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Vacancy complexes in GaAs: Effects on impurity compensation

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The energetics of shallow impurity compensation in GaAs via reactions of the type $V_{\mathrm{As}} \rightarrow (V_{\mathrm{Ga}} + \mathrm{Ga}_{\mathrm{As}})$, where V denotes a vacancy and $\mathrm{Ga}_{\mathrm{As}}$ a Ga-antisite defect is examined. It is proposed that in n-type GaAs this single-atom-displacement reaction is unstable with respect to a similar type of process, namely, $2V_{\mathrm{As}} \rightarrow (V_{\mathrm{As}} + V_{\mathrm{Ga}} + \mathrm{Ga}_{\mathrm{As}})$. The latter does not lead to any compensation of donors, thereby removing discrepancies between theoretical predictions and experimental results on donor passivation by native defects in GaAs.

Native defects such as Ga and As vacancies, antisites, or interstitials and complexes thereof can occur in bulk GaAs during high-temperature crystal growth and may become frozen-in as the temperature is lowered. A defect as simple as a vacancy can lead to the generation of a host of other more complex defects as a consequence of atomic motion and rearrangement.[1] For example, in the reaction

$$V_{\mathrm{As}} \rightarrow (V_{\mathrm{Ga}} + \mathrm{Ga}_{\mathrm{As}}) , \tag{1}$$

which is shown schematically in Figs. 1(a) and 1(b), a vacancy on an As site is transformed into a Ga-vacancy and a Ga-antisite defect as a result of the hop of a nearby Ga atom into the As vacancy. The energetics of such defect reactions are of considerable interest since they determine the relative abundances of various defect species.[1,2] For the above reaction, the atomic rearrangement has a major impact on the electrical activity of the defect.[1] The As-vacancy defect on the left-hand side of Eq. (1) gives rise to Ga dangling bonds with energies near the GaAs conduction-band minimum (CBM) and acts as a multiple donor. Both the V_{Ga} and $\mathrm{Ga}_{\mathrm{As}}$ defects resulting from the reaction are, however, strong acceptors. The relative stability of the defects on the two sides of Eq. (1), therefore, has a striking dependence on the Fermi-level position E_F with the total-energy difference changing sign as E_F is swept across the band gap.[1]

Baraff and Schlüter have examined the total energies of this and similar types of reactions using an *ab initio* self-consistent pseudopotential approach.[1] They have suggested that because of the very sizable Fermi-level dependence of the energy difference in Eq. (1) strong donor-acceptor transitions should occur as E_F is varied within the band gap. Their calculations predict that for E_F near the CBM it would be energetically favorable to create acceptor-type defects and as a result the reaction will be driven to the right. Conversely for E_F near the valence-band maximum, donorlike defects become energetically more favorable and the reaction is driven to the left.

In a recent Comment, Hurle[3] has raised questions concerning this self-compensation mechanism. Specifically, he points out that since there are about 10^{17}–10^{18}-cm^{-3} As vacancies in "as-grown" GaAs, any attempt to obtain n-type doping would lead to compensation until the donor concentration exceeds that of the As vacancies. The experimental observations are, however, contrary to this prediction in that doping levels much below the As vacancy concentration can be achieved.[3] Hurle has suggested that either the calculated reaction energies are significantly different from their true values or that some other competing reaction which leaves the reactants in an uncharged state occurs preferentially. In this paper we follow the latter suggestion and show that a very simple modification of the reaction given in Eq. (1) completely removes the discrepancy between the theoretical results and the exper-

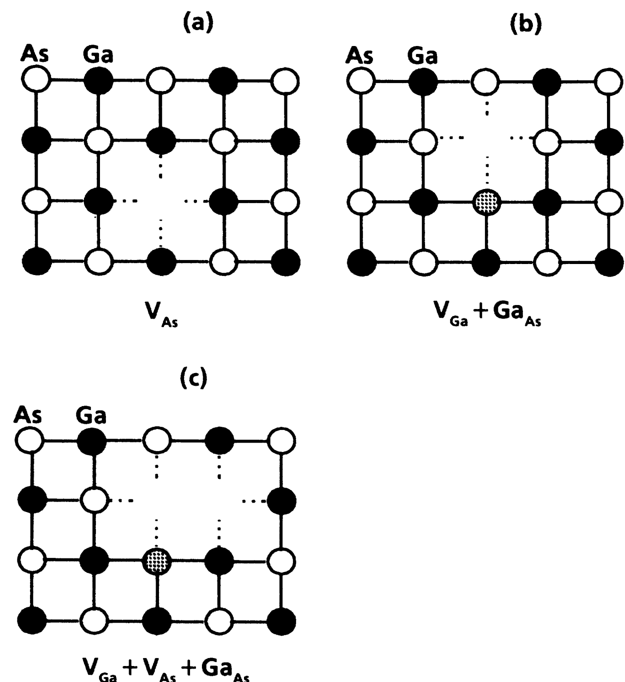

FIG. 1. (a) An arsenic vacancy in a GaAs lattice is shown schematically. Broken bonds are shown as dashed lines. (b) A $(V_{\mathrm{Ga}} + \mathrm{Ga}_{\mathrm{As}})$ vacancy-antisite complex obtained from (a) by a Ga nearest-neighbor hop where the antisite is shown as a shaded circle. This complex acts as a strong acceptor and would lead to the passivation of donors in n-type GaAs. (c) A defect complex consisting of $(V_{\mathrm{Ga}} + V_{\mathrm{As}} + \mathrm{Ga}_{\mathrm{As}})$ which results from the capture of a free As vacancy by the complex in (b). In n-type GaAs this divacancy-antisite complex is calculated to be energetically more favorable than the one shown in (b) and is calculated to be electrically inactive.

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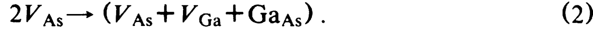
imental data.

Our idea is to add an As vacancy to each side of Eq. (1) so that the reaction is changed to



$$2V_{\mathrm{As}} \rightarrow (V_{\mathrm{As}}+V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}})\ . \qquad (2)$$

The defect complex on the right-hand side of Eq. (2), shown schematically in Fig. 1(c), consists of a divacancy coupled to a Ga antisite. Through simple electron counting and separately through tight-binding calculations,[4] we find that this new defect complex is *neutral*. The easiest way to see this is by using a fractional occupancy for the dangling-bond orbitals.[5] The As vacancy on the right-hand side of Eq. (2) acts as a donor and leads to three Ga dangling-bond orbitals each with $\frac{3}{4}$ electron on it. The Ga antisite is an acceptor. It needs $3\times\frac{5}{4}$ electrons to satisfy the bonding requirements with its three Ga nearest neighbors. Since it has only three valence electrons the $\mathrm{Ga}_{\mathrm{As}}$ antisite is a $\frac{3}{4}$ electron acceptor.[6] In addition, the two partially filled As dangling bonds created by the Ga vacancy also act as $\frac{3}{4}$ electron acceptors. Overall, the numbers of electrons in donor states matches exactly the number of electrons in acceptor states making the complex electrically inactive if charge transfer between the acceptorlike and donorlike states can take place.

The empirical tight-binding total-energy minimization method[4] was used to test these ideas more quantitatively. The approach is the same as that employed in previous surface studies.[4] Bloch functions constructed from s, p_x, p_y, and p_z atomic orbitals were used in the calculation of the electronic structure. Periodic boundary conditions were imposed on 32 (and 64 atom), body-centered-cubic (and cubic) unit cells. The tight-binding parameters (in eV) used in the electronic structure calculations are given by $E_s(\mathrm{Ga})=-3.19$, $E_s(\mathrm{As})=-8.21$, $E_p(\mathrm{Ga})=1.282$, $E_p(\mathrm{As})=3.473$, $V_{ss\sigma}=-1.69$, $V_{sp\sigma}=2.373$ (for Ga-s with As-p interaction), $V_{sp\sigma}=2.057$ (for As-s with Ga-p interaction), $V_{pp\sigma}=3.508$ eV, and $V_{pp\pi}=-0.963$. For this choice of parameters the bulk valence-band maximum is at zero eV. The evaluation of the total energy involves additional two-body terms which were determined from the cohesive energy, lattice constant, and the bulk modulus.[4] They are given (in eV) by $U_0=5.24$ eV, $U_1=-4.49$, and $U_2=13.58$.[7] Equilibrium atomic positions for the defects on the right-hand sides of Eqs. (1) and (2) were calculated by an iterative Hellmann-Feynman based total-energy minimization procedure.[4]

The results of the calculations show an extremely large lattice relaxation for the divacancy-antisite complex in Eq. (2). As expected from other studies on surfaces, the relaxations lead to a nearly sp^2-like bonding with angles of close to 117° at the Ga antisite and at the Ga dangling bond sites and to s^2p^3-like bonding with reduced angles of about 100° at the As dangling-bond sites.[4] The large orbital rehybridizations resulting from lattice relaxation lead to the desired charge transfer between the atoms. No defect states in the band gap is found for the relaxed structure in its neutral state. The relative energy difference between the two reactions given in Eqs. (1) and (2) were also examined. For n-type GaAs with E_F near the CBM, the reaction given by Eq. (2) is found to be at least 0.5 eV more favorable than its counterpart $2V_{\mathrm{As}} \rightarrow 2(V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}})$ obtained from a doubling of the defect concentrations given by Eq. (1). The stable state of the $(V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}})$ complex n-type GaAs is found to occur for a triply negative charge state. Inclusion of electronic repulsion effects which are neglected in the tight-binding calculation should make the $(V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}})$ complexes even less stable with respect to the $(V_{\mathrm{As}}+V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}})$ divacancy-antisite complex. The simple modification of Eq. (1) given by Eq. (2), therefore, resolves the discrepancy between theoretical predictions[1] of donor passivation in GaAs and experimental data[3] showing the absence of such an effect. The results of the calculations in n-type GaAs can be summarized by the following inequalities:

$$E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{Ga}_{\mathrm{As}}] < 2E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}] < 2E[V_{\mathrm{As}}]\ . \qquad (3)$$

The magnitudes of the energy differences in Eq. (3) can be obtained by combining the tight-binding results with those of Baraff and Schlüter[1] for the reaction in Eq. (1). We find

$$E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{Ga}_{\mathrm{As}}]-2E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}]=-0.5\ \mathrm{eV}$$

and

$$E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}]-E[V_{\mathrm{As}}]=-2.6\ \mathrm{eV}\ .$$

The divacancy-antisite complex is neutral and its energy does not vary with the Fermi energy. The Fermi-level dependence of the energy of the other defects in Eq. (3) has been previously calculated.[1] Using these results, we find the following relations for p-type GaAs:

$$E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{Ga}_{\mathrm{As}}] < 2E[V_{\mathrm{As}}] < 2E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}]\ , \qquad (4)$$

with

$$E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{Ga}_{\mathrm{As}}]-2E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}]=-4.9\ \mathrm{eV}$$

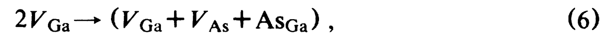
and

$$E[V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}]-E[V_{\mathrm{As}}]=+1\ \mathrm{eV}\ .$$

As a part of this study we have also analyzed the reactions analogous to those given by Eqs. (1) and (2), viz.,

$$V_{\mathrm{Ga}} \rightarrow (V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}) \qquad (5)$$

and



$$2V_{\mathrm{Ga}} \rightarrow (V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}})\ , \qquad (6)$$

in which the positions of the Ga and As atoms have been interchanged. The Ga vacancy is a strong acceptor whereas the As-vacancy and As-antisite defects on the right-hand side of Eq. (5) are strong donors. The energy difference between the two sides of Eq. (5) is again strongly E_F dependent and changes sign as E_F is swept through the gap with the reaction being pushed to the right in p-type GaAs.[1] The right-hand side of Eq. (6) is, however, predicted to be in a neutral charge state. In n-type GaAs, $(V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}})$ is more stable than $2V_{\mathrm{Ga}}$ and both are significantly more stable than $2(V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}})$, i.e.,

$$E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}] < 2E[V_{\mathrm{Ga}}] < 2E[V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}]\ , \qquad (7)$$

with $E[V_{\mathrm{Ga}}+V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}]-2E[V_{\mathrm{Ga}}]=-1$ eV and (using

the results of Ref. 1) $E[V_{Ga}]-E[V_{As}+As_{Ga}]=-3.4$ eV. Similarly, for p-type GaAs we find

$$2E[V_{As}+As_{Ga}]<2E[V_{Ga}]<E[V_{Ga}+V_{As}+As_{Ga}] \quad (8)$$

with $E[V_{As}+As_{Ga}]-E[V_{Ga}]=-2.2$ eV and $2E[V_{Ga}]-E[V_{Ga}+V_{As}+As_{Ga}]=-4.6$ eV. In obtaining these relations the Fermi-level dependence of the V_{Ga} and $V_{As}+As_{Ga}$ defects obtained previously by Baraff and Schlüter[1] has been used. Equation (8) shows that in p-type GaAs, $(V_{As}+As_{Ga})$ is by far the most stable of the three defects. Unlike the case for donors where Eq. (2) circumvents the passivation mechanism given by Eq. (1), acceptor compensation in GaAs can proceed via Eq. (5) if there are a sufficient number of Ga vacancies present. The concentration of free Ga vacancies at room temperature is probably too low, however, for the acceptor compensation to be noticeable.[8]

In conclusion, we have examined the electronic properties of vacancy-antisite complexes originating from simple Ga or As vacancies in GaAs. The effect of these complexes on shallow donor and acceptor compensation was studied. In particular, a *divacancy-antisite complex* [shown in Fig. 1(c)] arising from free As vacancies is proposed to be more stable than a vacancy-antisite complex [shown in Fig. 1(b)] and leads to a resolution of the experimental observation of a lack of donor passivation by As vacancies as is predicted by Eq. (1). The new defect complexes consisting of divacancies and antisites may also prove important in interpretation of positron-annihilation data of vacancy defects in GaAs.[9]

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[5]J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B **14**, 1623 (1976). In bulk GaAs, each Ga atom has three electrons and makes four bonds; therefore, there is formally $\frac{3}{4}$ electron in each Ga dangling-bond orbital. Similarly, there are $\frac{5}{4}$ electrons in each As dangling bond.

[6]In a threefold-coordinated configuration, Ga tends towards planar sp^2 bonding leading to an empty p_z orbital.

[7]Similar interatomic matrix elements were used for Ga-Ga and As-As interactions. Since the right-hand side of Eqs. (1) and (2) both contain a Ga antisite, the energy difference between the two defect complexes is not very sensitive to the empirical force constants.

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