Bistability and Metastability of the Gallium Vacancy in GaAs: The Actuator of *EL* 2?

G. A. Baraff and M. Schluter
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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We have used the Green's-function technique to carry out electronic-structure and total-energy calculations for the gallium vacancy in GaAs and for the nearest-neighbor (arsenic vacancy)-(arsenic antisite) pair which results when an adjacent arsenic atom hops over and fills the gallium vacancy. The results are interpolated with a tight-binding model for intermediate positions of the moving arsenic atom. The system shows bistability and metastability, and seems to describe many properties of the *EL* 2 center.

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*Bi*stability (the existence of two different atomic arrangements for two different charge states of a given defect) is well-known for extrinsic defects in covalent semiconductors. Oxygen in GaP,[1] Fe-Al pairs in silicon,[2] and, indeed, most situations in which large lattice relaxations occur[3] can be considered examples of this. *Meta*stability of a point defect can also occur: For a given charge state two configurations, separated by a barrier, may exist but one of the two configurations is more stable than the other, e.g., as in *EL* 2.

The deep electron trap in GaAs known as *EL* 2 is, because of both its technological importance and the fascinating behavior associated with that metastability, probably the most thoroughly investigated defect in any compound semiconductor.[4,5] Most of the experimental evidence seems to show that the transformation between its ground and metastable configurations occurs *within* a specific charge state.[6–10] The *M* center[11] in InP is probably another example of metastability, rather than bistability.

An interest in bistability and metastability and in the defect *EL* 2 has led us to calculate the properties of several native defects in GaAs. In this Letter, we present calculations which predict that a simple native defect in GaAs, namely, the isolated gallium vacancy, exhibits a charge-controlled bistability and, quite independently of this, an additional metastability. This metastability provides a mechanism by which *EL* 2 (whose identity is still unclear) can work. The situation that we have found is basically the following:

V_{Ga}, the isolated gallium vacancy, is a multiple *acceptor* which can be either neutral or negatively charged by the gain of up to three additional electrons. Starting with the neutral vacancy, a probable atomic motion during the annealing of the crystal is the hopping of one of the four nearest-neighbor arsenic atoms to fill the gallium vacancy.[12] This results in a nearest-neighbor (arsenic vacancy)-(arsenic antisite) (V_{As}-As_{Ga}) pair. This defect pair, however, is a multiple *donor* which can be neutral or positively charged by the loss of up to three electrons. We calculate that for the neutral (and all negatively charged) states the total energy of V_{Ga} is less than that of the pair, while for all the positively charged states, the total energy of the defect pair is lower than that of the vacancy. This is the bistability.

We introduce the configuration coordinate R as the position of the arsenic atom on the [111] axis. At $R = 0$, the arsenic atom fills the gallium vacancy and the defect is the nearest-neighbor V_{As}-As_{Ga} pair. At $R = 1$, it fills the arsenic vacancy and the defect is the isolated gallium vacancy. The total energy of the system depends on R and charge state as shown in Fig. 1 (bottom). We ignore the obvious metastability of charge state 0; it is not relevant here. Charge states

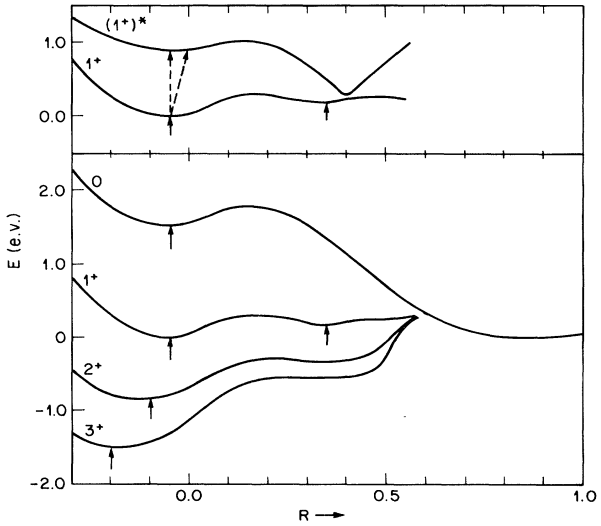

FIG. 1. Bottom panel: ground-state total energies for four of the charge states of the V_{Ga} ↔ (As_{Ga}-V_{As}) system as functions of the arsenic-atom position (R). Only the neutral charge state exists for the whole range of R. Upper panel: excited-state energy of the + charge state $(1+)^*$ with one of its electrons promoted from A to E, and the ground-state energy of the + charge state $(1+)$ with both of its electrons in the A state. The vertical transition and the no-phonon transition are indicated.

+, 2+, and 3+ exist only up to $R \approx 0.55$. Among these the state of + charge exhibits an additional metastable minimum near $R \approx 0.35$ which tends to disappear as the charge state is changed to 2+ and 3+. This is the additional metastability that we want to focus on.

Our calculations give two mechanisms for population of the intermediate metastable minimum by internal optical transition to an excited state. This state relaxes slightly and then deexcites to the ground state. The excited state from which the deexcitation occurs has a large vibrational overlap with the true minimum of the ground state and a small but finite one with the metastable minimum of the ground-state curve as can be inferred from Fig. 1 (top). Alternatively, by surmounting a small barrier in the excited state, the system relaxes to a configuration close to the metastable one. To reach the metastable minimum the amount of forward relaxation is large, and as a consequence, the donor levels are pulled deep down into the gap, as shown in Fig. 2. This quenches photoionization and internal excitation and causes a shift from donor to acceptor in the Hall conductivity. Insofar as the Fermi energy is tied to these donor levels, it will drop during the ground-to-metastable transition. This rather unusual scenario is in accord with many, but not all, of the experimental properties of $EL2$.[6–13,14] The importance of the scenario lies both in its connection to $EL2$ and in its role as a general prototype model for instability in III-V semiconductors.

Let us now briefly describe how these results were obtained. First, using the self-consistent Green's-function technique,[15] we calculated the electronic

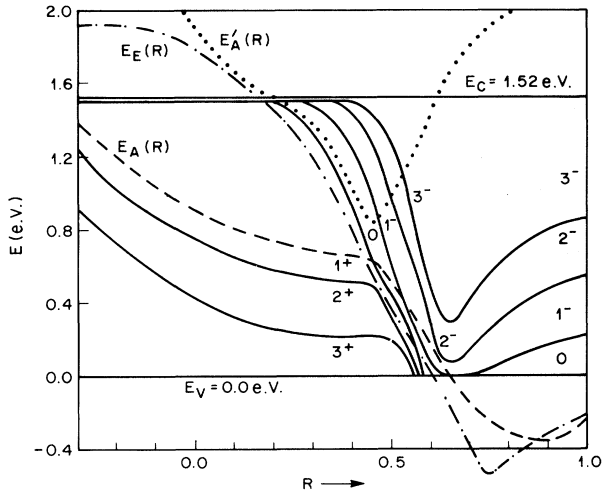

FIG. 2. Eigenvalues (broken lines) and electronic energy levels (solid lines) for the $V_{Ga} \rightarrow (As_{Ga}\text{-}V_{As})$ system as calculated by the Green's-function method and interpolated by a tight-binding scheme.

structure and total energy of both the isolated gallium vacancy (V_{Ga}) and the isolated V_{As}-As_{Ga} pair. Both calculations were carried out with the same low C_{3v}-symmetry Green's function, one which is extensive enough so that it reproduces accurately the extra degeneracies imposed by the T_d symmetry of the isolated gallium vacancy. The total-energy calculations show that the isolated neutral V_{As}-As_{Ga} pair is 1–2 eV higher in energy than the isolated V_{Ga}. The uncertainty arises from systematic and numerical errors in the calculations.[15] We take 1.5 eV as a reasonable estimate for the difference between the $R=0$ and $R=1$ values for $E^0(R)$, the total energy of the neutral defect. If $R=-1$, then we have three collinear defects: an arsenic interstitial, an arsenic vacancy, and a gallium vacancy. This configuration is calculated to be about 8 eV more energetic than the gallium vacancy alone and roughly determines the shape of $E^0(R)$ for $R<0$. The shape of the curve $E^0(R)$ for $0<R<1$ is rather smooth and featureless, showing the typical barrier for vacancy migration.[16]

Total-energy curves for excited and/or different charge states can be deduced from the basic total-energy curve if we know the electronic level structure as a function of R and use Slater's transition-state argument. For $R=0,1$ the level structure is obtained from our Green's-function results. Since the connection between these end points is far from obvious, we have interpolated the results to intermediate positions of the As atom using a simple tight-binding model. The model contains sp^3 orbitals on eight atoms in the crystal, including the central gallium and arsenic atoms. The perturbation representing the defect is taken to be a nearest-neighbor vacancy pair plus a movable arsenic atom. The shapes of the orbitals and defect potential were taken from the Green's-function calculations and matrix elements were evaluated numerically. The parameters of the perfect-crystal Hamiltonian were chosen so as to fit the defect eigenvalues and *wave functions* of the two Green's-function calculations described above. The fitting was done for the charge state which has two electrons on the state in the gap, giving an overall charge of 1+.

The strong variation of the total-energy curves with excitation or ionization results, of course, from a rich deep-level structure which changes drastically in character as R goes from 0 to 1. This is shown in Fig. 2. There are three defect-related eigenvalues (the broken lines in Fig. 2). They are labeled E_A, E'_A, and E_E. The subscripts A and E refer to the singly and doubly degenerate representations of the group C_{3v}. Counting spin, an A level can hold 0, 1, or 2 electrons and gives rise to two levels; an E state gives rise to four.

At $R=0$, the state E'_A at 1.87 eV is the antisite state, with three, rather than four, nearest neighbors. The states E_E at 1.75 eV and E_A at 0.87 eV are As va-

cancy states, made up of bonds from the three adjacent Ga neighbors, with very little contribution from the one wrong, i.e., As, neighbor. As R goes from 0 to 1, the states E_A and E_E drop and, at $R=1$, they coalesce to give the threefold-degenerate T_2 state of the isolated Ga vacancy at -0.26 eV. Concurrently, the antisite state drops into the gap, becomes deep (~ 0.8 eV near $R \approx 0.45$), interacts strongly with the state E_A, and rises out of the gap again as $R \rightarrow 1$.

Consider the levels shown as solid lines in Fig. 2 associated with these eigenvalues. These are constructed in the usual way by use of the Slater transition-state argument, but with account taken of how shallow states spread out and can become effective-mass-like if the charge is right. In Fig. 2, the area between the levels $\epsilon_R[(n+1)/n]$ and $\epsilon_R[n/(n-1)]$ is labeled by n, the charge state common to both levels. One interprets $\epsilon_R[n/(n-1)]$ in the usual way as the energy to transfer an electron from the valence band to the defect at R in charge state $n-1$, bringing it to charge state n. One interprets $E_C-\epsilon_R[n/(n-1)]$ as the energy needed to remove that same electron to the conduction band. Additionally, one can read Fig. 2 as a phase diagram, with the interpretation that a point at μ and R lying in the area labeled by n indicates that, for Fermi energy μ and coordinate R, the thermodynamically stable state has charge n. Note that the various stable charge states have limited regions of existence, with only the neutral state being permitted at all values of R (for some μ) and at all values of μ (for some R). In this diagram, the transformation of the defect from the *donor* V_{As}-As_{Ga} to the *acceptor* V_{Ga}, a feature of the transformation from the ground state to a metastable state, is clearly depicted.

We now describe the properties of the metastable donor As_{Ga}-V_{As} pair. In its ground state near $R=0$, it is a triple donor, having a shallow level which is effective-mass-like and has E symmetry. That level is deeper than the ordinary shallow donors in GaAs (6 meV) because of a strong attractive central-cell correction for E states. The wave function associated with the two deep donor levels has A symmetry. It is As-vacancy-like with the electron being concentrated on the three adjacent Ga atoms. The separation between the levels is approximately that of a typical vacancy, i.e., 0.2 to 0.3 eV. Occupancy by one electron gives the defect a charge of 2^+ and causes it to be paramagnetic.

There is a strong resonance of E symmetry low in the conduction band. It is sharp because it lies below the X and L conduction-band minima at an energy where the density of states (states associated with the Γ minimum) is still quite low. The wave functions associated with this resonance are similar to those of the deep A levels in that the electron is concentrated on the three adjacent Ga atoms.

The optical absorption spectrum of the defect contains, in addition to the bound-to-free transitions, a strong internal transition in which an electron in the deep A state is excited to the E resonance. The photon energy for a "vertical" transition (i.e., one which would be described classically as occurring at a fixed value of R) will be approximately equal to the difference in energy between the E and A eigenvalues because the Slater transition-state effects should not be very different in the two states. There is also an associated no-phonon transition at $A \rightarrow E$ symmetry as shown in Fig. 1, top panel. The $A \rightarrow E$ transition causes the system to relax towards higher values of R, and deexcitation, followed by back relaxation to the ground minimum or, much less probably, by forward relaxation to the metastable minimum, can then occur. Recovery from the metastable is by thermal excitation over the barrier.

In spite of an intriguing similarity with what is observed for $EL2$, there are several points of detail in which the metastable defect we have described is different. The most pointed of these is that the deep level in the gap is an As-vacancy–derived state, while the As_{Ga}-derived state has an eigenvalue so high that it will not normally be populated by a single electron. Thus, this defect would not exhibit an As_{Ga}-like spin-resonance signal. Experimentally, however, such a signal seems to be associated with the $EL2$ defect.[17,18] The association may be accidental: If the *isolated* antisite (here assumed to be a stable defect) had its first ionization level $(0/+)$ at an energy close to the higher deep level $(+/++)$ of the metastable As_{Ga}-V_{As} pair, then many of the seemingly mysterious experimental contradictions about $EL2$ would disappear: The change in Fermi energy caused by the metastable transition would affect the occupancy, and therefore the paramagnetism, of the isolated antisite. Thus, the presence of the antisite spin-resonance signal would be dependent on the state of the metastable defect. However, if the antisitelike spin-resonance signal is *directly* related to $EL2$, then either our calculation of the antisitelike state has put it at too high an energy,[19] or alternatively, there are additional features involved, lowering its energy. For instance, Van Vechten has suggested that during the growth process, a positively charged antisite and a negatively charged gallium vacancy will be attracted to second-nearest-neighbor positions.[20] The atomic jump that we have described would then transform this defect complex into *two* As_{Ga}-V_{As} pairs with the single V_{As} shared by both antisites.[21] Similarly, there may be complexes of other defects with the As_{Ga}-V_{As} pair forming a whole "family" of $EL2$ defects,[18] whose properties differ in slight detail from the model developed in this Letter. This is why we regard the underlying As_{Ga}-V_{As} pair as the actuator of $EL2$.

The essence of the model proposed here is an interplay between the electronic energy gain available from having a deep level sweep completely across the gap as an atom hops, and the energy penalty for creating an extra antisite. As one goes to more polar semiconductors, both of these energies increase, allowing still the possibility for bistability. The model detailed here for GaAs may thus have a much wider range of applicability.

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