Deep-Shallow Transitions and Loss of Amphoterism in Type-II Superlattices

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

Shang Yuan Ren and John D. Dow
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287
(Received 20 April 1992)

The traditional rules of effective-mass theory, that a substitutional dopant is a donor (acceptor) if it lies to the right (left) in the periodic table of the atom it replaces, are shown to be broken often in type-II-misaligned superlattices such as InAs/GaSb. Impurities commonly undergo deep-shallow transitions and transitions to "false valence," and group-IV substitutional dopants can lose their amphoterism as remote layer thicknesses are varied.

PACS numbers: 71.55.Eq, 71.70.−d, 73.20.Dx

The nature of substitutional dopants in semiconductors was first clarified by the effective-mass theory of Luttinger and Kohn [1], which explained the behavior of shallow donors and acceptors: For example, P in Si produces a rather delocalized hydrogenic effective-mass donor state that is easily ionized thermally and is responsible for n-type conductivity. The binding energy of a shallow impurity is of order $R^*=e^2/2\epsilon a^*$, where $a^*=\hbar^2\epsilon/m^*e^2$ is its Bohr radius, m^* is the adjacent band's effective mass, and ϵ is the dielectric constant of the host.

Implicit in the effective-mass theory is the idea that every substitutional impurity that lies to the right in the periodic table of the host atom it replaces is a donor, while an atom to the left is an acceptor. Absent from the theory is any explanation of why certain impurities produce levels energetically much deeper than R^* in the fundamental band gaps of their host semiconductors (such as O on a P site in GaP [2]), while some impurities actually change from donors to acceptors (such as In in $Pb_{1-x}Sn_xTe$, with increasing x [3]). Also missing is any criterion for why a particular impurity ion is stable in its host semiconductor. These deficiencies of the effective-mass theory were removed with the recognition that the theory omits rather large (often of order 4 eV or larger) "central-cell" corrections, which are responsible for dramatic alteration of the four bonds the impurity forms with its neighbors [4–7], as well as for shifts of the hydrogenic levels. For s- and p-bonded impurities, these altered bonds produce an s-like A_1 and a p-like T_2 impurity state in the vicinity of the fundamental band gap, and the location of those localized "deep level" states with respect to the Fermi energy and the band edges, not the position in the periodic table, determines the doping character of the impurity. For example, P in Si has both its s- and p-like deep levels *above* the conduction band minima of Si (and above the Fermi energy). Hence, although the extra electron of neutral P wants to occupy the lowest (s-like) deep level above the conduction minima, the electron spills out of the localized state, leaving P autoionized as P^+. Then the extra electron is bound by the effective-mass Coulomb potential of P^+, occupying a rather delocalized hydrogenic orbital with a radius of order a^* and shallow binding energy of order R^*.

Few physicists realize that, if the s-like deep level of P had fallen not in the conduction band but well in the fundamental gap of Si, then P would not have been a shallow donor: Its stable ground state in otherwise intrinsic Si would not have been P^+, but P^0 in the central cell, and P would have been a deep impurity with a level in the gap occupied by one electron and one hole (when neutral) —capable of trapping an electron or a hole and tending to make the material semi-insulating, rather than n type. In fact, by alloying Si with Ge as suggested by Newman and Dow [8], Bunker *et al.* observed this deep level of Si descend into the gap, which corresponds to a shallow-to-deep transition in the doping character of the impurity [9]. Moreover, had this s-like deep level fallen energetically in the valence band of Si, the ground state of the impurity would have been P^-, and P would have become a shallow *acceptor*, doping Si *p type* (see Fig. 1). In this last case, P, when viewed from the framework of effective-mass theory, appears to have a valence different by two (P^- instead of P^+) from what is expected, termed a "false valence." Such a false valence was proposed by Lent *et al.* [3] to explain the behavior of In in $Pb_{1-x}Sn_xTe$ crystalline alloys as a function of alloy composition x (substitutional In is a donor in PbTe, but an acceptor in SnTe), but has never before been proposed for a III-V semiconductor.

The purpose of this Letter is to show theoretically that type-II-misaligned superlattices are especially prone to having impurities exhibit doping characters that are anomalous in the framework of effective-mass theory: Expected shallow donors are often either deep traps or false valence shallow acceptors, and expected acceptors are traps or donors; group-IV impurities in III-V compounds, which are expected to be amphoteric (donors on cation sites and acceptors on anion sites), can lose their amphoterism in such superlattices. Indeed, for III-V semiconductors type-II superlattices are the structures most likely to exhibit false valence.

A type-II-misaligned superlattice, such as [001] $N_{InAs}\times N_{GaSb}$ InAs/GaSb, is one in which the fundamental band gap and the conduction band edge of one constitu-

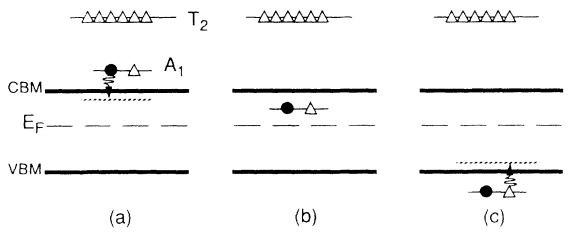

FIG. 1. Schematic illustration of three conceivable deep level positions for a single substitutional impurity such as P in bulk intrinsic Si: In all cases, we assume that the p-like T_2 level is well above the conduction band edge. (a) Shallow donor case, with the s-like A_1 level above the conduction band minimum (CBM), wanting to be occupied by one electron and one hole when P is neutral. The electron (solid circle) is autoionized, because the level is above the CBM and the Fermi energy. P^+ is formed and binds the extra electron in the shallow donor level from which it can be thermally ionized, leading to semiconductivity. (b) The deep trap case: The s-like deep level is in the gap and, in otherwise intrinsic material, is occupied by an electron and a hole (open triangle) and can trap either an electron of opposite spin or a hole but, for most energies, is too far from either band edge to be thermally ionized. (c) False valence acceptor case (cannot occur for P in Si): The deep level is resonant with the valence band and the hole in it is autoionized, forming P^- and a shallow acceptor. Group-IV donors, such as C_{In} in InAs layers of InAs/GaSb, can correspond to either case (a), (b), or (c), depending on the layer thicknesses of the superlattice. Antisite defects in InAs, such as As_{In}, when neutral, have two electrons in the A_1 level, not just one.

ent (InAs) lie lower in energy than the valence band edge of the other (GaSb). The conduction and valence band edges of such a type-II-misaligned superlattice can be manipulated (by choosing layer thicknesses) to occur almost anywhere throughout the range of energies from the higher conduction band edge of the two constituents (GaSb; the limit $N_{InAs} \rightarrow 0$) to the lower valence band edge (of InAs; for $N_{GaSb} \rightarrow 0$). Hence, by varying the layer thicknesses N_{InAs} and N_{GaSb}, it is possible to select a valence-band-maximum energy *for the superlattice* [10] anywhere from the valence band edge of InAs ($N_{GaSb}=0$) to the valence band edge of GaSb ($N_{InAs}=0$)—namely, anywhere in the fundamental gap of InAs, plus in the valence band of GaSb and above the conduction band edge of InAs. Similarly, the conduction band edge of the superlattice can be chosen anywhere in the forbidden gap of GaSb, and even below GaSb's valence band maximum, down to the conduction band minimum of InAs. The physics involved is that, as N_{GaSb} increases from zero, the conduction band of InAs experiences quantum confinement due to the GaSb barriers; similarly, the GaSb valence band experiences decreasing confinement as N_{GaSb} increases. Thus the conduction and the valence band edges of the superlattice move upwards in energy. The characteristic layer thickness below which such confinement occurs is an effective-mass Bohr radius a^*, typically tens or hundreds of angstroms.

Since deep impurity levels have wave functions with radii of only a few angstroms, they are virtually unaffected by the changes in layer thickness on the tens or hundreds of angstroms scale that alter the superlattice's band edges rather dramatically, and one can think of the band edges being altered without altering the deep levels. *Hence all of the impurities that produce deep levels in the fundamental band gaps of either bulk InAs or bulk GaSb can have those levels "covered up" by engineering the superlattice's layer thicknesses so that those deep levels of either InAs or GaSb lie resonant with either the conduction band or the valence band of the superlattice.* For an otherwise undoped superlattice, when this covering up occurs the deep traps become shallow impurities, and the impurities change their doping characters, most often from semi-insulating to n type (deep levels in the conduction band) or to p type (levels in the valence band). Shallow donors in InAs, such as group-IV impurities on In sites (e.g., C_{In}), may have their deep levels resonant with the conduction band in bulk InAs, but may become deep traps in some $N_{InAs} \times N_{GaSb}$ InAs/GaSb superlattices as the superlattice conduction band edge passes up through one of the deep levels (e.g., the s-like A_1 level of C_{In}) as N_{GaSb} increases from zero (InAs); some can even become shallow false valence acceptors in other superlattices (as the fundamental band gap passes up through the deep level until the level lies resonant with the valence band), even though their local environments do not change; see Fig. 2. For this reason, the type-II-misaligned superlattices will be especially interesting laboratories for studying the physics of impurities in semiconductors: the transitions of impurities from shallow to deep, and the transitions from deep to false valence shallow—such as a group-IV impurity on an In site in InAs becoming an acceptor in some superlattices.

To explore this physics, we have computed the conduction and valence band edges of $N_{InAs} \times N_{GaSb}$ [001] superlattices, and the positions of the s-like deep levels of the group-IV impurities C, Ge, and Si, and the group-V "antisite" defects As, P, and Sb, all on an In site near the center of an InAs layer, as functions of N_{InAs} and N_{GaSb}, where this notation means a superlattice whose fundamental period is N_{InAs} bilayers of InAs and N_{GaSb} bilayers of GaSb. The band structures of the superlattices are computed using the empirical tight-binding model of Vogl, Hjalmarson, and Dow [11], which, by design, obtains conduction band edges accurately—a feature of few electronic structure theories other than empirical tight-binding and empirical pseudopotential theory [12], and rather cumbersome self-energy-corrected *a priori* methods [13]. The deep-level theory follows the work of Hjalmarson *et al.* [6], which solves the secular equation

$$\underline{V}^{-1} = P \int dE' \, \delta(E'\underline{1} - \underline{H}_0)/(E - E') ,$$

where $\underline{V}$ is the defect central-cell potential matrix, approximated as localized in a single unit cell, after Hjal-

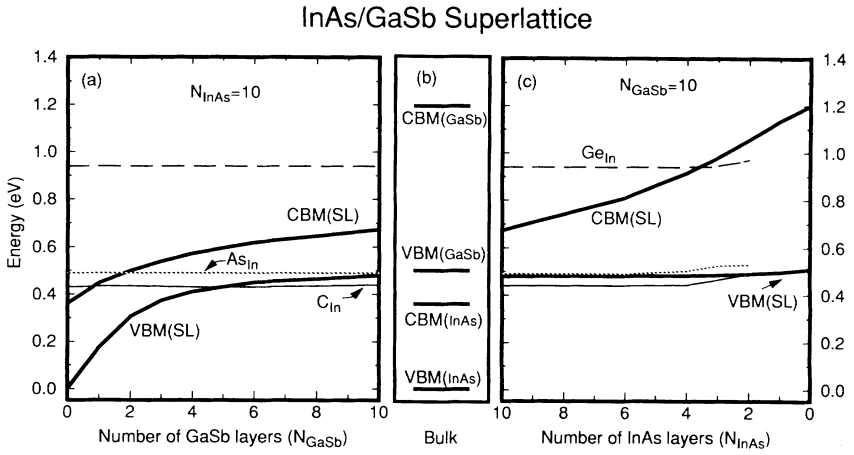

FIG. 2. Calculated band edges and deep levels of In-site C, As, and Ge in [001] $N_{InAs} \times N_{GaSb}$ superlattices at 300 K. P, As, Sb, and Si lie approximately 0.03, 0.05, 0.39, and 0.54 eV above the C level. (a) $N_{InAs}=10$, with varying N_{GaSb}; (b) the band edges of bulk InAs and GaSb; and (c) $N_{GaSb}=10$, with varying N_{InAs}. Note that the abscissa is reversed in (c).

marson *et al.*, $P\int$ denotes a principal-value integral over all energies E', and $\underline{H}_0$ is the host (perfect superlattice) Hamiltonian operator, in the empirical tight-binding representation. In this well-accepted approximation, the long-ranged Coulomb potential responsible for shallow donor or acceptor states is omitted, and treated as a perturbation later. The resulting deep levels and band edges are given in Fig. 2, as functions of N_{InAs} and N_{GaSb}. The shallow donor (acceptor) levels follow the conduction (valence) band edges and lie an energy of order R^* from them in the gap, and so are not distinguished from the band edges in Fig. 2.

Concentrating on the fact that we make allowances for any theoretical uncertainty below, we first consider the predictions for the antisite defect As_{In}. In bulk InAs, the s-like A_1 level of this defect lies within the conduction band, and its two extra electrons spill out of that level, forming As^{++}, which produces a shallow (double) donor, doping the material n type. When, for increasing layer thickness N_{GaSb}, the gap ascends through the level, the extra electrons are trapped on the deep level, and the stable ground state of antisite As in an InAs layer becomes As^0 (in otherwise intrinsic material), and As_{In} becomes a deep hole trap. When the valence band edge of the superlattice moves up through the deep level (as it does for 20×20 InAs/GaSb; in Fig. 2 it almost descends into the valence band for the 10×10 superlattice), the level is filled by two electrons, the impurity is electrically neutral, and the defect only a short-ranged scatterer of free carriers—relatively inactive and inert. Hence, with increasing N_{GaSb}, antisite As changes from a donor to a deep hole trap to an inert impurity with a (doubly) filled s-like deep level in the valence band.

In-site C exhibits similar behavior, as discussed above and displayed in Fig. 2. Not shown in the figure is the fact that C on an As site produces deep A_1 and T_2 levels in the valence band, and hence is a shallow acceptor for all values of the layer thicknesses N_{InAs} and N_{GaSb}. Hence the theory predicts that, on an As site, C is always an acceptor, while on an In site in the superlattice it is sometimes a donor (as in bulk InAs) but sometimes an acceptor—and hence loses its amphoteric doping character whenever N_{GaSb} is large enough that C_{In} is not a donor; see Fig. 2.

The essential physical feature for achieving these two phenomena, (i) the change of character of the As antisite defect from a double donor to a hole trap to an inert center with a deep level in the valence band, and (ii) the change of C on the In site from a donor to a deep trap to a false valence acceptor, with its attending loss of amphoterism, is the type-II-misaligned character of the InAs/GaSb band edges: The conduction band edge of bulk InAs and the As_{In} and C_{In} s-like deep levels all lie at lower absolute energy than the valence band edge of GaSb. Thus the effect of "superlatticing" the GaSb with the InAs, as the GaSb layer thickness increases from zero, is first to move the InAs conduction band edge upwards in energy, through the deep levels that were just above the conduction band edge of bulk InAs, and then second to move the valence band edge of the superlattice through the deep levels also. Hence, changes of doping character (shallow to deep and deep to false valence shallow) are likely to be common in type-II-misaligned superlattices, for any impurities that have their deep levels energetically rather near one of the constituents' band gaps.

The predictions of the theory for a given defect potential $\underline{V}$ are very accurate, because they follow from the analytic structure of the theory of deep levels [6]. However, the association of a given defect potential matrix with a specific impurity can introduce errors as large as 0.3 eV in the predicted energy levels [14]. Thus the predictions must be viewed as appropriate for a *class* of impurities, and the impurities assigned to a specific level may have to be revised in the light of experiments. For example, if the

C_{In} deep level were to lie in the gap of InAs rather than in the conduction band as predicted, the impurity scale should be shifted downwards more or less rigidly, until the theory and the data coincide. This would very likely bring Si to a level similar to the predicted C level—and the physics predicted here would still hold, but for Si rather than C. We do note that shallow donor and acceptor levels associated with the group-IV impurities Ge, Si, and Sn have been reported for InAs [15], facts fully consistent with the theory.

Carbon doping of InAs, according to the lore, has little effect on the carrier concentration. This lore probably means either (i) that C occupies anion and cation sites almost without preference, producing self-compensating shallow levels, or (ii) that our predicted C level for the In site could be at slightly lower energy, in the gap. Since there is an emerging consensus that C preferentially occupies anion sites in most other III-V semiconductors, the possibility that C produces a deep level in the fundamental band gap of InAs should be considered seriously—and implies that C will become a false valence acceptor on the In site in some InAs/GaSb superlattices. Thus, even if p doping with C is difficult to achieve in bulk InAs, this may not be the case in certain InAs/GaSb superlattices.

In any case, the present *picture* of impurity behavior is qualitatively very sound, and the predictions of interesting physics, shallow-deep transitions, and false valence impurities in type-II-misaligned superlattices are expected to be confirmed.

S.Y.R. and J.D.D. gratefully acknowledge the support of the U.S. Air Force Office of Scientific Research (Contract No. AFOSR-91-0418).

[1] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, pp. 258–321; J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 969 (1955).

[2] D. J. Wolford, W. Y. Hsu, J. D. Dow, and B. G. Streetman, J. Lumin **18/19**, 863 (1979).

[3] C. S. Lent, M. A. Bowen, R. S. Allgaier, J. D. Dow, O. F. Sankey, and E. S. Ho, Solid State Commun. **61**, 83 (1987).

[4] W. Y. Hsu, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. B **16**, 1597 (1977).

[5] C. A. Swarts, D. L. Miller, D. R. Franceschetti, H. P. Hjalmarson, P. Vogl, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. B **21**, 1708 (1980).

[6] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[7] S. Y. Ren, Sci. Sin. **XXVII**, 443 (1984), and references therein.

[8] K. E. Newman and J. D. Dow, Solid State Commun. **50**, 587 (1984).

[9] B. A. Bunker, S. L. Hulbert, J. P. Stott, and F. C. Brown, Phys. Rev. Lett. **53**, 2157 (1984).

[10] The valence band maximum (conduction band minimum) of the superlattice is the same as the $n=1$ quantum-well state of the valence (conduction) band.

[11] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983). We adjusted the parameter $E_{s,c}$ for InAs, GaSb, InSb, and GaAs, respectively, to -2.8142, -4.0418, -3.5515, and -2.8285 eV to obtain room-temperature band gaps of 0.36, 0.69, 0.17, and 1.43 eV, respectively.

[12] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **10**, 5095 (1974); **14**, 556 (1976).

[13] C. S. Wang, M. R. Norman, W. E. Pickett, and H. Krakauer, Bull. Am. Phys. Soc. **32**, 820 (1987); M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986); Phys. Rev. Lett. **55**, 1418 (1985).

[14] We have omitted charge-state splittings of the deep levels. With each additional electron occupying it, a deep level moves up in energy of order 0.1 eV. See G. Kim, J. D. Dow, and S. Lee, Arabian J. Sci. Eng. **14**, 513 (1989); Phys. Rev. B **40**, 7888 (1989).

[15] M. I. Guseva, N. V. Zotova, A. V. Koval, and D. N. Nasledov, Fiz. Tekh. Poluprovodn. **9**, 901 (1975); **8**, 59 (1974); [Sov. Phys. Semicond. **9**, 591 (1975); **8**, 34 (1974)].