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Binding and formation energies of native defect pairs in GaAs

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The formation energies of native lattice-site point defects and of nearest-neighbor lattice-site defect pairs in GaAs have been calculated by use of the self-consistent Green's-function technique. From these results, we deduce a binding energy of $\sim 2\pm 1$ eV for the pairs $V_{\mathrm{As}}+V_{\mathrm{Ga}}$, $\mathrm{As_{Ga}}+\mathrm{Ga_{As}}$, $\mathrm{As_{Ga}}+V_{\mathrm{As}}$, and $\mathrm{Ga_{As}}+V_{\mathrm{Ga}}$. We also obtain end-point energy differences for the vacancy migration hops $V_{\mathrm{Ga}}\rightarrow V_{\mathrm{As}}+\mathrm{As_{Ga}}$ and $V_{\mathrm{As}}\rightarrow V_{\mathrm{Ga}}+\mathrm{Ga_{As}}$. For these latter reactions, violent donor-acceptor transitions occur and the Fermi energy determines the stable form.

At the high temperatures associated with crystal growth, the solid phase of a compound semiconductor in equilibrium with the liquid or gas can exist over a narrow but finite range of atomic composition, i.e., with small deviations from exact stoichiometry.[1] As the temperature drops, the extent of this so-called existence region shrinks and eventually goes to zero. At the lowered temperatures, however, atomic diffusion rates have become so small that deviations from stoichiometry are frozen into the low-temperature crystal.[2]

Any deviation from exact stoichiometry implies the existence of defects to accommodate the imbalance. Whether the excess of (say) arsenic atoms in (say) GaAs will be accommodated as As^i (an arsenic atom in a normally empty interstitial position), as $\mathrm{As_{Ga}}$ (an arsenic atom on a gallium lattice site), as V_{Ga} (a gallium vacancy), or even as macroscopic As aggregates, will be determined in part by thermodynamic considerations and in part by kinetic ones. That is, are the atoms mobile enough to move towards an equilibrium which is itself changing as the temperature drops?

In this work, we address the defect distribution in equilibrium. We present calculations of the electronic structure and total energy for four nearest-neighbor, native, lattice-site defect pairs in GaAs. These calculations complement our recent work[3] on the electronic structure and thermodynamic properties of eight elementary native point defects in GaAs.

The calculations are done in the Green's-function scheme as described in Ref. 4, with the use of local-density theory, the Ceperly-Alder form of the exchange correlation energy, and first-principles pseudopotentials of the Hamann-Schlüter-Chiang type.[5] The Green's function used here, with the C_{3v} symmetry appropriate to nearest-neighbor defect pairs, extends over 26 lattice sites and carries eight Gaussian orbitals per site. The Green's functions used in Ref. 3, by comparison, had the T_d symmetry appropriate to isolated point defects and, for the substitutional site defects, extended over 29 lattice sites and carried 19 Gaussian orbitals per site. This latter set of orbitals gave a well-converged band structure of GaAs and a "scissors shift"[4,6] of $\Delta=0.6$ eV was used to adjust the conduction-band minima at X and L. In calculating the total defect energies, however, the effect of the scissors operator was evaluated and explicitly removed so that the total energies presented in Ref. 3 were local-density-theory values. For the smaller orbital set used in the C_{3v} Green's function, the band structure is less accurate, i.e., the gap opens up and no scissors shift is needed ($\Delta=0$).

Binding energies for the defect pairs were calculated by comparing results for isolated point defects and defect pairs, all calculated using the same C_{3v} Green's function. Most of the convergence error cancels out of the energy difference taken to evaluate the binding energy. The total (formation) energies, on the other hand, were evaluated by using the highly converged T_d Green's function to obtain the energy of the isolated defects,[3] and correcting these (where appropriate) by the binding energy. Atomic relaxations have not been taken into account in any of these calculations. Our experience has been that lattice relaxations will lower total energies by not more than a few tenths of an eV and we shall focus on properties unaffected by this uncertainty.

Let us now discuss the electronic structures of the nearest-neighbor pairs. The antistructure pair $\mathrm{As_{Ga}}$-$\mathrm{Ga_{As}}$ has a single E state (twofold orbital degenerate) in the gap and is neutral when this state is occupied by four electrons. The wave function associated with this level is composed of "wrong" Ga—Ga bonds which have been pushed up from the valence band, much as they would have been for the isolated GaAs antisite. The $\mathrm{As_{Ga}}$-like state of the pair, As—As antibonds pulled down from the conduction band, are not pulled far enough below the X and L minima to fall into the gap. This is in contrast to the isolated $\mathrm{As_{Ga}}$ antisite. The predicted level structure for the antistructure pair is that of a single donor, with the level $\epsilon(0/+)$ at $E_v+0.3$ eV.

The divacancy pair, V_{As}-V_{Ga}, has two states, an A and an E, in the gap. The A state is (except for three broken bonds instead of four) like the A_1 state of the isolated V_{As} while the E state is (again, except for three broken bonds instead of four) like the T_2 state of the isolated V_{Ga}. These two states are well separated spatially. It turns out that adding an electron to either of them causes its energy to move up higher than the other. Thus, the *Aufbauprinzip* of occupying all lower levels by an integer number of electrons and leaving all higher ones empty cannot be implemented here. This same problem occurs in certain atomic calculations within local-density theory.[7] We adopt the same somewhat heuristic solution as is customarily used.[7] We assign a fractional number of electrons to each of the two states, choosing that fraction so as to have the correct total charge, subject to the condition of lowest total energy, which implies that the occupancies are adjusted so as to make the two eigenvalues degenerate. The resulting level structure turns out to have four levels in the gap, with a separation of roughly 0.2 eV between them. This is smaller than the level spacing associated with most other point defects in GaAs.[3] It results from the delocalization caused by the simulataneous participation of all six broken bonds in one level. (This situation did not occur for the antistructure pair, where the two sets of wrong bonds maintained their separate identities.)

The pair V_{As}-$\mathrm{As}_{\mathrm{Ga}}$ is of interest, not only as the first step in the migration of the V_{Ga} (i.e., a nearest-neighbor As atom hops into the vacant gallium site and the above pair results), but also as a possible candidate for the structure of the midgap donor known as *EL*2, as first proposed by Lagowski *et al.*[8] We have described the properties of the pair elsewhere[9] and will not repeat that discussion here.

The fourth pair, V_{Ga}-$\mathrm{Ga}_{\mathrm{As}}$ is of interest as the first step in the migration of V_{As}. This pair has an E state in the gap which is a mixture of V_{Ga} and $\mathrm{Ga}_{\mathrm{As}}$ states. This state, being capable of holding four electrons, will give rise to four levels in the gap ranging from about $E_v+1.0$ eV for $\epsilon(3-/2-)$ down to $E_v+0.3$ eV for $\epsilon(0/+)$, with a spacing of about 0.2 eV between levels.

In Fig. 1, we give the binding energies of all four defect pairs as a function of the Fermi energy μ. The μ dependence arises because the levels of the defects as isolated entities and their levels as nearest-neighbor pairs do not coincide. Thus, electrons occasionally have to be transferred between the defects and a reservoir with energy μ during the process of pair formation or dissolution. Figure 1 shows that the μ dependence of the binding energy is, except for the last pair, relatively small and that the binding energy of all four pairs is positive (i.e., it costs energy to break up each pair) for all values of μ. Figure 1 also shows that the average binding energy is ~ 2 eV ± 1 eV regardless of the nature of the nearest-neighbor pair. The energy of 2 eV is roughly the energy of one bond or half the cohesive energy per atom.

Let us now consider the formation energy of three of the defect pairs, namely, the antistructure pair, which can be created from the perfect crystal by interchanging two nearest-neighbor atoms, the pair V_{As}-$\mathrm{As}_{\mathrm{Ga}}$ which can be created from the crystal containing an isolated V_{Ga} by a single As atom hop, and the pair V_{Ga}-$\mathrm{Ga}_{\mathrm{As}}$ which can be created from the isolated V_{As} by a single Ga atom hop. These three formation energies are shown in Fig. 2, again as functions of μ. These curves were obtained by combining the isolated defect total energies taken from Ref. 3 with the binding energies shown in Fig. 1.

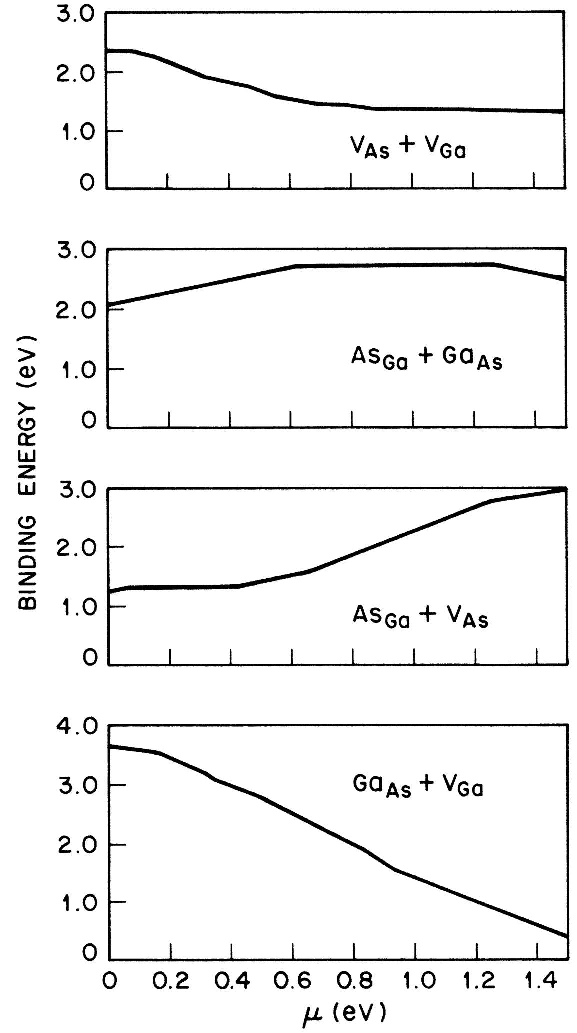

FIG. 1. Binding energy and its dependence on the Fermi-level position μ of the four nearest-neighbor native lattice-site defect pairs in GaAs.

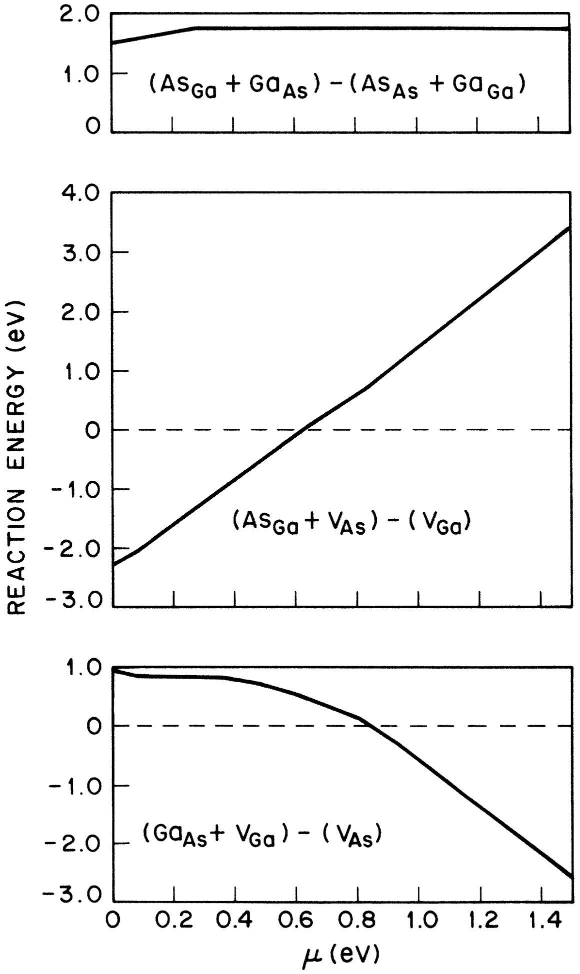

FIG. 2. Formation energies for the reactions (top) $\mathrm{As}_{\mathrm{As}}+\mathrm{Ga}_{\mathrm{Ga}} \rightarrow \mathrm{As}_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}$, (middle) $V_{\mathrm{Ga}} \rightarrow V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}$, and (bottom) $V_{\mathrm{As}} \rightarrow V_{\mathrm{Ga}}+\mathrm{As}_{\mathrm{Ga}}$ as a function of μ.

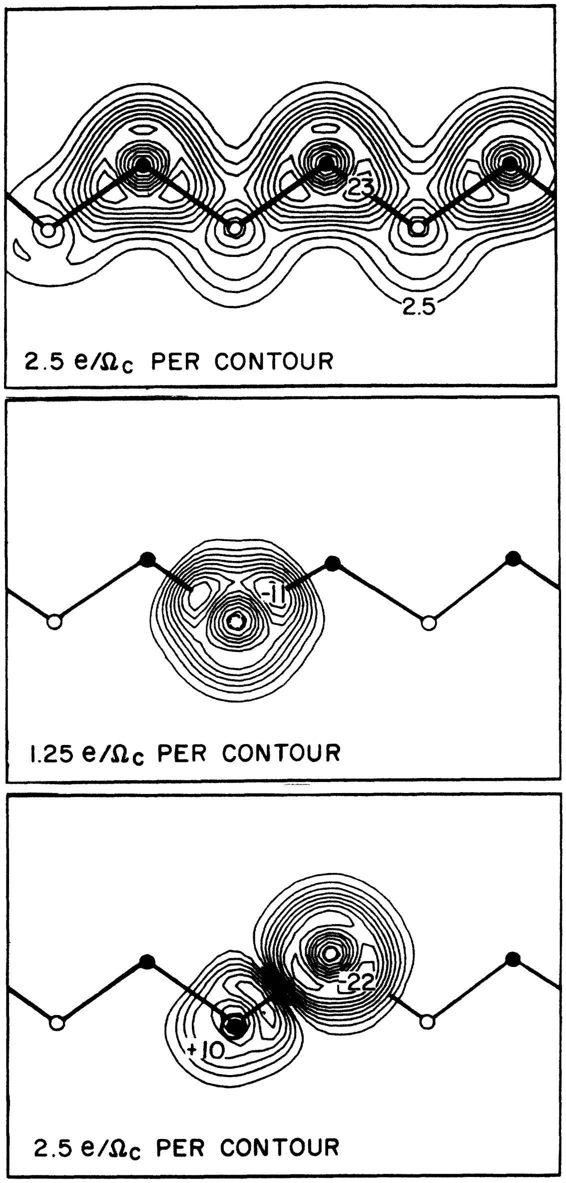

FIG. 3. Charge densities in the 110 plane: (top), total charge density for the perfect crystal; (middle), change in charge density of the isolated V_{Ga}; and (bottom), of the defect pair $V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}$.

The antistructure pair-formation energy is only weakly dependent on μ. Its value, roughly 1.7 eV, is significantly higher than Van Vechthen's earlier estimate[10] of 0.7 eV but comparable to Kraut and Harrison's[11] estimate of 2.28 eV. Nonetheless, the antistructure pair is still the least expensive defect to create from the perfect crystal, although it may be somewhat less abundant than previously assumed. The formation energy of ~ 1.7 eV puts a value of about ~ 0.3 eV on the formation of single "wrong" bond, i.e., a weakening of $\sim 15\%$.

The μ dependence of the formation energies of the other two pairs is much more striking. Each of these pair reactions, $V_{\mathrm{Ga}}\rightarrow V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}$ and $V_{\mathrm{As}}\rightarrow V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}$, represents the transformation between a strong donor V_{As} and a strong acceptor V_{Ga} by a single atom hop. The associated antisite defect is a much weaker perturbation on the crystal than is either vacancy, as is evident from the charge plots in Fig. 3. The formation energies for the pairs can be either positive or negative depending on μ because so many electrons are transferred to or from the defect during the reaction. As a result, the pair $V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}$ is stable relative to V_{Ga} at low values of μ while the pair $V_{\mathrm{Ga}}+\mathrm{Ga}_{\mathrm{As}}$ is stable relative to V_{As} at high values of μ.

It is interesting to note that as *separated* defects, V_{As} and $\mathrm{As}_{\mathrm{Ga}}$ are not stable relative to V_{Ga},[3] and that it is the binding energy which makes the energies of $V_{\mathrm{As}}+\mathrm{As}_{\mathrm{Ga}}$ and V_{Ga} comparable. The transfer of electrons to or from the defect can change the stable form from the isolated defect to the pair. This interplay between the energy needed to transform one form of the defect to the other and the energy available by having electrons in levels that sweep across the gap is at the heart of many of the bistable and metastable properties of deep level defects.[9] The calculations presented here make it likely that the isolated V_{As} would exhibit these same phenomena. Perhaps the reason that they have not been observed is that Ga-rich GaAs, which might be thought to contain isolated V_{As}, actually prefers to accommodate the Ga excess as isolated $\mathrm{Ga}_{\mathrm{As}}$ antisites, as was suggested in Ref. 3. However, it may also be the case that present technological interest has focused more attention on the As-rich forms of GaAs than on the Ga-rich ones.

In summary, these calculations have indicated that nearest-neighbor V_{As}-$\mathrm{As}_{\mathrm{Ga}}$ pairs should be an abundant defect in GaAs, and that although there may be antistructure pairs present, they are more costly to produce than has been previously assumed.

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