Metastability of the Isolated Arsenic-Antisite Defect in GaAs

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We propose that a neutral As-antisite defect in GaAs has a stable fourfold and a metastable, threefold interstitial configuration differing by 0.24 eV in their energies. The barrier height from the metastable to the normal state is calculated to be 0.34 eV. The metastable geometry is predicted to have a low optical excitation probability and to be electron-paramagnetic-resonance inactive. The two structural states of the antisite provide the simplest explanation for the unusual properties of the $EL2$ defect center in GaAs.

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The anion antisite defect As_{Ga} in GaAs where an As atom occupies a Ga site has attracted a great deal of attention because it is believed to be at the core of the very unusual and technologically important $EL2$ center in GaAs.[1] A distinguishing feature of $EL2$ is its metastability. Experimental evidence indicates that the neutral defect has two states: a normal stable configuration, and an excited metastable configuration $EL2^*$ which can be reached from the stable geometry by exposure to $\simeq$1-eV light.[2-5] The precise relationship between these states and the antisite has been the subject of many studies. Proposed models involve an As_{Ga} defect, either by itself,[5-7] or in combination with other defects such as a Ga-As divacancy[8] or an As interstitial As_i.[9-11]

The challenge faced by each model is to explain both the normal- and the excited-state properties of $EL2$ within the same unified framework. Electronic structure calculations,[11] and electron-paramagnetic-resonance[6,12] (EPR), photocapacitance,[7] and stress- and magnetic-field-dependent optical-absorption[5] measurements show that the isolated As_{Ga} antisite provides a good description for the normal $EL2$ center. The model provides no clues, however, as to the structure of the metastable $EL2^*$ state. As a result more extended defect complexes have been examined in order to explain the two states of this defect.[8-11] The possibility that both $EL2$ and $EL2^*$ arise from an isolated As_{Ga} defect has not received general acceptance up to now because of the lack of a suitable low-energy metastable structure for this defect.

The primary purpose of this Letter is to show that an As_{Ga} defect does indeed have two distinct atomic configurations which are remarkably close in energy but which have very different electronic properties. These structures are shown to provide good agreement with $EL2$-derived experimental data on charge state,[7,13] thermal stability,[14] EPR activity, Fermi-level pinning position, and the energy barrier[3,4] between the stable and metastable geometries.

Our calculations are based on an *ab initio* pseudopotential total-energy method.[15] The exchange and correlation potentials are approximated by the Wigner interpolation formula.[16] Norm-conserving nonlocal pseudopotentials[17] and a momentum-space formalism[18] were employed. An eighteen-atom hexagonal supercell with its c axis oriented along the [111] direction and with a $\sqrt{3}a\times\sqrt{3}a\times\sqrt{6}a$ periodicity, where $a\simeq4$ Å is the (111) planar lattice constant, was used. In the initial configurations the As—As and Ga—As bond lengths were chosen to be equal. Hellmann-Feynman forces[19] were calculated and used to optimize the atomic coordinates and minimize the energies. The atomic coordinates were further optimized by tight-binding calculations[20] on 144-atom $2\sqrt{3}a\times2\sqrt{3}a\times2\sqrt{6}a$ supercells.

The two different structures for the As antisite are shown in Fig. 1. The structure in Fig. 1(a) with the antisite bonded to four nearest-neighbor As atoms represents the one ordinarily associated with the As_{Ga} defect. The configuration in Fig. 1(b) shows the proposed new metastable geometry for the antisite. In this structure the central As atom breaks one of its four As—As bonds and moves to an interstitial position 0.29 Å below the

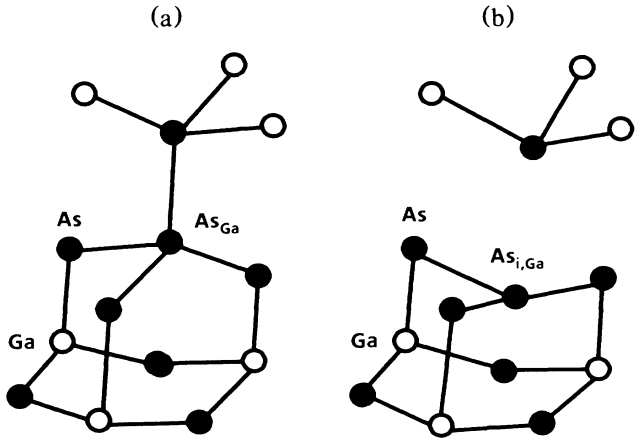

FIG. 1. The atomic structures for (a) the stable, fourfold coordinated, antisite, As_{Ga}, and (b) the metastable, threefold coordinated, interstitial antisite, $As_{i,Ga}$, defects in GaAs.

plane of its three remaining neighbors. This structure denoted in the following by $As_{i,Ga}$ gives rise to two threefold-coordinated As atoms with different environments. The results of our calculations for the structural and electronic properties of the two structures shown in Fig. 1 are examined below. The normal As_{Ga} state in Fig. 1(a) shows *large* atomic relaxations around the antisite.[21] The two donor electrons of the As antisite occupy an antibonding level which leads to weaker than normal As–As bonds. The energy-minimized configuration shows that all four As neighbors of the antisite move radially away from it by $\simeq 0.19$ Å leading to As–As bond lengths of 2.64 ± 0.03 Å.[22] The relaxation energy is calculated to be 0.54 eV for an 18-atom cell and $\simeq 1$ eV in a 144-atom cell. We have also examined the atomic structure of the positively charged As_{Ga}^{+} center and find smaller As–As bond lengths of 2.58 ± 0.03 Å resulting from a reduction in the number of antibonding electrons.

The metastable $As_{i,Ga}$ configuration in Fig. 1(b) is found to have a larger relaxation energy than the normal state: 1.6 eV in an 18-atom cell with an additional 0.6-eV relaxation in a 144-atom cell. The difference in total energies between the stable and metastable configurations is 0.38 ± 0.03 eV from the 18-atom/cell self-consistent pseudopotential calculations and 0.24 ± 0.1 eV from the combined self-consistent and tight-binding calculations on 144-atom cells. The 0.14 eV difference between the two calculations is equal to the difference in the 0.6- and 0.46-eV residual relaxations of the metastable and normal states when placed in a 144-atom cell. Similarly, the energy barrier to go from the metastable to the stable configuration is calculated to be 0.20 eV from the self-consistent 18-atom/cell calculations and is estimated to be 0.34 ± 0.1 eV for the larger 144-atom unit cell. The calculations show that the top of the barrier is reached when the $As_{i,Ga}$ atom moves from 0.29 Å below to 0.18 Å above the plane of its three nearest-neighbor As atoms.

The optimized atomic structure of the metastable center shown schematically in Fig. 1(b) is very unusual. The bond angles around the interstitial antisite atom are 119° and one $As_{i,Ga}$-As-Ga angle of 80° occurs on each neighboring As atom. The largest relaxation occurs for the antisite defect. It moves 1.2 Å along a [111] direction, away from its "ideal" Ga substitutional position, and breaks one of its bonds by stretching it to $\simeq 3.6$ Å. The remaining three As–As bond lengths of 2.49 ± 0.003 Å are significantly shorter than the $\simeq (2.64 \pm 0.03)$-Å separations in the normal state and lead to a stronger As–As bonding in the metastable configuration. The $\simeq 120°$ bond angles instead of the ordinarily preferential 97° angles for trivalent As make the antisite behave more like a Ga than an As atom. The Ga-type behavior is consistent with the loss of electronic charge from this site as discussed below.

The total valence electronic charge density for the

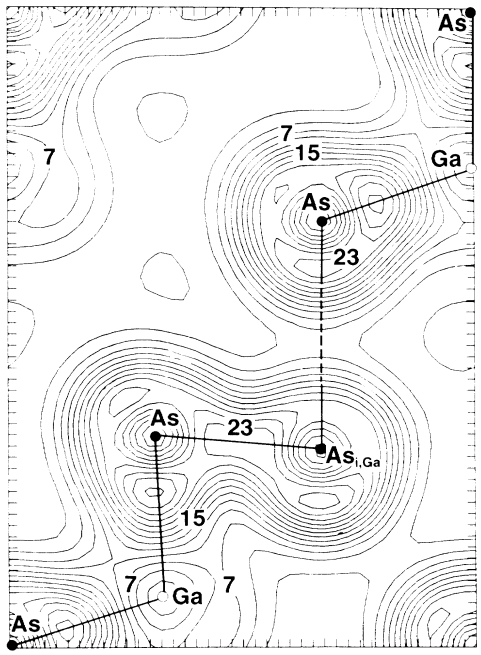

FIG. 2. The total electronic charge density for the fully relaxed $As_{i,Ga}$ structure of Fig. 1(b) is shown in a $[1\bar{1}0]$ plane. The vertical and horizontal directions are along the cubic [111] and $[11\bar{2}]$ axes, respectively. The contour lines are in units of electrons per bulk GaAs unit cell volume.

$As_{i,Ga}$ defect is shown in Fig. 2 where the broken As–As bond is represented by a dashed line. The charge-density contours are seen to reach a minimum near the center of the broken bond. The calculated electronic structure for $As_{i,Ga}$ shows one state associated with each of the two threefold As atoms (Fig. 3). The highest filled level, at 0.2 ± 0.1 eV with respect to the bulk valence-band maximum, is doubly occupied and is associated with the Ga-bonded As atom as shown in Fig. 3(a). The charge-density contours of the empty state shown in Fig. 3(b) are localized on the interstitial antisite. The pseudopotential calculations place the empty level at $\simeq 0.5$ eV below the conduction-band minimum. The electronic charge-density contours shown in Fig. 3 clearly demonstrate the degree of localization for the two states and indicate that charge is transferred from the antisite to the trivalent Ga-bonded As atom. The charge-density contours in Fig. 3 also suggest that the dipole matrix element connecting the filled and empty states of the interstitial antisite should be an order of magnitude smaller[23] than typical valence- to conduction-band matrix elements because of the small wave-function overlaps.

The structural models proposed here explain many of the properties associated with the $EL2$ center. In their ground states both the As_{Ga} and $As_{i,Ga}$ defects are predicted to be neutral[7,13] and EPR inactive,[6,9] in agreement with experiment. The calculated energy barrier of

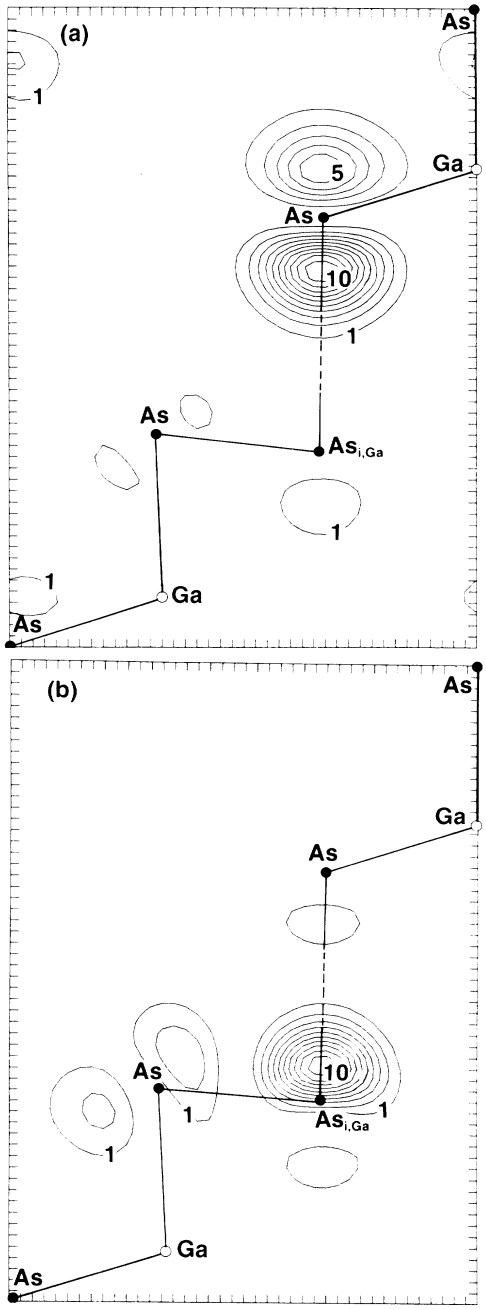

FIG. 3. (a) The electronic charge densities of the highest occupied state of the metastable $As_{i,Ga}$ defect. (b) The corresponding charge-density contours for the first empty state. The same atomic plane and charge-density units as in Fig. 2 are used.

0.34 ± 0.1 eV to go from the metastable to the stable configuration is in very good agreement with the experimental value of 0.34 eV.[3,4] The larger relaxation energy of the metastable state compared to the stable state is consistent with the experimentally derived inference from photocapacitance measurements.[2] The low[4-7,9] but nonzero[24] optical excitation probability for $EL2^*$ which makes it inaccessible for EPR is also consistent with the model.

Overall, the isolated antisite model does better in explaining $EL2$ than the As_i-As_{Ga} pair defect model.[9-11] The major difficulties with this model are these: (i) The observed thermal stability[14] of $EL2$ and its stability against electron-hole recombination[25] are difficult to explain since the diffusion of an As_i atom away from the antisite should lead to a disappearance of the center. (ii) The ground-state configurations of $EL2$ and $EL2^*$ have to be *positively* charged in order for them to be EPR inactive. (iii) For $EL2$ concentrations above those of acceptors the Fermi-level is pinned at the conduction-band minimum instead of at midgap.

The above problems do not arise from the simple antisite model. However, three experiments[26-28] indicating a trigonal C_{3v} instead of T_d symmetry[5] for $EL2$ have been interpreted to be in conflict with this model. The dichroism[26] in the optical absorption of $EL2$ at low temperatures T after stress has been applied at high T and removed at low T may be explainable in terms of *frozen-in* stresses which alter its underlying T_d symmetry. This question needs to be clarified by further experiments. The results of phonon transmission experiments[27] may also be ambiguous because of a drop in the Fermi level in going from the normal to the metastable state of $EL2$. This can cause a change in the charge state and scattering intensity[27] of a trigonally symmetric defect which is not directly related to $EL2$. Finally, the problem of uniqueness of interpretation in optically detected electron-nuclear double-resonance measurements[28] needs to be raised since if $EL2$ does in fact have T_d symmetry then it would not show any magnetic circular dichroism and would not be observed by this experiment. The observation of metastability effect is a *necessary but insufficient* condition for the identification of $EL2$.

In summary, we have shown that a neutral As antisite defect in GaAs has a stable fourfold and a metastable, threefold interstitial configuration which explain most of the experimentally observed properties of the normal and excited states of the $EL2$ defect center.

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[22]A small departure (0.03 Å) from T_d symmetry was found for the eighteen-atom/cell calculations which have built-in trigonal symmetry. No such departures from T_d symmetry were found for a cubic cell.

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