Cation Antisite Defects and Antisite-Interstitial Complexes in Gallium Arsenide

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The atomic geometries of Ga and B antisites in GaAs are proposed to be strongly bistable. As the Fermi level is lowered towards the valence-band maximum, a structural change from fourfold to threefold coordination is predicted to occur. The Ga antisite is found to be metastable with respect to atomic exchange in the presence of an As interstitial. The antisite-interstitial complex has a large 2.9-eV binding energy but a small 0.3-eV barrier to Ga-As exchange.

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Antisites are among fundamental intrinsic defects in compound semiconductors. Two types of antisites are possible in a III-V semiconductor such as GaAs: an anion antisite defect As_{Ga} in which an As atom occupies a Ga lattice site, and conversely, a cation antisite defect Ga_{As} in which a Ga atom occupies an As site. The As_{Ga} antisite in GaAs has been extensively studied.[1] It exhibits an interesting photoinduced structural metastability, which strongly affects its electronic properties. The underlying physical mechanisms and microscopic origin for the metastability are now well understood.[2] In comparison, very little is known about the structural states of cation antisites in GaAs and their associated electronic[3-6] properties. Gallium or boron antisites can result from nonstoichiometric growth[5] or through impurity boron incorporation during Czochralski growth where boron nitride and liquid boric oxide are used.[7,8]

In this Letter we propose that Ga_{As} and B_{As} antisite defects in GaAs possess strong structural bistabilities as a function of the Fermi-level position in the band gap. As a result the two antisites act as *shallow* acceptors in *n*-type but as *deep* acceptors in *p*-type GaAs. We also show that Ga antisites form low-energy metastable complexes (and undergo exchange reactions) with mobile As interstitials.

Our computational approach is based on the *ab initio* self-consistent pseudopotential method within the local-density-functional approximation.[9] The electron-electron correlation energy was determined from the Wigner interpolation formula.[10] Plane-wave bases with kinetic-energy cutoffs of 6.5 Ry for Ga_{As} and 12.0 Ry for B_{As} were used in the expansion of the wave functions.[11] Supercells containing 18 atoms for B_{As} and 32 atoms for Ga_{As} per cell were employed. A Hellmann-Feynman energy-minimization scheme[12,13] was used in the search for the stable atomic configurations. Our results are converged to within 0.1 eV with respect to energy cutoff, cell size, and Brillouin-zone sampling. The Fermi-level-dependent energy of the defect was obtained from

$$E(N,\mu) = E_{\rm tot}(N) - \mu N , \quad (1)$$

where $E_{\rm tot}(N)$ is the total energy for the defect in charge state N and μ is the Fermi energy defined with respect to the valence-band maximum (VBM).

The calculated energy of Ga_{As} as a function of μ is shown in Fig. 1 for various charge states. A transformation from a doubly negative to a neutral charge state is predicted to occur for Ga_{As} (B_{As}) antisite defects for $\mu \leqq 0.17$ eV ($\leqq 0.23$ eV). The *neutral* defect is found to be stable only in a *threefold*-coordinated configuration shown in Fig. 2(a). This configuration induces a large lattice relaxation which traps two holes in the broken-bond region and gives rise to a deep acceptor level at $\epsilon(0/--) \simeq 0.17$ eV above the VBM.[14] The normal fourfold-coordinated substitutional configuration shown in Fig. 2(b) is calculated to be stable for the doubly negative charged state and to give rise to a shallow level near the VBM.

Our calculations start with a cation antisite on a tetrahedral substitutional site. This structure gives rise

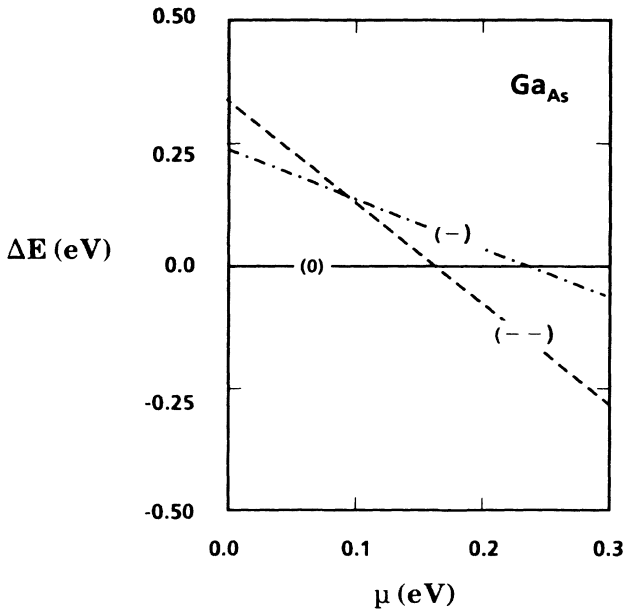

FIG. 1. Defect energy E (in eV) vs chemical potential μ for the Ga_{As} antisite defect in GaAs.

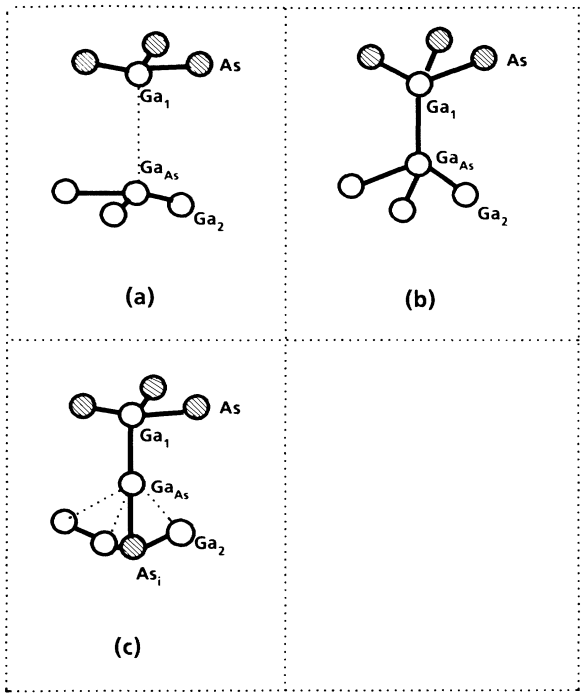

FIG. 2. Structural models for the Ga antisite determined from our calculations are shown. (a) The broken-bond configuration for the neutral charge state of Ga_{As}. (b) The fourfold-coordinated substitutional site model for the negatively charged state. (c) An *sp*-bonding model for the intermediate metastable state of the Ga_{As}-As_i^+ complex.

to a threefold-degenerate level in the gap. The states are filled by four, five, and six electrons for the neutral, single-negative, and double-negative charge states of the defect, respectively. For the singly negative charged state, there is a C_{3v} symmetric Jahn-Teller distortion in which the antisite moves by a small distance along the antibonding direction. The motion lifts the threefold orbital degeneracy and leads to a set of occupied twofold-degenerate levels and to a half-occupied nondegenerate level. The neutral state, however, undergoes a very large atomic relaxation in which the antisite is spontaneously driven into a *broken-bond* configuration without having to overcome any potential barrier along the way.

In the threefold-coordinated configuration for the neutral charge state of Ga_{As}, the antisite and one of its Ga neighbors (labeled as Ga_1 in Fig. 2) move away from each other, relaxing towards their three nearest neighbors to form sp^2-type planar bonds. The dangling-bond orbitals of both atoms are empty: The excess $\frac{3}{4}$ electron in the Ga_1 dangling bond is transferred to the "back bonds" of the Ga_{As} antisite.[15] Overall, the defect remains neutral. The calculated 3.30-Å separation between the two Ga atoms is 34% larger than the ideal Ga-As bond length of 2.46 Å.[16] The remaining bond lengths (bond angles) are 2.38 Å (117.7°) for the Ga_{As} and 2.39 Å (117.5°) for the Ga_1 atom, respectively. The similarity in the bond lengths and angles arises from the absence of occupied p_z states at the two sites. An empty optical level with a p_z character lying 0.2 eV above the VBM is found. Because of the large lattice relaxation of the neutral state [Fig. 2(a)], the level $\epsilon(0/-)$ is found to be at 0.24 eV above the VBM. In contrast, $\epsilon(-/--)$ is 0.09 eV above the VBM. This indicates, therefore, that Ga_{As} is a small "negative-*U*" system.

A similar situation [Fig. 2(a)] is found for the threefold-coordinated neutral B_{As}. Compared with the sum of atomic radii of 2.14 Å,[17] the separation between the B_{As} and Ga_1 atoms (>3.0 Å) is large. Since boron is a first-row element, the B-Ga_2 bond length is substantially smaller than the normal GaAs bond length where Ga_2 denotes any of the three equivalent Ga neighbors shown in Fig. 2. This gives rise to even larger relaxations than for Ga_{As}. The bond length and bond angles are 2.14 Å and 118.3°, respectively. An empty optical level 0.2 eV above the VBM is also obtained for this configuration.

The Fermi-level-induced structural transitions at Ga and B antisites explain two unexpected experimental observations.[6,8] In a recent deep-level transient spectroscopy (DLTS) experiment on Ga_{As} a shallow (0.07–0.08 eV) and a deep (0.2 eV) level were observed for *n*-type GaAs using a minority-carrier (holes) optical filling pulse.[6] The DLTS signal of the deep level is an order of magnitude larger than that of the shallow level. In *p*-type samples, the levels were also observed as majority-carrier (holes) traps. However, the signal intensities were reversed. The shallow level is instead an order of magnitude stronger than the deep level. These results are consistent with our theory. All the Ga_{As} sites are doubly charged in *n*-type samples. The optical filling process creates more two-hole (neutral) states as opposed to one-hole (singly charged) state since this is a negative-*U* system. In *p*-type samples the deep level is empty; hence it cannot act as a hole trap. The predicted energy positions, $\epsilon(0/-)=0.24$ eV and $\epsilon(-/--)=0.09$ eV, are also in good agreement with the experimental values (0.2 eV and 0.07–0.08 eV, respectively).

In another experiment the local B_{As} vibrational mode is seen to suddenly disappear for $\mu \leqq 0.23$ eV.[8] This provides further strong experimental evidence in favor of the fourfold-to-threefold structural transformation proposed in this paper. The result had been explained previously as arising from the complexing of the B_{As} with a nearby vacancy[8] which is qualitatively similar to the coordination change predicted from our calculations. We have calculated the B stretching-mode frequency along a [111] direction for the doubly negative charge state. The theoretical value of 540 cm^{-1} is in reasonable agreement[18] with the experimental value of 601 cm^{-1}.[8] For *neutral* B_{As} we predict that the B stretching frequency should be in the range 240–330 cm^{-1},[19] or about one-half that for the negatively charged state. The charged-to-neutral transformation occurs when μ is below

$\epsilon(0/--)=0.1$ eV, in reasonable agreement with the experimental value of 0.23 eV. For a Ga antisite, the local vibrational mode in the negatively charged state is less well localized because of the nearly equal Ga and As atomic masses.

We now examine the stability of a Ga antisite defect in the presence of an As interstitial atom denoted by As_i. As_i behaves as a triple donor with three electrons in a doubly degenerate level above midgap. Since Ga_{As} is a double acceptor, the combined complex [see Fig. 2(c)] is expected to be a single donor. The binding energy for the Ga_{As}-As_i^+ is determined to be 2.9 eV. In comparison, other antisite-interstitial-based complexes such as As_{Ga}-As_i^+ and As_{Ga}-Ga_i^+ have much smaller binding energies of 0.5–0.7 eV.

The As_i of the Ga_{As}-As_i complex is calculated to be strongly bonded to the Ga antisite. The Ga_{As}-As_i and Ga_{As}-Ga_1 bond lengths are 2.20 and 2.27 Å, respectively. The bonds are about 10% shorter than the bulk GaAs bond length. Three Ga_2-As_i bonds with bond angles of 115° are formed to replace the Ga_2-Ga_{As} bond (which are now elongated to 2.97 Å). The new Ga_2-As_i bond lengths are 2.57 Å, about 4.5% longer than the bulk GaAs bond length. In order to release the stress caused by the Ga_{As}-As_i interaction, the Ga_1 atom relaxes towards its back neighbors. This results in bond lengths (bond angles) of 2.41 Å (117.4°) between Ga_1 and its three As neighbors. The electronic charge distribution of the complex is shown in Fig. 3. The Ga antisite atom is an essentially twofold-coordinated *sp*-bonded configuration with a 180° bond angle. A similar geometry has been previously reported for a GaAs (100) surface terminated with a half-monolayer Ga coverage.[20]

Despite its relatively large 2.9-eV binding energy, the Ga_{As}-As_i complex is found to be unstable with respect to the Ga_{As}-As_i interchange reaction:

$$Ga_{As}\text{-}As_i \rightarrow As_{As}+Ga_i\,. \qquad (2)$$

The reaction releases 0.96 eV in energy and there is a small 0.3-eV barrier for the exchange. This implies that under normal conditions, excess As incorporated in the lattice as interstitials will tend to eliminate Ga_{As} defects, creating Ga interstitials in the process. The barrier was calculated by displacing the antisite Ga atom towards the interstitial site in a (110) plane (see Fig. 3). The maximum barrier height is at 60% of the total displacement to the final position at which the optical gap is closed indicating that the *sp* configuration of Ga_{As}^+ is replaced by an s^2 configuration of Ga_i^+. The two-step reaction discussed above assumes a postively charged As_i^+. This choice is valid in *p*-type GaAs. For *n*-type GaAs the energetics of the reaction for As_i^0 are expected to be the same as for As_i^+ since the additional electron is not involved in the bonding and its energy level is found to be essentially unchanged during the transition.

In summary, we have studied the structural and electronic properties of Ga and B antisite defects in GaAs. The *broken-bond* configuration shown in Fig. 2(a) is predicted to be the stable configuration in a *neutral* charge state. The normal fourfold-coordinated substitutional site is found to be the preferred geometry in a negatively charged state. The proposed Fermi-level and charge-state-dependent structural changes suggest that cation antisites behave as shallow double acceptors in *n*-type samples but as deep acceptors in *p*-type GaAs. Experiment data[8] on the disappearance of the local vibrational model of B_{As} when the Fermi level comes near the VBM provide strong support for the large lattice relaxation model proposed here. The Ga antisite is found to form a low-energy metastable complex with an As interstitial and to be unstable towards an exchange reaction with the interstitial.

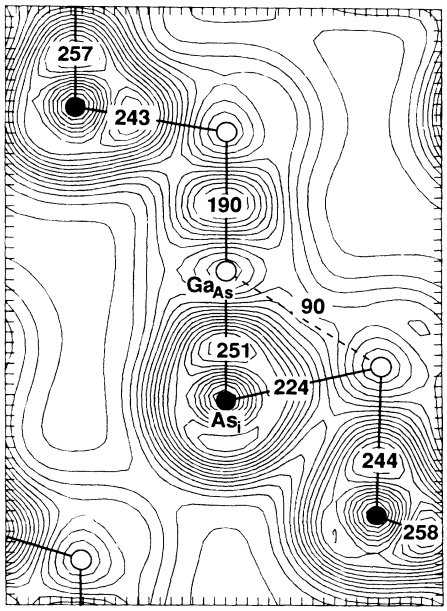

FIG. 3. Total charge densities in a (110) plane for the Ga_{As}-As_i^+ complex. The contour spacings are fifteen electrons per unit-cell volume. The unit-cell volume is 412.7 $Å^3$.

The large lattice relaxation geometry for the neutral state of a cation antisite in GaAs is very similar to that proposed earlier for the *positively charged* A^+ state of an *acceptor* such as As in ZnSe.[21] We have previously suggested that large lattice relaxations of this type can lead to a simple mechanism for self-compensation of acceptors in ZnSe. In both GaAs and ZnSe, a localized two-electron perturbation of the bond charge drives the relaxation. Similar atomic relaxation effects were predicted when an impurity induces an excess electronic charge in the bond region, as in the case of As-antisite-derived *EL*2,[22] and Si- or S-derived *DX* centers[14,23] in GaAs.

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[18]The discrepancy arises from the incomplete convergence in the calculation and can be reduced by (i) increasing the kinetic-energy cutoffs in the calculation, and (ii) making the theoretical local vibrational mode orthogonal to more phonon modes by adding more atomic shells.

[19]The calculated local B vibrational frequency for the neutral state shows some dependence on the geometry of the supercell. It is 240 cm^{-1} for an 8-atom cell (in which the Ga_I back relaxation can fit the relaxation of the B_{As}) and 330 cm^{-1} for an 18-atom cell (in which the Ga_I back relaxation cannot fit the relaxation of the B_{As} well).

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