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Energetics of the As vacancy in GaAs: The stability of the 3+ charge state

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Total-energy calculations predict that the As vacancy in GaAs adopts a 3+ charge state under p-type conditions, and that the formation energy of V_{As}^{3+} is competitive with that of the gallium interstitial Ga_i^{3+}. After a breathing-mode relaxation, which reduces the energy by more than 1.5 eV, the nearest-neighbor Ga atoms exhibit a nearly sp^2 bonding configuration. On the basis of our results we propose that charged anion vacancies with sp^2-bonded cation neighbors should be examined as possible mechanisms for the compensation of p-type doping in III-V and II-VI semiconductors, and as possible facilitators of acceptor diffusion and anion self-diffusion in these materials.

Point defects play a potentially important role in determining the position of the Fermi level in III-V and II-VI semiconductors.[1-3] Charged defects reduce the doping efficiency if their concentrations are comparable to those of the dopant atoms: p-type doping efficiencies are reduced by the formation of positively charged defects and n-type doping is inhibited by formation of negatively charged defects. Defects also mediate dopant diffusion and self-diffusion in GaAs. Under As-rich and n-type conditions the charged Ga vacancy mediates both Ga self-diffusion and the diffusion of donors residing on the group-III lattice sites.[4-9] Under the combination of p-type and Ga-rich conditions, the charged Ga interstitial is believed to be the dominant defect and to mediate the diffusion of acceptors.[6,10,11]

The motivation for calculating formation energies is to determine which defects are most abundant and therefore most likely to mediate diffusion or give rise to compensation effects. The III-V semiconductor GaAs has served as a model system for theoretical studies of point defects, but although several calculations of the energetics of point defects have been published,[1,6,12-14] the possibility of a 3+ charge state of the As vacancy has, to our knowledge, not been reported. The exploratory survey of native defect reaction energies performed by Baraff and Schlüter[1] indicated that if lattice relaxation is neglected, then the As vacancy would exist in the 1+ charge state over most of the gap, with the 2+ charge state occurring when the Fermi level is very close to the valence-band maximum. In this work we show that under p-type conditions a 3+ charge state of the As vacancy is stabilized by a large lattice relaxation in which the Ga atoms move away from the vacancy and adopt a nearly sp^2 bonding configuration. We find that the formation energy of V_{As}^{3+} has a minimum value of about 0.8 eV, and is competitive in energy with the triply charged Ga interstitial. This result leads us to suggest that charged anion vacancies, with sp^2-bonded cation neighbors, should be considered as possible mechanisms for the compensation of p-type doping in III-V and II-VI semiconductors (e.g., ZnSe). Such vacancies may also be important facilitators of acceptor diffusion and anion self-diffusion in this class of materials.

The present total-energy and force calculations are performed using the local-density-functional approximation and first-principles pseudopotentials as in our previous work.[6,7] We employ a supercell containing 32 lattice sites: 15 As atoms, 16 Ga atoms, and one As vacancy. The solutions to the Kohn-Sham equations are expanded in a plane-wave basis with a kinetic-energy cutoff of 8 Ry. The Brillouin-zone sums include two special k points.

The charge state of an As vacancy is specified by the number of electrons which occupy the a_1 and t_2 orbitals. The nondegenerate a_1 orbital corresponds to the fully symmetric combination of the four dangling hybrids of the Ga atoms surrounding the vacancy. In the 1+ charge state of an As vacancy the a_1 orbital is doubly occupied, and its Kohn-Sham single-particle energy is about 0.1 eV above the valence-band maximum. The threefold-degenerate t_2 complex is empty for all positively charged states. A 3+ charge state is obtained by removing the two electrons from the a_1 orbital.[15] By itself, this removal of electrons would initially lead to a very unstable configuration, *but as the four Ga atoms undergo a rehybridization towards sp^2 bonding the formation energy of the 3+ charge state decreases by more than 1.5 eV* and the energy of the (empty) a_1 orbital increases to a value about 1.1 eV above the valence-band maximum. In the fully relaxed configuration the four Ga atoms are each displaced from their ideal positions by 0.55 Å. This breathing mode relaxation results in a nearly planar sp^2 bonding configuration, with the Ga atoms located 0.25 Å above the plane formed by their three As neighbors. *This rehybridization is likely to be a general feature for the anion vacancies in III-V and II-VI semiconductors in which the a_1 orbital is empty.*

In previous calculations[6,7] we determined the formation energy of the 1+ state of the As vacancy to be (in electron volts):

$$\Omega(1+)=3.0+\mu_e-\tfrac{1}{2}\Delta\mu.$$

In this expression μ_e is the electron chemical potential measured from the valence-band maximum and $\Delta\mu$ is the differ-

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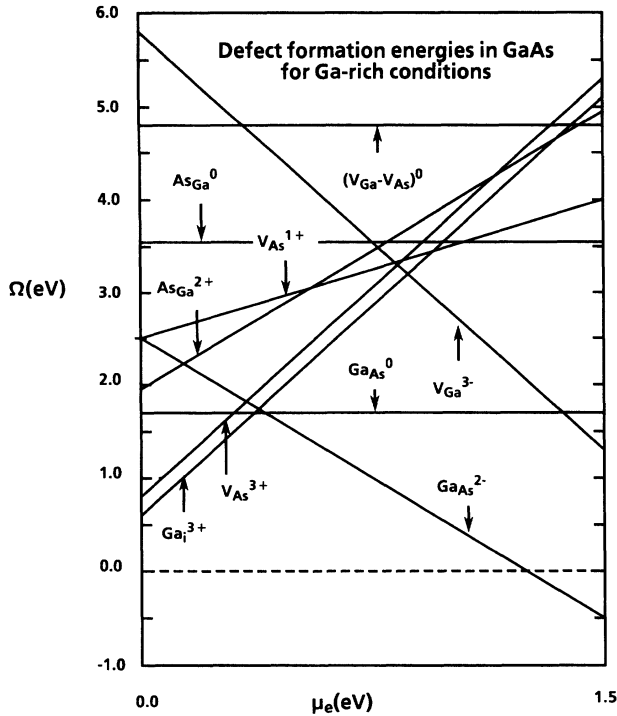

FIG. 1. Defect energies for the Ga-rich limit. In this limit the Ga chemical potential is equal to the calculated energy per atom of bulk Ga, and the corresponding As chemical potential is determined by equilibrium with bulk GaAs: $\mu_{\mathrm{As}}=\mu_{\mathrm{GaAs(bulk)}}-\mu_{\mathrm{Ga(bulk)}}$.

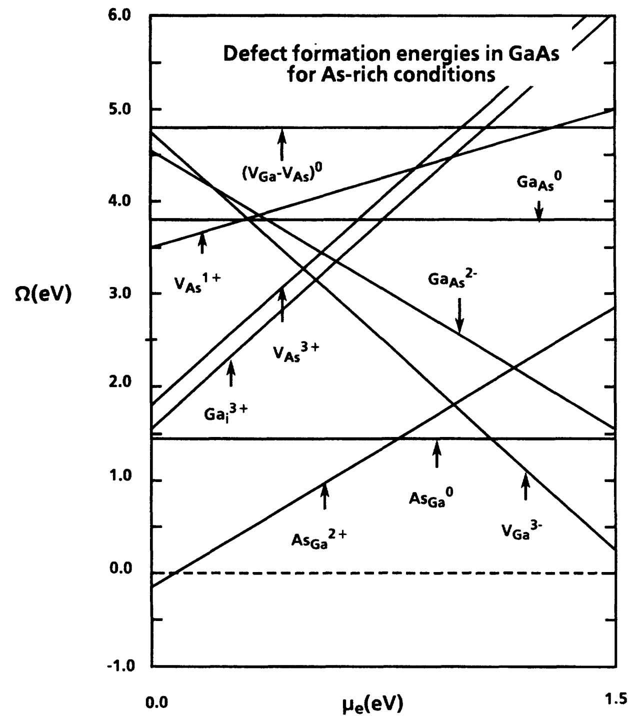

FIG. 2. Defect energies for the As-rich limit. In this limit the As chemical potential is equal to the calculated energy per atom of bulk As, and the corresponding Ga chemical potential is determined by equilibrium with bulk GaAs: $\mu_{\mathrm{Ga}}=\mu_{\mathrm{GaAs(bulk)}}-\mu_{\mathrm{As(bulk)}}$.

ence between the atomic chemical potentials of Ga and As: $\Delta\mu=(\mu_{\mathrm{Ga}}-\mu_{\mathrm{As}})-(\mu_{\mathrm{Ga(bulk)}}-\mu_{\mathrm{As(bulk)}})$. The values for μ_e range from 0 to E_{gap}. ($E_{\mathrm{gap}}\sim 1.5$ eV.) Values for $\Delta\mu/2$ range from -0.5 eV (As-rich limit) to 0.5 eV (Ga-rich limit). The present calculations for the triply charged As vacancy give

$$\Omega(3+)=1.3+3\mu_e-\tfrac{1}{2}\Delta\mu .$$

The thermodynamic transition level, defined as the electron chemical potential for which the formation energies of the two charge states are equal, is 0.85 eV. Thus in both intrinsic and p-type GaAs the 3+ charge state is energetically favorable with respect to the singly charged state, and when the Fermi level lies near the valence-band maximum the 3+ charge state is lower in energy by about 1.7 eV. The minimum formation energy occurs for p-type and Ga-rich conditions where $\mu_e=0.0$ and $\Delta\mu/2=0.5$ eV. Under these conditions $\Omega(3+)=0.8$ eV. This is comparable to the formation energy obtained for the triply charged Ga interstitial (in the As tetrahedral configuration), which we have found to be 0.6 eV under these conditions. The expected accuracy of the calculations is the same order as the 0.2-eV difference in energy between the interstitial and the vacancy. Therefore, it is possible that either, or both, of these defects play a role in mediating diffusion in GaAs. Specifically, arsenic self-diffusion in GaAs could occur via a second-nearest-neighbor hopping mechanism involving V_{As}^{3+} under p-type doping conditions. This would be analogous to the self-diffusion of Ga which is thought to be mediated by gallium vacancies.[8]

The formation energies of the As vacancies are shown in Fig. 1 along with those of several other native defects for comparison. The results shown are for the maximum possible Ga chemical potential that is $\mu_{\mathrm{Ga}}=\mu_{\mathrm{Ga(bulk)}}$. When μ_e is close to the valence-band maximum the interstitial $\mathrm{Ga}_i^{\,3+}$ and vacancy V_{As}^{3+} are the dominant defects. The formation energy of V_{As}^{+} is relatively high under all conditions. As μ_e increases above midgap the formation energy of the antisite $\mathrm{Ga}_{\mathrm{As}}^{\,2-}$ decreases to values less than 1 eV and actually becomes negative for $\mu_e>1.2$ eV. This result implies that under extreme Ga-rich conditions it should be impossible to move the Fermi energy more than about 1.2 eV above the valence-band maximum and maintain thermodynamic equilibrium.[16]

Under As-rich conditions the defect formation energies assume the values indicated in Fig. 2. It is clear that the As vacancies are not abundant under these conditions. Instead the Ga vacancy is dominant for n-type material, while the $\mathrm{As}_{\mathrm{Ga}}$ antisites are dominant for p-type material.

Also shown in these figures is the calculated energy of the neutral As-Ga divacancy. Its formation energy, which is independent of μ_e and $\Delta\mu$, is found to be 4.8 eV. On the basis of this result we should expect neutral divacancies to be essentially nonexistent in GaAs under equilibrium conditions. (Note: charged divacancies were not examined.) From the calculated value of the formation energies of V_{Ga}^{3-} and V_{As}^{3+} the binding energy of the vacancy pair is determined to be 1.8 eV. This large binding energy arises primarily from the elimination of one As and one Ga dangling bond by the formation of the pair from two isolated vacancies. Surface energy calculations for GaAs(110) indicate that the forma-

tion energy of a pair of Ga(sp^2) and As(s^2p^3) dangling bonds is approximately 1.2 eV.[17] The rest of the binding energy presumably arises from the reduction in Coulomb energy.

In summary, total-energy calculations predict that As should exhibit a 3+ charge state under p-type conditions, and that the corresponding formation energy is competitive with that of the Ga interstitial. We propose that anion vacancies, with nearly sp^2-bonded cations, should be considered as possible mechanisms for compensation in III-V and II-VI semiconductors. They, along with the cation interstitials, may also play a role in mediating the diffusion of acceptors and anion self-diffusion in these materials.

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[15] Even if the Kohn-Sham energy of the a_1 orbital is less than the valence-band maximum when the defect is in the 1+ charge state, it may happen that the energy of the a_1 orbital will move into the gap following the breathing mode relaxation. This may lead to a stable 3+ charge state.
[16] Still, n-type GaAs grown under Ga-rich conditions may be achieved if the Fermi energy remains near midgap during the high-temperature growth and the concentration of $Ga_{As}{}^{2-}$ which corresponds to this Fermi level is "frozen in" as the Fermi energy moves to the conduction band during the cooldown to room temperature.
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