Electronic Structure, Total Energies, and Abundances of the Elementary Point Defects in GaAs

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The electronic structure and total energies of eight elementary isolated-T_d-site point defects in GaAs have been calculated with use of the self-consistent Green's-function technique. We evaluate reaction energies and from these, using simple thermodynamic considerations, we predict which native defects should be abundant in As-rich or Ga-rich and in *n*-type or *p*-type material. Comparison with available experiments confirms our findings.

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A primary goal of the study of point defects in semiconductors is to identify them. The electronic structure of a defect, i.e., its ionization energies, its internal excitation energies, and the symmetry of its localized states, is a powerful clue to its identity because that structure can be both measured experimentally and calculated theoretically with reasonable confidence.[1] In the compound semiconductors, like, e.g., GaAs, there is another powerful experimental tool available, namely, crystal growth under conditions of controlled nonstoichiometry. The crystal containing an excess of, say, As must contain a concentration of defects to accommodate that excess. Whether it will be accommodated by a concentration of interstitials As^i, of antisites $\mathrm{As_{Ga}}$, or of vacancies V_{Ga}, by complexes of these, or even by macroscopic As aggregates will, in equilibrium, be determined by thermodynamic considerations involving the total energies of the defects.

In this Letter, we report calculations of defect total energies[2-5] for the purpose of predicting the abundances of the native defects in a compound semiconductor. We have studied GaAs, and we deduce the dominant defect for As-rich versus Ga-rich material, for both undoped and doped material. We have investigated all eight possible elementary point defects with T_d symmetry and all possible reactions in which the defects can participate. Each reaction of the type $N_A A + N_B B \rightleftharpoons N_C C + N_D D$ has an associated temperature-dependent equilibrium constant K:

$$\frac{[C]^{N_C}\times[D]^{N_D}}{[A]^{N_A}\times[B]^{N_B}} \equiv K(T) = e^{-\Delta G/kT}, \qquad (1)$$

where $[A],\ldots,[D]$ are the concentrations of $A,\ldots,D$, and where $\Delta G = \Delta E - T\Delta S$ is the change in Gibbs free energy associated with the reaction. Each allowed reaction thus establishes a constraint among the various defect concentrations. Each defect also represents a deviation from stoichiometry and so for a crystal composed of N_{As} atoms of As and N_{Ga} atoms of Ga, the deviation from stoichiometry $\delta \equiv (N_{\mathrm{As}} - N_{\mathrm{Ga}})/(N_{\mathrm{As}} + N_{\mathrm{Ga}})$ can be expressed in the form $\delta = M_A[A] + M_B[B] + \ldots$, where $M = +2$ for $\mathrm{As_{Ga}}$, $M = +1$ for As^i, $M = -2$ for $\mathrm{Ga_{As}}$, etc. Knowledge of δ and of all the various K provides enough constraints to determine the defect concentrations.

Posing the problem of defect abundances in this way presupposes several conditions. It presupposes, first of all, that the growth and annealing process is sufficiently slow that true equilibrium can be reached, secondly, that all of the possible defects, i.e., not only the point defects but their complexes as well, are included in the description, and finally, that the Gibbs free energy ΔG can be evaluated with acceptable accuracy.

Our program is somewhat more modest than this. Because the state of the art of evaluating total defect energies is primitive compared to the needs of chemical accuracies, we confine ourselves to those situations where the calculational uncertainties will not invalidate our conclusions. Second, we neglect the $T\Delta S$ contribution to ΔG because the uncertainties in the calculated values of ΔE already exceed any reasonable estimate of $T\Delta S$. Third, we do not consider the role of defect complexes; these are beyond our computational ability at present. And finally, in this survey we do not study the effect of allowing atoms near the defect to relax, which would lower the defect total energy and alter the electronic structure. Our experience with other defects[6] has been that energy changes due to relaxation are in the range of 0.2 to 0.6 eV. In spite of these approximations and uncertainties several unambiguous results emerge from the calculations.

The calculations are done in the Green's-function scheme as described in Ref. 2, with use of local-density-functional theory, the Ceperley-Alder form of the exchange correlation energy, and first-principles nonlocal pseudopotentials of the Hamann-Schlüter-Chiang type. The resulting band structure for the perfect crystal yields a conduction-band structure too low with respect to experiment. Therefore, before evaluating the Green's function we shift the conduction bands rigidly upward by $\Delta = 0.6$ eV which approximately adjusts the X and L minima to experiment. We have shown[2] that this procedure which alters the total defect energy can be explicitly corrected for, to regain approximately the total energy as given by local-density-functional theory.

Let us now describe the results. We have studied the defects V_{Ga} and $\mathrm{As}_{\mathrm{Ga}}$ at the Ga site, V_{As} and $\mathrm{Ga}_{\mathrm{As}}$ at the As site, and As^i and Ga^i at T_{d1} (T_{d2}), the interstitial site of T_d symmetry for which the four nearest neighbors are As (Ga) atoms. The results of these calculations are summarized in the eight panels presented in Figs. 1 and 2, whose meaning we now explain, using As^i as an example.

The defect As^i has a state of T_2 symmetry in the gap, and when that state has $N_{T_2}=0$, 1, 2, or 3 electrons, the charge of the defect is 3+, 2+, 1+, or 0. The energy of the defect with charge N and a reservoir with chemical potential μ is then

$$\Delta E(N,\mu)=\Delta E(N)-\mu N, \qquad (2)$$

where $\Delta E(N)$ is the total energy as evaluated by the Green's-function method for the defect in the charge state N and where $\mu=0$ is the top of the valence band. The curves plotted in Figs. 1 and 2 are made up of line segments, i.e., the lowest value of $\Delta E(N,\mu)$ plotted versus μ. The breaks in the curve occur at those values of μ for which the charge of the lowest-energy state changes, a value of μ which, by definition, is an "energy level" in the gap. The defect energies are arbitrarily normalized such that the total energy of a unit cell of GaAs is equal to $E_0^{\mathrm{cell}}=-7.9$ eV.

Figures 1 and 2 convey several interesting findings. First, for the $\mathrm{As}_{\mathrm{Ga}}$ antisite, the levels we calculate here, $\epsilon(0/+)=1.50$ eV and $\epsilon(+/++)=1.25$ eV, are higher by about 0.4 eV than those given in our earlier calculation[7] as a result of improved numerical procedures. The agreement with the simplest interpretation of the experimental findings of Weber *et al.*[8] has therefore deteriorated although the inclusion of spin-polarization effects may improve it again. Second, for the $\mathrm{Ga}_{\mathrm{As}}$ antisite, two groups have seen levels which they attributed to this defect. Our calculation here, $\epsilon(--/-)=0.62$ eV and $\epsilon(-/0)=0.30$ eV, is more consistent with the observations of Wang, Lebedo, and Grimmeiss[9] (0.70 and 0.40 eV) than with those of Yu *et al.*[10] (0.23 and 0.077 eV). Third, in contrast to some analyses of defect abundances which assumed that Ga^i is an acceptor, our calculations here show it to be a donor, just like As^i. Fourth, our calculations show that at all values of μ, the Ga vacancy and Ga interstitial have opposite charges and thus attract each other, increasing the probability that they will mutually annihilate. The As vacancy and As interstitial, on the other hand, are both donors and tend to avoid each other. Once formed, they are more likely to last. This provides a first explanation of why, in the experiments of Pons and Bourgoin[11] on electron-irradiation–

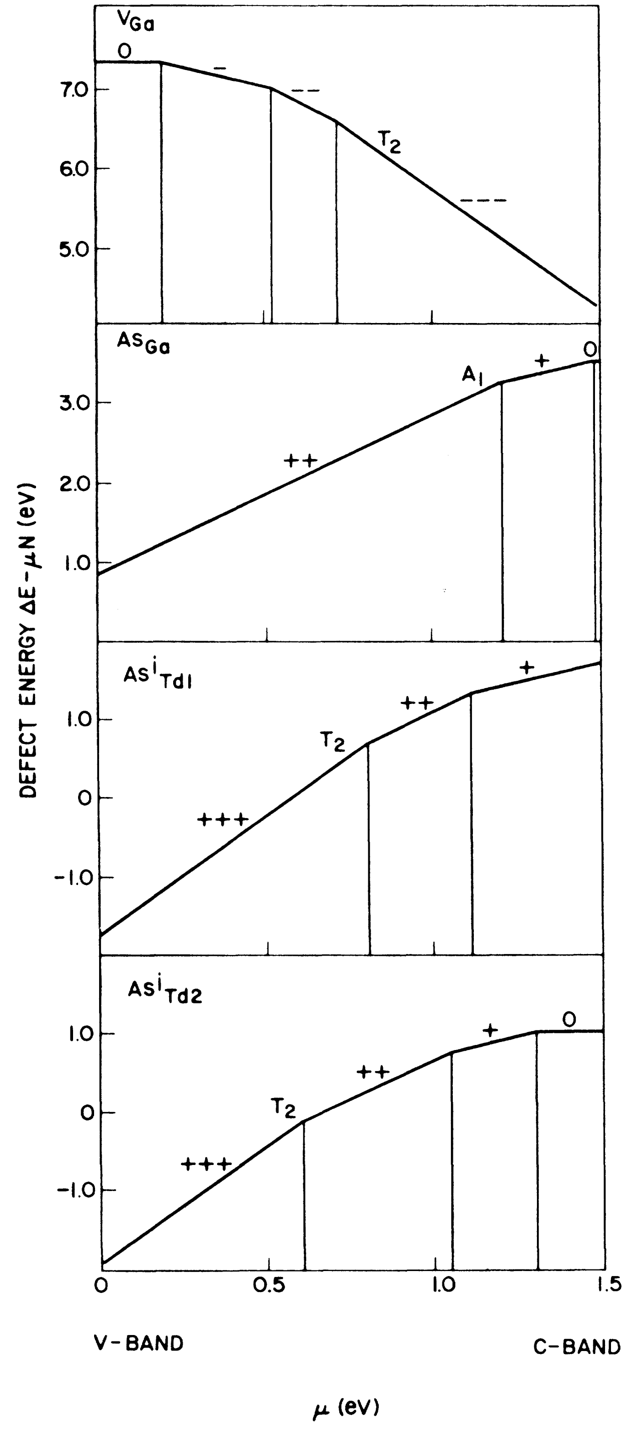

FIG. 1. Total energy $\Delta E-\mu N$ for different simple defects in GaAs. Shown are the defects occurring in As-rich material: V_{Ga}, $\mathrm{As}_{\mathrm{Ga}}$, $\mathrm{As}^i_{T_{d1}}$, and $\mathrm{As}^i_{T_{d2}}$. The lowest-energy charge states are plotted vs μ, the position of the Fermi level; the changes in charge state at deep levels and the character of the deep levels (A_1 or T_2) are indicated. The zero of energy has no intrinsic significance here.

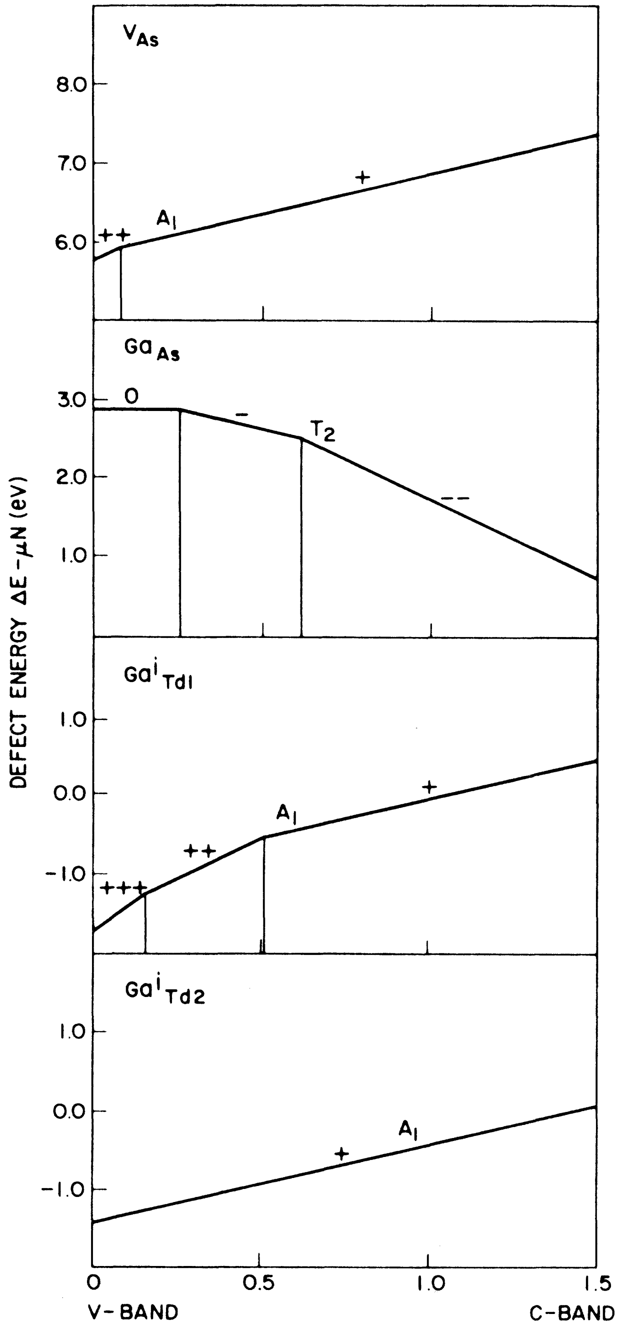

FIG. 2. As Fig. 1, but for Ga-rich material.

produced defects, the observed defects were, at the lowest values of electron beam energy, those produced by motion of As atoms, not Ga atoms.

In Fig. 3, we show reaction energies for three defect reactions, $0 \rightarrow V_{\mathrm{Ga}} + \mathrm{Ga}^i$, $0 \rightarrow V_{\mathrm{As}} + \mathrm{As}^i$, and $\mathrm{As}_{\mathrm{Ga}} + V_{\mathrm{As}} \rightarrow V_{\mathrm{Ga}}$. Here the energy scale is absolute. The first and second of these are related to the electron-irradiation defect-production experiments of Pons and Bourgoin.[11] They describe the extra energy stored in an *adiabatically* produced, infinitely separated vacancy-interstitial pair. These energies are in the 4–8-eV range, which is below, by a reasonable amount, the *barrier* of 7–11 eV which Pons and Bourgoin found for defect production. The third reaction (bottom panel of Fig. 3) is the reaction studied by Lagowski *et al.*,[12] who found that the abundance of $\mathrm{As}_{\mathrm{Ga}}$ antisites was severely inhibited by the inclusion of donors during the crystal growth process. As argued by them, our calculations demonstrate that the electrons needed to balance the reaction electrically help drive it to the right, and that four to six electrons are needed for each V_{Ga} produced by the disappearance of each $\mathrm{As}_{\mathrm{Ga}} + V_{\mathrm{As}}$ defect pair. Figure 3 emphasizes this, in that the defect energy is *strongly*

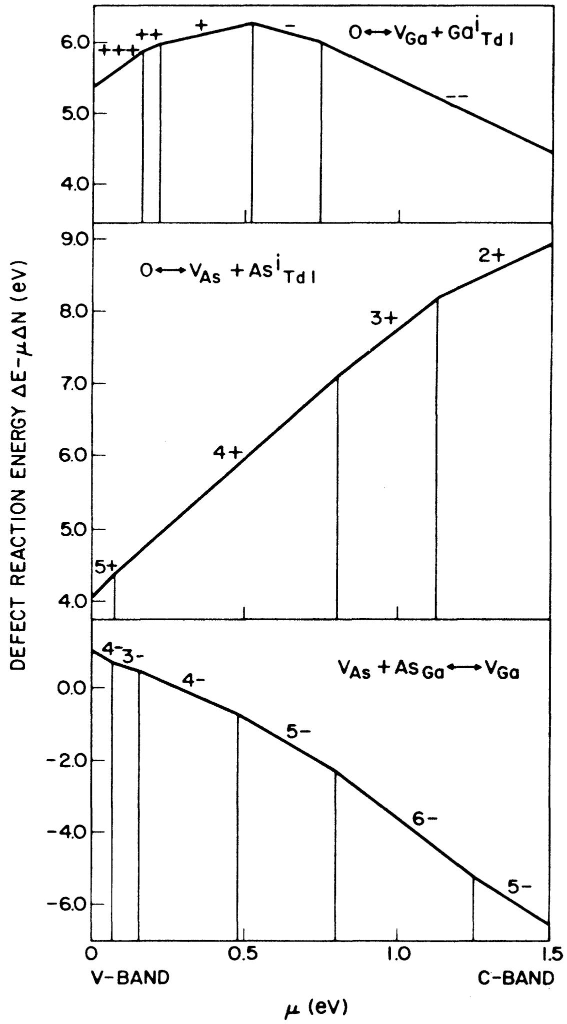

FIG. 3. Total reaction energies $\Delta E - \mu\, \Delta N$ for the defect reactions $0 \leftrightarrow V_{\mathrm{Ga}} + \mathrm{Ga}^i$, $0 \leftrightarrow V_{\mathrm{As}} + \mathrm{As}^i$, and $\mathrm{As}_{\mathrm{Ga}} + V_{\mathrm{As}} \leftrightarrow V_{\mathrm{Ga}}$, plotted vs μ, the position of the Fermi level.

dependent on μ, so that the reaction is driven to the left in p-type material and to the right in n-type material.

Finally, we discuss defect abundances: If all of the reaction constraint equations of the form (1) are solved under the conditions of, say, large As excess, the concentration of those defects which accommodate Ga excess, i.e., V_{As}, $\mathrm{Ga}_{\mathrm{As}}$, and Ga^i, will be so low that they can be ignored. In that case, we need to consider only the concentrations of the defects that accommodate As excess, i.e., V_{Ga}, $\mathrm{As}_{\mathrm{Ga}}$ and As^i. The reactions which establish equilibrium among these three are

$$V_{\mathrm{Ga}}+\mathrm{GaAs}\leftrightarrow \mathrm{As}^i, \quad \mathrm{As}_{\mathrm{Ga}}+\mathrm{GaAs}\leftrightarrow 2\mathrm{As}^i,$$

in both of which the crystal loses one unit cell when the reaction goes to the right. For a given deviation from stoichiometry the equilibrium concentrations can be computed if the reaction energies are known. Because the reaction energies are μ dependent[13] the concentrations found will also depend on μ. We find that for As-rich material, $\mathrm{As}_{\mathrm{Ga}}$ is the dominant defect in strongly p-type material while V_{Ga} is dominant in n-type material. The dominance of one or another type is not so great in Ga-rich material but, with somewhat less confidence, our calculations suggest $\mathrm{Ga}_{\mathrm{As}}$ to be the dominant defect in both p- and n-type material, with a possibility that V_{As} also appears in p-type material. One of the main results emerging from our calculations is that the isolated-T_d-site interstitials are thermodynamically much less likely under all conditions for which defect equilibration reactions can occur. This does not in principle exclude the possible existence of other, less simple, interstitial configurations. However, on general energetic grounds this is not likely.

Suppose now that the GaAs is intrinsic, so that μ itself is determined by the native defect content. Ga-rich material, containing the acceptor $\mathrm{Ga}_{\mathrm{As}}$, will grow p type. In contrast, however, As-rich material, assumed p (n) type, will contain the donor $\mathrm{As}_{\mathrm{Ga}}$ (acceptor V_{Ga}), thus growing n (p) type. The contradiction here means that there is no consistent solution for high or low μ, and μ will be driven to midgap so that both native defects $\mathrm{As}_{\mathrm{Ga}}$ and V_{Ga} are present in comparable abundance. Intrinsic material will thus, under As-rich growth conditions, be semi-insulating. These conclusions are in accord with what is observed in both Ga-rich and As-rich material.[14]

In summary, total-energy calculations of reaction energies of simple native point defects in GaAs can predict the natural abundance of defects induced by nonstoichiometric growth conditions. The results are in agreement with experiments where available.

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[1] See, e.g., *Proceedings of the Thirteenth International Conference on the Defects of Semiconductors, Coronado, California, 1984,* edited by L. C. Kimerling and J. Parsey (AIME Press, New York, 1984).

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[13] Thermodynamically, an equilibrium constant K should depend only on the temperature if the concentration of all the reactants and products, including any electrons or holes, is included in the definition. Our usage, for convenience here, leaves out their concentrations which of course depend on μ. One can easily use the values presented here to obtain constants K which are in fact μ independent by multiplying our values by the μ-dependent carrier concentrations.

[14] J. Lagowski and H. C. Gatos, in Ref. 1, p. 73.