{1-x}As$ has a deep level for $x=0$ (GaAs) above the conduction-band edge that descends into the gap for alloys with $x>0.22$. In GaAs-rich ma-

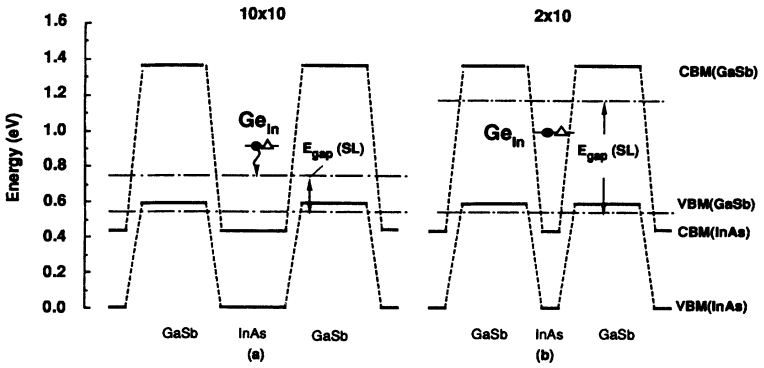

FIG. 1. Illustrates the quantum-well effect on the band gap E_{gap} (SL) of a $N_{InAs} \times N_{GaSb}$ InAs/GaSb superlattice: (a) $N_{InAs} = N_{GaSb} = 10$ and (b) $N_{InAs} = 2$, $N_{GaSb} = 10$. The band edges of the superlattice are denoted by chained lines. The zero of energy is the valence-band maximum *of InAs*.

terial, the Si is a shallow donor, but for $x > 0.22$ it is a deep electron trap—very likely the essential element of the *DX* center.

False valence occurs when a deep level in the conduction band passes all of the way through the gap into the valence band (or vice versa) as a result of a change in the parent impurity's environment. (See Fig. 3.) An example of false valence is In_{Te} in $Pb_{1-x}Sn_xTe$, which is a normal valence (triple) acceptor in SnTe but a false valence (triple) donor in PbTe.[3] A *p*-like deep level of In lies in the valence band of SnTe but passes through the band gap with increasing Pb content until it lies in the conduction band of PbTe. This deep level would hold three electrons and three holes if In_{Te} were neutral and the level were in the gap (where it would not be autoionized, because there are no host states degenerate with it). But when the level lies degenerate with the valence band of SnTe, the holes bubble up to the top of the valence band and the In is negatively charged, producing a shallow acceptor level. (If we neglect Coulomb effects, the In is In^{-3}, and acts as a triple acceptor.) In PbTe, the deep *p*-like level is in the conduction band and the three electrons that would occupy its six spin orbitals if the levels were in the gap, instead fall to the conduction-band minimum, forming In^{+3}, which binds (three) electrons in shallow-donor states. Note that in the simple one-electron approximation, the In is triply ionized In^{+3}, and the conventional notion that In on a Te site should become In^{-3} has the apparent valence incorrect by six—the number of electrons a *p* level can hold. So, in PbTe, In_{Te} has a false valence, different from its true valence by six. Every impurity produces deep levels associated with the central-cell impurity potential, although these deep levels often

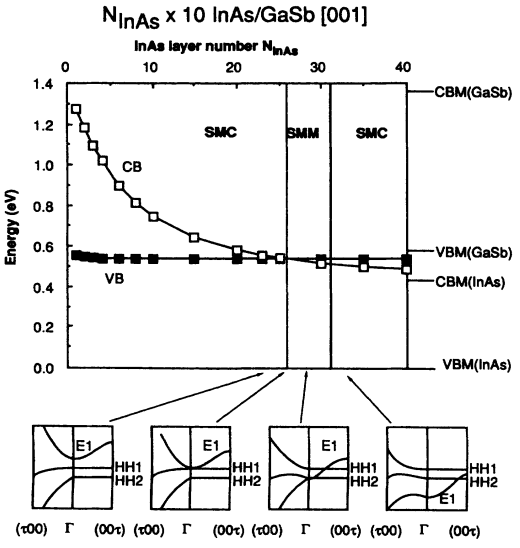

FIG. 2. Predicted conduction- and valence-band edges of $N_{InAs} \times 10$ InAs/GaSb [001] superlattices. The conduction-band edge crosses the valence-band edge at $N_{InAs} = 26$ (= 79 Å), corresponding to a semiconductor-semimetal transition. SMC denotes semiconductor; SMM denotes semimetal.

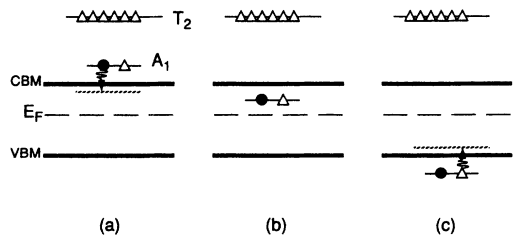

FIG. 3. Schematic illustration of the deep-level structures one might conceive of for an impurity such as P in bulk Si: (a) the A_1 level above the conduction minimum of Si, (b) the *s*-like A_1 deep level in the fundamental band gap, and (c) the A_1 level in the valence band. We have assumed that the T_2 level in all cases lies above the conduction-band minimum. In case (a), P becomes P^+ and produces a shallow donor impurity because the Fermi energy lies below the deep A_1 level in the conduction band, and so the electron (solid circle) spills out of the level, falls down to the conduction-band edge, and leaves P ionized as P^+—which then binds the electron in a shallow donor state. In case (b), the deep level is in the gap, presumably above the Fermi energy (dashed line), the stable ion is P^0, and the impurity can trap an electron of opposite spin in the hole (open triangle). Here P is a deep trap that tends to make the material semi-insulating. In case (c), the hole bubbles up to the valence-band maximum, P becomes P^-, and the ion binds a hole in its shallow acceptor level. Of course, case (a) is the common shallow-donor case for P in Si; case (b), the deep trap, occurs for O_P in GaP, and for selected x, for P in $Ge_{1-x}Si_x$ alloys (Ref. 2). Case (c) has P as a shallow *acceptor* in Si, and has P with a "false valence" as P^-, different by two from its normal valence. False valence does not occur in nature for P-doped Si, but similar false valences occur for other impurity-host combinations, such as In-doped $Pb_{1-x}Sn_xTe$.[3]

do *not* lie energetically within the band gap. When one of these levels passes through the conduction- or valence-band edge, the doping character of the impurity changes: (i) if none of the deep levels lies in the gap, then the impurity will be a shallow donor or acceptor, obey hydrogenic effective-mass theory, and following the conventional wisdom; (ii) if at least one deep level lies in the gap, the impurity will be a deep trap; and (iii) if one of the deep levels has crossed the gap as the host atom has been transmuted into an impurity, the shallow donor or acceptor will have a false valence. One purpose of this paper is to predict how, by varying superlattice layer thicknesses such changes of doping character can occur.

II. FORMALISM

To develop a theory of doping character, we must be able to predict the valence- and conduction-band edges in superlattices rather accurately. Of the various electronic-structure theories, only the empirical pseudopotential[5] and empirical tight-binding[6] models do a rather good job of predicting conduction-band edges. For this reason, and because we wish to display explicitly the chemistry of sp^3 binding, we employ the empirical tight-binding model of electronic structure, using an sp^3s^* basis.[6] In this model, there are one s orbital and three p orbitals per atomic site, as well as a fictitious excited s orbital s^* that simulates states at higher energy. The formalism to describe the [001] InAs/GaSb superlattices is similar to what we used in Ref. 7 for the type-I $GaAs/Al_xGa_{1-x}As$ superlattices.[6,8] A major difference occurs at the interfaces where there is a common anion (As) in the $GaAs/Al_xGa_{1-x}As$ superlattice but not in the InAs/GaSb superlattice. In addition to the InAs and GaSb bonds within their bulk layers, there are GaAs and InSb bonds at the interfaces. We have used four sets of tight-binding parameters (i.e., those for InAs, GaSb, InSb, and GaAs) to appropriately describe the actual bonding of the atoms. To account for the valence-band offsets, the constants 0.0, 0.58, 0.75, and -0.17 eV have been added to the tabulated diagonal matrix elements of InAs, GaSb, InSb, and GaAs parameters, respectively.[9,10]

The theory of deep levels in the type-II InAs/GaSb superlattice is the same as the one applied to the type-I $GaAs/Al_xGa_{1-x}As$ superlattices.[7,8] The Green's-function theory of Hjalmarson *et al.*[11] is extended to the superlattice and superlattice special points are used to evaluate the Green's functions.[7,12] The point-group symmetry of a general substitutional defect in the InAs/GaSb superlattice is C_{2v}. The A_1 and T_2 deep levels of the bulk InAs or GaSb produce two a_1 levels of the superlattice (one s-like, derived from the A_1 level and one T_2-derived p_z-like), one b_1 level [(p_x+p_y)-like], and one b_2 level [(p_x-p_y)-like]. Of course, for impurities far from an InAs/GaSb interface, the s-like a_1 level will have an energy very close to the energy of a bulk A_1 level, and the p_z-like a_1 level and the b_1 and b_2 levels will lie close to the bulk T_2 level also. We normally expect to find the T_2-derived a_1 level between the b_1 and b_2 levels but, if the level lies close to the valence-band maximum, then the splitting of the valence-band edge into a (p_x+p_y)- and (p_x-p_y)-like maximum with a p_z-like edge at slightly lower energy (because of the smaller effective mass) may cause the a_1 deep level to lie lower in energy than the b_1 and b_2 levels by a comparable energy. Note that this splitting exists even for defects distant from the interface and is a consequence of the different host spectral densities in the superlattice for a_1 and b_1 and b_2 states.

III. RESULTS

A. Host band gap

Unlike the type-I $GaAs/Al_xGa_{1-x}As$ superlattice, the type-II InAs/GaSb superlattice has its quantum wells for electrons (conduction band) and for holes (valence band) in different layers (Fig. 1), with the former in the InAs layers and the latter in the GaSb layers. So the conduction-band edge energy *of the superlattice* is more sensitive to the InAs layer thickness and the valence-band edge is more sensitive to the GaSb layer thickness. This is demonstrated by the calculated results of Fig. 4. Here, one must keep in mind that the superlattice is a periodic structure with its own conduction- and valence-band edges. This is especially important in the type-II InAs/GaSb system whose valence- and conduction-band edges are mixtures of the InAs and GaSb edges—in contrast with GaAs/AlAs type-I superlattices, for which the $n=1$ GaAs quantum-well states are the superlattice conduction- and valence-band edges.

When the InAs layer thickness (N_{InAs}) increases, the conduction-band mininum of the superlattice [CBM(SL)]

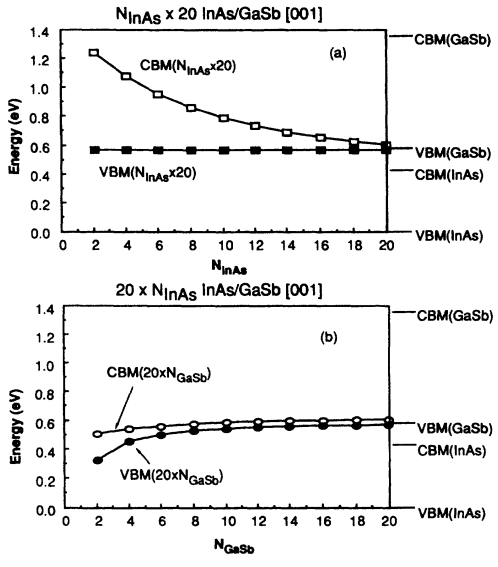

FIG. 4. Predicted energies (in eV) of the superlattice conduction-band minima and valence-band maxima with respect to the valence-band maximum of *bulk InAs* for an InAs/GaSb [001] superlattice versus reduced layer thicknesses N_{InAs} and N_{GaSb} for various $N_{\mathrm{InAs}}\times 20$ and $20\times N_{\mathrm{GaSb}}$ [001] InAs/GaSb superlattice. The calculations are based on the low-temperature band structures of InAs and GaSb, with bulk band gaps of 0.43 and 0.78 eV, respectively. For all cases, the valence-band maximum and the conduction-band minimum are found at Γ ($k=0$).

decreases from CBM(GaSb) toward CBM(InAs), and the valence-band maximum of the superlattice [VBM(SL)] remains almost a constant. Similarly, when the GaSb layer thickness (N_{GaSb}) increases, VBM(SL) increases from VBM(InAs) toward the VBM(GaSb), the CBM(SL) changes from near the CBM(InAs) but at a smaller rate than when N_{InAs} increases. The CBM and the VBM of the superlattice are found to be at $\Gamma(000)$ for all cases, so that *the gap is always direct.* When the InAs layer thickness increases further (Fig. 2), CBM(SL) crosses VBM(SL). In this case, the electrons in the GaSb valence band will "flood" into the InAs conduction band, corresponding to a semiconductor-semimetal transition. This transition was first predicted by Sai-Halasz *et al.* and later experimentally confirmed by Chang *et al.*,[13] who measured the layer-thickness dependence of the superlattice's Hall carrier concentration. A sudden increase by an order of magnitude of the carrier concentration in the neighborhood of 100-Å-thick ($N_{InAs} \approx 33$) InAs layers was observed. According to Fig. 2, the on-site InAs layer thickness of the transition is $N_{InAs}=26$ (≈ 79 Å), for $N_{GaSb}=10$, in good agreement with the experiment. The interesting thing is that after the superlattice becomes a semimetal, with increasing N_{InAs} the carrier concentration reverses its trend and *drops down* also an order of magnitude. Chang *et al.* interpreted this drop as due to the superlattice becoming a series of isolated heterojunctions. This is true when the charge transfer causes severe band bending at the interfaces. Here, our calculation shows that the concentration drop can also happen due to another reason: *the superlattice becomes a semiconductor again* when the InAs layer thickness increases further. (See Fig. 2 insets.) In the figures, we can see that the two heavy-hole bands (HH1, HH2) do not move much when the InAs layer thickness increases, while the light conduction band moves down (E_1). At an InAs layer thickness of 79 Å ($N_{InAs}=26$), the conduction band crosses the upper (heavy-hole) valence band, the gap is zero, and the superlattice undergoes a semiconductor-semimetal transition. At InAs layer thickness $N_{InAs} \approx 32$, the conduction band (E_1) moves down further so that a gap opens up at $\mathbf{k}=(00\tau)$ [where $\tau=1/(N_{InAs}+N_{GaSb})$], so that the superlattice is a semiconductor again, which makes the carrier concentration drop. A similar phenomenon was also predicted in type-III HgTe/CdTe superlattices.[14]

The sensitivity of the superlattice conduction-band edge to the InAs layer thickness is important for the physics of deep levels in superlattices because, as we shall see below, the deep levels have energies relative to the InAs valence-band maximum that vary relatively little with the thickness of the InAs layers. Hence, a deep level that is near the conduction-band edge but within the gap in an InAs quantum well can be "covered up" and autoionized by the conduction-band edge when the InAs layer thickness is increased and the conduction-band edge descends in energy, while the deep level remains at a relatively constant energy (Fig. 5). Here, it is important to remember that we use the definition of a deep level[11] as one that originates from the perturbation caused by the central-cell potential. (This contrasts with the old definition as a level that lies within the band gap by at least 0.1 eV.) As a result, there are "deep resonances" that lie in the conduction band, above the band gap. We shall see below that Ge in InAs, although producing only shallow levels in the band gap of bulk InAs (i.e., its deep levels are all resonances that lie in the conduction band), is a candidate for producing a deep level in the band gap of an InAs/GaSb superlattice, in the thin InAs quantum-well limit. For neutral Ge in an otherwise intrinsic semiconductor superlattice, this level, when in the fundamental band gap and electrically neutral, will be occupied by one electron (and one hole). It is a trap for either an extra electron or hole, and tends to make the superlattice semi-insulating. When the InAs layer thickness increases, this level is covered up by the falling conduction-band edge and becomes a resonance. The electron in the resonant level is autoionized and relaxes (e.g., by phonon emission) to the conduction-band edge,

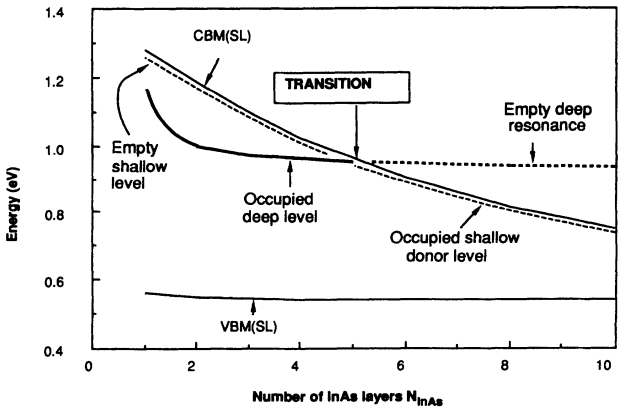

FIG. 5. Illustrates the deep-to-shallow transition as a function of InAs layer thickness N_{InAs} in an InAs/GaSb $N_{InAs} \times 10$ [001] SL for a Ge impurity on an In site in the center of an InAs layer of the superlattice host. The CBM and VBM are indicated by light solid lines. The Ge deep level is denoted by a heavy line, which is solid when the level is in the gap but dashed when the level is resonant with the conduction band. The deep level in the band gap for $N_{InAs} < 5$ is covered up by the conduction band as a result of changes in the host for $N_{InAs} > 5$. The impurity's deep level lies in the gap for $N_{InAs} < 5$ and is occupied by the extra Ge electron; the Ge, in this case, is thus a "deep impurity." For $N_{InAs} > 5$, the deep level lies above the conduction-band edge as a resonance. The daughter electron from the Ge impurity which was destined for this deep level is autoionized, spills out of the deep resonance level, and falls to the conduction-band edge (light solid line) where it is subsequently bound (at low temperature) in a shallow level associated with the long-ranged Coulomb potential of the donor (indicated by the short dashed line). It is important to realize that *both* the deep level and the shallow levels coexist and are distinct levels with qualitatively different wave functions. The issue of whether an impurity is "deep" or "shallow" is determined by whether or not a deep level associated with the impurity lies in the band gap. The computed deep-shallow transition occurs for $N_{InAs}=5$ layers. While the qualitative physics is completely reliable, it is possible that the transition-layer thickness may differ somewhat from the predicted value $N_{InAs}=5$ in real superlattices. All energies are with respect to the valence-band maximum *of InAs.*

where it is a shallow-donor electron, donated by the Ge and orbiting the Ge^+ ion. (In the present theory, which neglects the long-ranged Coulomb potential of the donor, the binding energy of a shallow donor is zero; in a more complete theory, the Coulomb potential would trap this electron at zero temperature in a hydrogenic orbit.)

B. Defect levels

The substitutional defect energy levels for sp^3-bonded impurities can be evaluated using the techniques of Hjalmarson *et al.*,[11] as described above for superlattices. When interpreting the predictions, one should remember that the absolute energy levels predicted by this theory have a theoretical uncertainty of a few tenths of an eV. This is, of course, comparable with the uncertainties of the other sophisticated theories of deep levels that have been presented to date.[15] Nevertheless, the theoretical uncertainty is a significant fraction of the band-gap energy, and so one must not use the theory in a futile attempt to predict precise energy levels. Rather, the theory should be employed to understand the chemical trends in the deep energy levels, to study qualitative changes in level structures (such as a deep resonance descending into the fundamental band gap—the shallow-deep transition), or to suggest experiments for testing hypotheses about impurity states. One of the reasons that the model of Hjalmarson *et al.*[11] has been so successful is that the tight-binding Hamiltonian has been constructed with manifest chemical trends in its parameters, following ideas developed originally by Harrison.[16] Earlier theories sometimes obtained tight-binding parameters by performing least-squares fits to the band structures of the semiconductors being studied. Such fits, while having given impressive band structures, often lacked the essential chemistry that determines deep levels and, as a result, those theories have not been as successful as the theory of Hjalmarson *et al.* Indeed, because the Hamiltonian employed in the theory of Hjalmarson *et al.* has manifest chemical trends and also has (by construction) the correct band gaps, the method of Hjalmarson *et al.* is comparably accurate with far less simple theories of deep levels.[15,17]

C. Dependence on layer thickness

Figure 5 displays the dependence on InAs reduced layer thickness N_{InAs} of the deep In-site A_1 level of a Ge impurity *in the middle of* an InAs layer in an InAs/GaSb superlattice. As the size N_{InAs} of the InAs layer shrinks, the *deep* levels remain relatively constant in energy with respect to the InAs valence-band maximum while the conduction-band edge of the superlattice increases in energy—progressively uncovering the once-resonant deep level of Ge and converting this shallow-donor impurity into a deep trap. This shallow-deep transition as a function of InAs well size N_{InAs}, to our knowledge, has not been anticipated in the literature—and has consequences for InAs/GaSb superlattice and quantum-well devices, because it implies that the common dopant, Ge, may become a deep electron trap rather than a shallow donor in InAs.

Also note (Fig. 5) that when Ge in an InAs quantum well becomes a deep impurity with its deep level in the fundamental gap of the superlattice, this level (with respect to the InAs valence-band maximum) generally lies at a higher energy than the bulk InAs band gap, at lower energy than the Ge deep level in a GaSb layer, and below the superlattice and bulk GaSb conduction-band edges. Because Ge in a GaSb layer produces a deep level that lies in the conduction band of GaSb, it is possible to move the conduction-band edge up by reducing the width of the InAs layers and to achieve a situation in which Ge in an InAs layer is a deep level, but that Ge in an GaSb layer is still a shallow donor with respect to the superlattice.

Because of uncertainties in the theory, we cannot estimate with precision the layer thickness N_{InAs} at which the Ge level in InAs should undergo the shallow-deep transition. Based on the general structure of the curves of Fig. 5, it probably occurs for $N_{\mathrm{InAs}} \approx 5$ and an InAs layer thickness of order ~ 15 Å or less.

D. Cation-site carbon a_1 levels

When C substitutes for either In or As in *bulk* InAs, it produces an *s*-like A_1 level and three *p*-like T_2 levels. When C is on the anion site, the A_1 and T_2 levels are all resonant with the valence band. Since the higher energy of these deep levels lies below the valence-band maximum and the Fermi energy, an extra hole attributable to the valence difference between C and As is autoionized and bubbles up to the valence-band edge, leaving C as a negative ion. The Coulomb potential of the negative ion binds a hole, causing C_{As} to be a shallow acceptor. When C is on the cation site, the A_1 and T_2 levels are all in the conduction band. The extra valence electron of neutral C is not stable in the resonant deep levels and thus falls to the conduction-band edge, leaving C as a positive ion. This ion then binds the electron (at zero temperature) in a Coulombic shallow donor level. Thus C in bulk InAs is amphoteric, being a donor on the In site and an acceptor on an As site.

According to the theory, this amphoteric character of C in InAs is lost in a 10×10 InAs/GaSb superlattice, even though the C occupies substitutional sites in InAs layers. (See Fig. 6.) The superlattice valence-band maximum is sensitive to changes in the GaSb layer widths because GaSb is the quantum well for holes in these superlattices. In a thin-GaSb-layer superlattice, the superlattice's valence-band maximum is near the valence-band maximum of InAs; in a thick-layer superlattice, the valence-band maximum approaches that of GaSb. In a 10×2 superlattice, the superlattice valence-band edge lies between the valence extrema of bulk InAs and bulk GaSb. Nevertheless, it lies sufficiently low in energy (~ 0.3 eV) that the A_1 C_{In} level is exposed in the superlattice fundamental band gap: C is a deep trap for either electrons or holes. When the GaSb layer thickness increases, the superlattice valence-band maximum moves up while the C_{In} A_1 deep level stays virtually at the same position, until finally the deep level is covered up by the superlattice valence-band maximum (e.g., 10×10 InAs/GaSb). Once the level is covered, the hole in the

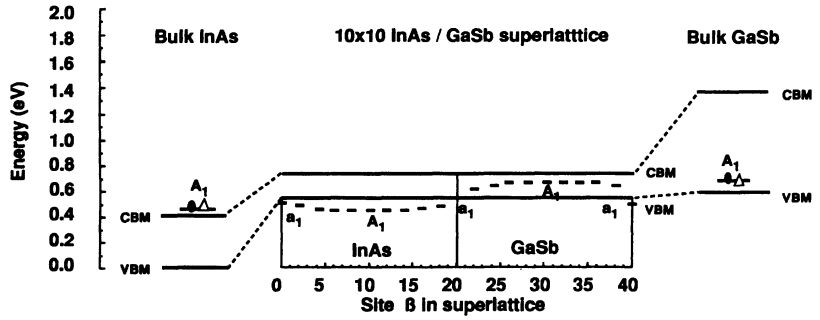

FIG. 6. Predicted energy levels of a C_{In} impurity in an 10×10 InAs/GaSb [001] superlattice, as a function of β, the position of the impurity (even values of β correspond to cation sites). The zero of energy is the valence-band maximum of bulk InAs, and the corresponding valence-band (VBM) and conduction-band (CBM) edges and deep levels in bulk InAs and bulk GaSb are given to the left and right of the central figure, respectively. The top of the central figure is the conduction-band edge of the superlattice. The A_1 level in the GaSb layer of the superlattice is higher than the corresponding level in the InAs layer, because of the band offset of 0.58 eV. The electron (hole) occupancies of the deep levels in bulk InAs and bulk GaSb are denoted by solid circles (open triangles). The C_{In} deep level in the bulk InAs is resonant with the conduction band and donates an electron to the conduction band. In the superlattice, the C_{In} level is covered up by the valence band of the superlattice and thus its extra hole becomes unstable and bubbles up to the valence-band edge, making the impurity an acceptor (false valence).

level is no longer stable and bubbles up to the superlattice valence-band edge, forming the C^- ion whose long-ranged Coulomb potential binds a hole—making C_{In} a shallow acceptor (false valence).

Figure 6 displays the predicted deep energy levels in the band gap of a cation-site carbon impurity in a $N_{InAs}=N_{GaSb}=10$ InAs/GaSb superlattice, as a function of β, the z component of the position of the impurity in the superhelix or superslab.[7] At the center of the thick quantum well or barrier, the local environment of a point defect is almost bulklike. So the impurity levels near the center of the layers almost line up with the ones in the respective bulk (labeled A_1). As the impurity approaches the interfaces (typically within three atomic layers), the deep levels shift slightly (≈ 0.1 eV). The A_1 C_{In} level in an InAs layer lies at lower energy than the C_{Ga} level in a GaSb layer because the band offset lifts the A_1 level in the GaSb layers in the superlattice. The A_1 level at the interface ($\beta=20$) lies higher in energy because the interfacial In atom belongs half to a higher-energy InSb bond. (Recall that the valence-band maximum of InSb lies 0.78 eV higher in energy than that of InAs.)

E. Cation vacancy levels

The A_1 bulk levels for cation vacancies in InAs and in GaSb all lie very deep in the host valence bands and are not near the fundamental band gap, either in the bulk or at an interface of an InAs/GaSb superlattice. The T_2-derived cation vacancy levels produce deep levels near the valence-band maxima of bulk InAs, bulk GaSb,[18,19] and the superlattice. (See Fig. 7.) In the Hjalmarson *et al.* theory, the uncertainty in the predictions of absolute energies is typically a few tenths of an eV and tends to be somewhat larger for the T_2 levels than for the A_1 levels. Therefore, in what follows, the reader should not interpret our predictions for the cation vacancy too literally or too quantitatively. Rather, the predictions illustrate the very interesting properties of a cation-site deep-T_2 level that lies near but below the valence-band

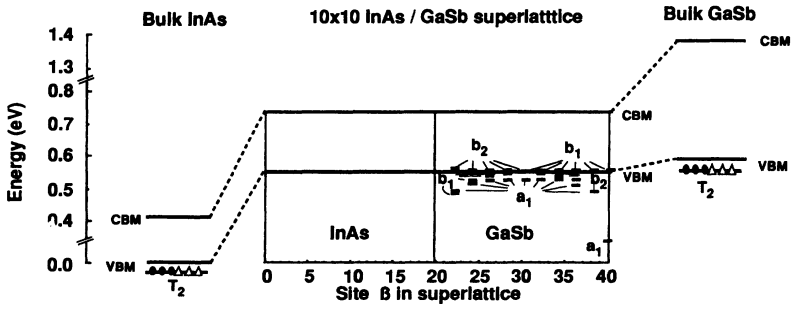

FIG. 7. Predicted T_2-derived levels of a cation vacancy in a 10×10 InAs/GaSb [001] superlattice, as a function of site index β, the position of the vacancy. The zero of energy is the valence-band edge of bulk InAs, and the corresponding valence-band and conduction-band edges and deep levels in bulk InAs and bulk GaSb are given to the left and right of the central figure, respectively. The top of the central figure is the conduction-band minimum of the superlattice. Electrons occupying the bulk levels are denoted by solid circles. Holes are denoted by open triangles. When, as in bulk InAs or GaSb, the holes are initially in levels *below the valence-band maximum,* they bubble up to the valence-band maximum where the long-ranged Coulomb potential can trap them in shallow acceptor levels (not shown). The cation vacancy in the superlattice is predicted to be a (triple) shallow acceptor, providing three such holes to the valence band. The lowest energy level is often of a_1 symmetry, and the highest is typically either of b_1 or b_2 symmetry; but exceptions to this rule do occur.

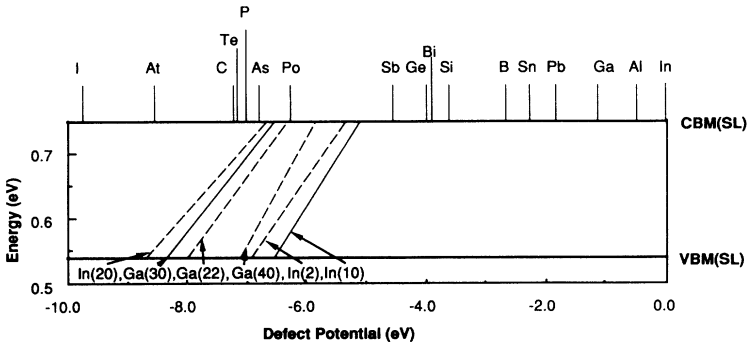

FIG. 8. Predicted energies of A_1-derived s-like a_1 deep levels of the indicated defects (Ref. 21) for an InAs/GaSb [001] superlattice with $N_{\mathrm{InAs}}=10$ InAs layers and $N_{\mathrm{GaSb}}=10$ GaSb layers in its unit supercoil. The dashed lines denote the predictions for defects at or near an InAs/GaSb interface: in the $\beta=20$ layer for the interface, levels for In-site defects and, in the $\beta=2$ and $\beta=22$ layers adjacent to interface layers, for In-site defects (in InAs) and Ga-site defects in GaSb, respectively. The solid lines denote the same levels for defects at or near the center of InAs and GaSb layers, respectively. In viewing this figure, remember that the theory is not precise, but that the general shape of the figure is reliable. The zero of energy is the valence-band maximum *of bulk InAs*. The valence- and conduction-band edges of the superlattice are denoted by VBM(SL) and CBM(SL), respectively.

maximum of GaSb. The T_2 In vacancy level is predicted[11,19] to lie ≈ 0.03 eV below the valence-band maximum in bulk InAs, and to lie much deeper relative to the valence-band maximum (not shown) of a 10×10 InAs/GaSb superlattice because the band offset raises the valence band about 0.5 eV. Thus, the In vacancy either in bulk InAs or in the superlattice is nominally a triple acceptor. In bulk GaSb, the predicted Ga vacancy level is ≈ 0.035 eV below the valence-band maximum, so the vacancy is a triple acceptor. In the 10×10 superlattice, GaSb layers are the quantum wells for holes and the valence-band maximum of the superlattice lies 0.04 eV below that of the bulk GaSb. The T_2 cation vacancy level splits into a_1, b_1 and b_2 sublevels. Some of these sublevels may lie in the gap of the superlattice.

If the predictions are taken literally, then the cation vacancy produces a very interesting level structure, depending on the site of the vacancy. The b_1 and b_2 levels in a GaSb layer lie typically ≈ 0.03 eV above the a_1 level, when we might have expected the a_1 level to lie between them. This expectation is not met because the T_2 levels are near the valence-band maximum and, in the superlattice, the T_2-like valence-band maximum is split into a_1 and b_1 and b_2 edges. Hence the a_1 valence-band edge has a stronger quantum-well confinement effect: the band edge for a_1 (p_z-like) states lies 0.14 eV below the edge for b_1 and b_2 states. The a_1 defect states lie lower because the valence-band states that repel them are at lower energy in the superlattice. The p_z-like a_1 level decreases in energy as the vacancy moves from the center of the GaSb layer toward the interface. The initial decrease is due to quantum-well confinement, and begins when the vacancy wave function significantly overlaps the InAs. However, as the vacancy becomes quite close to the interface, its wave function penetrates thoroughly into the InAs layer and feels the electronegativity of the InAs layers, due mainly to the band offset.

The neutral Ga vacancy in the bulk of GaSb (assuming its deep level lies in the valence band) is a triple acceptor (Fig. 7). (A Ga vacancy is created by adding three holes—to remove the three Ga electrons—and letting the defect potential become infinite.[20]) Consider this vacancy at the near-interfacial site $\beta=22$ in a GaSb layer of the superlattice; its levels, in order of decreasing energy, are b_2, a_1, and b_1. In all of the cases of Fig. 7, the cation vacancy is either a triple shallow acceptor or a deep trap for both an electron and a hole, having at least one partially filled deep level in the gap. If it were the case that a cation vacancy near an interface had only one of its sublevels in the gap and two sublevels resonant with the

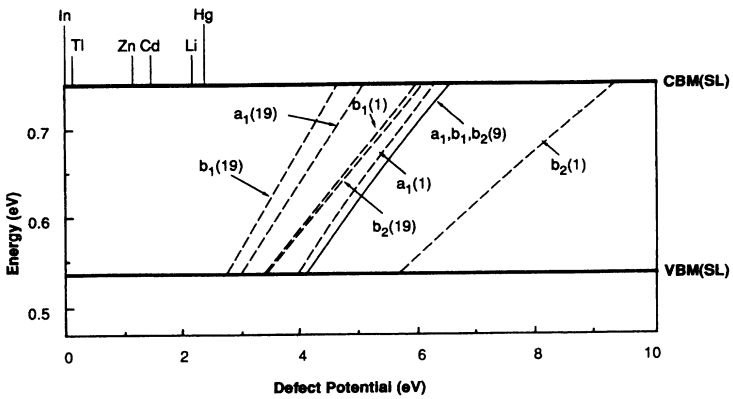

FIG. 9. The predicted T_2-derived deep levels for the indicated As-site defects (Ref. 21) in a 10×10 InAs/GaSb [001] superlattice. For As-site defects, the solid lines correspond to T_2-derived a_1, b_1, and b_2 levels (which are almost degenerate) in the center of InAs layers. The dashed lines denote the predictions for defects at ($\beta=1$) or near ($\beta=19$) an InAs/GaSb interface.

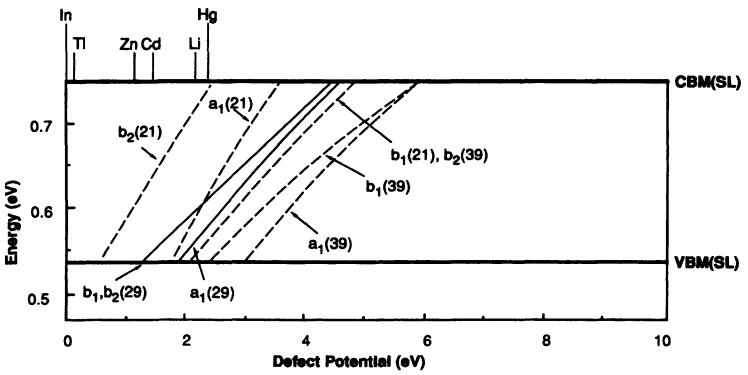

FIG. 10. The predicted T_2-derived deep levels for the indicated Sb-site defects (Ref. 21) in a 10×10 InAs/GaSb [001] superlattice. For Sb-site defects the solid lines correspond to T_2-derived a_1, b_1, and b_2 levels (which are almost degenerate) in the center of InAs layers. The dashed lines denote the predictions for defects at ($\beta=21$) or near ($\beta=39$) an InAs/GaSb interface.

valence band of the superlattice, then the vacancy would be a single acceptor, because only three electrons are available for four spin orbitals: the hole in the fourth spin orbital would "bubble up" to the valence-band maximum. Relatively small amounts of lattice relaxation or charge-state splitting of the defect levels could alter the predictions. Nevertheless, we think that studies of the character of the Ga-vacancy wave function in InAs/GaSb superlattices are warranted—and could possible reveal this shallow-deep transition in the character of the cation vacancy.

F. Deep levels of other sp^3-bonded impurities

The predicted deep energy levels of substitutional sp^3-bonded impurities in a InAs/GaSb superlattice are given in Figs. 8–10 for a superlattice with $N_{\mathrm{InAs}}=N_{\mathrm{GaSb}}=10$.[21] These levels' energies E are obtained by solving the secular equation (17) with the defect potential V of Hjalmarson *et al.*[6] In these figures, we display results for impurities at or near an InAs/GaSb interface and near the center of the InAs and GaSb layers. In the superlattice, the As-site and Sb-site s-like levels are all resonant either in the valence band or in the conduction band of the superlattice.

For the A_1- or s-like levels on the cation site (Fig. 8), most interfacial impurities (labeled 2, 22, and 40) have energy levels roughly midway between the levels for impurities near the center of the InAs and the GaSb layers. There are two types of cation sites: In (in InAs) and Ga (in GaSb); the near-interface In-site ($\beta=2$) defects have nearly the same deep levels as defects at the centers of the InAs layers (In at $\beta=10$) because the defect is at least one layer distant from the interface (namely, the As layer or $\beta=1$). Hence, these deep levels are only weakly perturbed by the atoms on the other side of the interface. The interface In-site ($\beta=20$) defect has an As plane ($\beta=19$) on one side and an Sb plane ($\beta=21$) on the other side. Its deep levels are shifted upward from those of the defects at the centers of the InAs layers due to the large positive-band offset (≈ 0.75 eV) of InSb with respect to the valence-band maximum of InAs. A similar situation holds for the Ga-site defects at the center ($\beta=30$), near the interface ($\beta=22$), and at the interface ($\beta=40$) in the GaSb layers. All T_2-derived p-like cation-site deep levels are resonant either in the valence band or in the conduction band of the superlattice.

There are three T_2-derived levels for each anion-site impurity in the superlattice; a_1 (p_z-like), b_1 ($[p_x+p_y]$-like), and b_2 ($[p_x-p_y]$-like) (Figs. 9 and 10). Again, these T_2-derived levels are split according to whether the impurity is near the layer center ($\beta=9$ for As, $\beta=29$ for Sb), near the interface ($\beta=19$ for As, $\beta=39$ for Sb), or at the interface ($\beta=1$ for As, $\beta=21$ for Sb). For an impurity near or at the interface, the amount of the level shifting depends on whether the orbitals are directed toward the interface or away from it. Generally, the level shifts most if the impurity is at the interface and its orbitals are oriented toward the interface (the $\beta=1$ As b_2 level and the $\beta=21$ Sb b_2 level), because its wave function penetrates most into the other side of the interface and thus is severely perturbed. The most dominant factor influencing the relative positions of deep levels in InAs and GaSb layers is the large band offset between the materials.

IV. SUMMARY

The calculations presented here call into question the common assumption that the character of an impurity in a superlattice will always be the same as in the bulk. We have presented calculations that indicate that the normal shallow dopant Ge in InAs may become a deep trap in a thin InAs quantum well, and that the common donor C_{In} in InAs may become an acceptor in a thick InAs quantum well of an InAs/GaSb superlattice.

We have elucidated the physics of deep levels in superlattices, and have found splittings of T_2 bulk levels and shifts of A_1 levels of order 0.1–0.2 eV for defects at the interface and less for impurities within two or three atomic planes of an interface. For impurities more distant from an interface, the effect of the superlattice is primarily to change the *window of observability* of the deep level: If one imagines the deep levels as being relatively fixed in energy, the role of the superlattice is to provide the band gap. As a result, for example, superlattices with small InAs quantum wells have sufficiently large band gaps that deep levels that are covered up by the bands in bulk InAs are uncovered and observable in the superlattice.

ACKNOWLEDGMENTS

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