Arsenic-antisite defect in GaAs: Multiplicity of charge and spin states

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We find that the As-antisite defect in GaAs which is the source of the stable EL2 and metastable EL2* centers can exist in at least *eight* different combinations of charge and structural states, twice as many as currently envisaged. In particular, results from first-principles calculations indicate that EL2* which is normally considered to be a neutral defect can also occur in $+1$, -1, and -2 charge states. The existence of charged states for EL2* is consistent with experimental data which indicate that EL2* is a more complex defect than originally anticipated.

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The arsenic-antisite defect (As_{Ga}) arising from the occupation of a Ga lattice site by an As atom is one of the most extensively studied defects in GaAs because it can pin the Fermi level at midgap, thereby enabling the production of semi-insulating substrates that are needed in high speed field-effect transistor applications. The defect exhibits fascinating optical and electronic properties that have attracted a great deal of attention. The As antisite is known to be the source of the EL2 defect in GaAs. The most important characteristic feature of EL2 is photoinduced metastability as demonstrated by the photoquenching of its optical absorption when it is exposed to sub-band-gap light in the 1.1–1.2-eV range.[1,2] This is accompanied by a quenching of photocapacitance,[1,2] photoluminescence,[3] and of the electron paramagnetic resonance[4] (EPR) associated with $EL2^+$. The photoquenching phenomena result from the transformation of EL2 into a metastable EL2* state. The original state of the antisite is recovered upon annealing to temperatures around 140 K in semi-insulating GaAs and 45 K in *n*-type material.[2] Optical recovery of EL2 from EL2* is also possible with near-band-gap energy photons and less efficiently with 0.8-eV light.[5,6]

Important experimental information on the symmetry and structure of EL2 and EL2* has come from intracenter optical absorption[7,8] and photoluminescence measurements[9] under uniaxial stress. Results from these measurements show that the normal EL2 state has T_d symmetry[7,9] and strongly support the identification of EL2 with an isolated As-antisite defect in a symmetric fourfold coordinated state. More recently, it has been shown[10] that electron-nuclear-double-resonance (ENDOR) data on EL2 can also be best explained with an isolated As_{Ga} model without an additional paired As-interstitial component as originally believed.[11] Stress-dependent measurements of the recovery of optical absorption during the transformation of EL2* to EL2 reveal a trigonal symmetry[8] for EL2* that is consistent with the theoretical prediction that EL2* corresponds to an antisite in an interstitial position, as shown in Fig. 1.[12,13] Previous theoretical and experimental work has generally assumed that EL2* is a neutral entity with a unique atomic structure. However, an accumulation of experimental data strongly indicates that EL2* is a more complex defect.[14–17] The most intriguing features exhibited by EL2* are enhanced photoconductivity under prolonged exposure to 1.1 eV light followed by long-lived persistent photoconductivity[14–16] in Czochralski grown samples.

In this paper, we re-examine the structural and electronic properties of the As-antisite defect in GaAs. Three-dimensionally periodic 64- and 32-atom cubic unit cells were used for a detailed investigation of the structure of the stable and metastable states of As_{Ga}. The first-principles pseudopotential total-energy calculations were done using a plane-wave basis[18] with up to 16-22 Ry energy cutoffs for the kinetic energy using Troullier-Martins potentials[19] and the Kleinman-Bylander[20] scheme. Zone center and boundary wave vectors were used in sampling the Brillouin zone.

In the following EL2 is used to denote the tetrahedrally symmetric state of As_{Ga} and EL2M (instead of EL2*) to denote configurations in which the antisite undergoes a large displacement away from T_d symmetry. The most important results concern EL2M for which we find the possibility of three new charge states with charges of $+1$, -1, and -2. We also find that the -2 charged state can exist in two

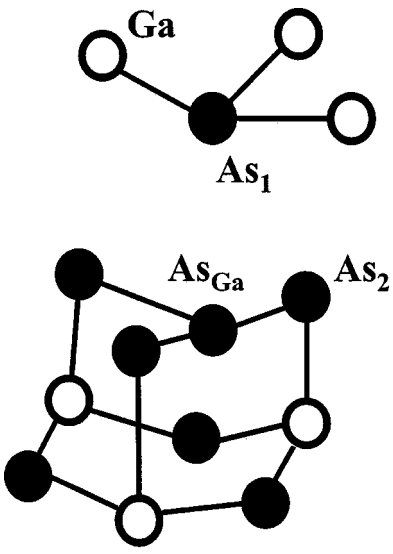

FIG. 1. Metastable configuration for the neutral state (EL2M) of the As-antisite defect in GaAs. This configuration with a smaller $As_1 - As_{Ga}$ separation is the *ground state* for negatively charged states of the As antisite in *n*-type GaAs when the Fermi level lies at the conduction band edge or higher.

distinct structures with practically the same energy. The main results of the calculations and their experimental implications are described below.

Our results for the structure of the stable EL2 state are similar to those obtained before,[12,13] and are reviewed briefly here. The structure has T_d symmetry with an As_{Ga}-As separation of 2.55 Å. The $(+/0)$ level of the defect is calculated to be at $E_c-0.75$ eV where E_c represents the CBM. The midgap state is very localized with s-like symmetry around the central antisite. A resonance state with p-type symmetry on As_{Ga} is found very close to the CBM. A much more localized As_{Ga}-derived triply degenerate p state is found at 0.6 eV above the CBM. The positively charged state of EL2 is found to be a positive-U defect in that the reaction:

$$2\mathrm{EL2}^{+}\rightarrow \mathrm{EL2}^{0}+\mathrm{EL2}^{2+} \tag{1}$$

is endothermic by 0.04 eV.[21]

The largest displacement of the As-antisite from its tetrahedral site occurs in $EL2M^0$, the *neutral* metastable state of EL2. The As_{Ga} atom moves by 1.41 Å into a trigonally symmetric interstitial position as shown in Fig. 1. The As_1 atom also undergoes a sizable displacement of 0.4 Å towards the antisite. The magnitude of all other atomic movements are 0.1 Å or smaller. The nearest-neighbor As-As distance in EL2M is 2.48 Å and the As_1-As_{Ga} separation is 3.46 Å. Energetically, EL2M is only about 0.13 eV higher in energy than EL2. It gives rise to an empty level heavily localized on the antisite and its three nearest-neighbors at approximately $E_c-0.16$ eV. This level is probably the one involved in the optical recovery of EL2 from EL2M with near-band-gap light.[14,15] A more delocalized occupied state similar in character to the As-derived states at the valence-band-maximum is found slightly above E_v.

The most important result obtained from the current calculations is the finding that EL2M can exist in $+1$, -1, and -2 charged states. Structurally, the main difference between the charged states and the neutral $EL2M^0$ state is the degree of relaxation that the antisite and the As_1 atom in Fig. 1 undergo. The hybridizations between the s and p orbitals on the two threefold coordinated As_{Ga} and As_1 atoms are sensitive to bond angles around these atoms and they determine the position of electronic levels in the gap. These orbitals can be approximately in either $s+p$ or $s-p$ combinations and the varying electronic occupation of these orbitals is what allows for the unusual negative charge states of the antisite.

Among the metastable charged states, $EL2M^+$ is closest in structure to $EL2M^0$. The antisite moves by 1.36 Å towards the interstitial position while As_1 moves by 0.22 Å from its bulk position towards the antisite. The As_{Ga}-As_1 separation of 3.60 Å in $EL2M^+$ is the largest among all the metastable states. The electronic structure of $EL2M^+$ is similar in some ways to that of a *negatively* charged *Ga-vacancy* defect in GaAs[22] i.e., the wave function of its half-filled resonance level that lies at $E_v+0.1$ eV has essentially zero amplitude on As_{Ga} and is primarily As p-type in character with a larger amplitude on As_1 than other As atoms. $EL2M^+$ has an empty level at about $E_c-0.03$ eV that is heavily localized at the antisite and its three nearest-neighbors. The possibility of a $+2$ charged state of EL2M was considered. The $(+2/1+)$ level of $EL2M^{2+}$ is found to lie slightly below the VBM; therefore, a $2+$ state of the antisite with a large lattice relaxation is not likely to occur in GaAs.

Free hole capture represented by

$$\mathrm{EL2M}^{0}+h_{\mathrm{VBM}}\rightarrow \mathrm{EL2M}^{+} \tag{2}$$

is calculated to be about 0.1 eV endothermic. The $EL2M^+$ state resulting from hole capture or from optical excitation of $EL2M^0$ should be EPR active. Experimentally, a trigonally symmetric EPR center in semi-insulating and p-type GaAs that is very different in nature from the stable $EL2^+$ state and which has a hyperfine splitting due to either ^{75}As or a combination of ^{69}Ga and ^{71}Ga isotopes is seen.[23] The defect was speculated to be a Ga antisite; however, it exhibits photoquenching[23] when exposed to near band gap light of 1.4-1.5 eV energy, similar to that observed in the optical recovery of EL2 from EL2M,[14,15] indicating a closer link to the As-antisite defect than to a Ga-antisite defect. The energy difference between $EL2^+$ and $EL2M^+$ is calculated to be around 0.38 eV.

Perhaps the most unusual features of EL2M are its negatively charged states. The As antisite is a double door center and it is surprising that it can be converted into a double acceptor defect through simple lattice relaxation. The basic features of the atomic structures of the negatively charged states are similar to those for the neutral metastable state of the antisite, i.e., they involve the motion of the As antisite into an interstitial site, as shown in Fig. 1. The magnitudes of the atomic relaxations, especially for the antisite, are quite different, however, for the different charge states. The displacement of the antisite is 1.41 Å in $EL2M^0$, 1.16 Å in $EL2M^-$, and 0.94 Å in $EL2M^{2-}$. The corresponding relaxations of the As_1 atom towards the antisite are 0.40, 0.46, and 0.54 Å for the three structures and the As_{Ga}-As_1 separation decreases from 3.46 to 2.85 Å in going from $EL2M^0$ to $EL2M^{2-}$. In addition, the smaller relaxations of the As nearest-neighbors of the antisite increase from 0.1 Å in $EL2M^0$ to 0.2 Å in $EL2M^{2-}$. The relaxations change the hybridization between s and p orbitals on the two threefold As atoms and the position of gap states by changing their bond angles from 114.4° (for As_{Ga}) and 97.1° (for As_1) in $EL2M^0$ to 119.8° and 93.6° in $EL2M^{2-}$. These relatively small changes in bond angles have a large effect on the electronic levels of the defects.

$EL2M^-$ has a half-filled electronic level at $E_c-0.35$ eV localized on As_{Ga} and its three nearest-neighbor As atoms. The electronic charge distribution for this state is similar to that for the first empty state of EL2M very close to the CBM examined previously.[12] The state is brought deep into the gap as a result of the different relaxations of atoms in EL2M as compared to $EL2M^-$. An intracenter optical transition at about 0.85 eV is expected for this center as a result of excitation into an electronic state with a large amplitude on As_{Ga} at $E_c+0.5$ eV. EL2M can compensate shallow donors in n-doped GaAs. Electron capture from the CBM represented by

$$\mathrm{EL2M}^{0} + e_{\mathrm{CBM}} \rightarrow \mathrm{EL2M}^{-} \quad (3)$$

releases approximately 0.24 eV in energy. The capture of a second electron by $\mathrm{EL2M}^{-}$ is even more exothermic, i.e.,

$$\mathrm{EL2M}^{-} + e_{\mathrm{CBM}} \rightarrow \mathrm{EL2M}^{2-} \quad (4)$$

releases an additional 0.43 eV in energy, indicating a negative-U nature for this defect with a U of -0.19 eV. This should make it difficult to detect $\mathrm{EL2M}^{-}$ via EPR experiments. The small energy difference of about 0.13 eV between $\mathrm{EL2}^{0}$ and $\mathrm{EL2M}^{0}$ suggests that in n-doped GaAs, EL2 centers can compensate shallow donors by getting converted into $\mathrm{EL2M}^{2-}$ centers. The ground state of the As antisite in the presence of free electrons is, therefore, the $\mathrm{EL2M}^{2-}$ state.[24] The tetrahedrally coordinated antisite is found to be metastable in the presence of free electrons in the conduction band. The disappearance of the electron trap at $E_c - 0.82$ eV trap associated with EL2 in n-doped GaAs[25] when the carrier concentration exceeds $10^{17}/\mathrm{cm}^3$ is consistent with a transformation of this defect (EL2) into a new state ($\mathrm{EL2M}^{2-}$). The existence of negatively charged states of the As antisite with very different atomic relaxations than the neutral metastable state also provides an explanation for the reduced thermal barrier for the transformation of the metastable state to the stable state in n-doped GaAs. Experimentally, it is known that the thermal barrier is reduced from about 0.34 eV in semi-insulating GaAs to 0.11 eV in the presence of free electrons in the conduction band.[2] As discussed above, the difference in the magnitude of the displacement of the antisite into an interstitial site is almost 0.47 Å between EL2M and $\mathrm{EL2M}^{2-}$ with the latter undergoing a substantially smaller lattice relaxation and $\mathrm{As_{Ga}}$-$\mathrm{As_1}$ separation.

$\mathrm{EL2M}^{2-}$ is found to occur in two distinct but energetically nearly degenerate structures. The first structure has C_{3v} symmetry as described earlier while the new structure has only twofold mirror symmetry[26] and is shown schematically in Fig. 2. In this structure two atoms, $\mathrm{As_{Ga}}$ and $\mathrm{As_2}$, undergo large motions. The principle direction of displacement for the antisite is along a cubic [110] axis with the antisite moving by 1.06 Å from its tetrahedrally coordinated site.[27] The $\mathrm{As_2}$ atom moves by 0.98 Å along an antibonding direction into an interstitial position. The resulting $\mathrm{As_{Ga}}$-$\mathrm{As_1}$ and $\mathrm{As_{Ga}}$-$\mathrm{As_2}$ distances of 2.94 and 2.75 Å, respectively are significantly larger than 2.55 Å in the tetrahedrally symmetric $\mathrm{EL2}^{0}$ state and 2.51 Å in the trigonally symmetric $\mathrm{EL2}^{+}$ state. The antisite in Fig. 2 is essentially twofold coordinated. Its displacement brings it within 2.82 Å of a distant Ga atom in the lattice (not shown in Fig. 2). The electronic structure of the two -2 charged states of EL2M are very different. The C_{3v} symmetric structure has an optical level at $E_c - 0.4$ eV while the structure with C_{1h} symmetry has an optical level at $E_v + 0.4$ eV. Changing the charge state of the low symmetry structure from -2 to -1 leads to a large decrease in atomic relaxations which make its atomic structure and electronic properties very close to that of the trigonally symmetric $\mathrm{EL2M}^{-}$ state and we will not distinguish between them, although in principle, two different states with different symmetries are involved.

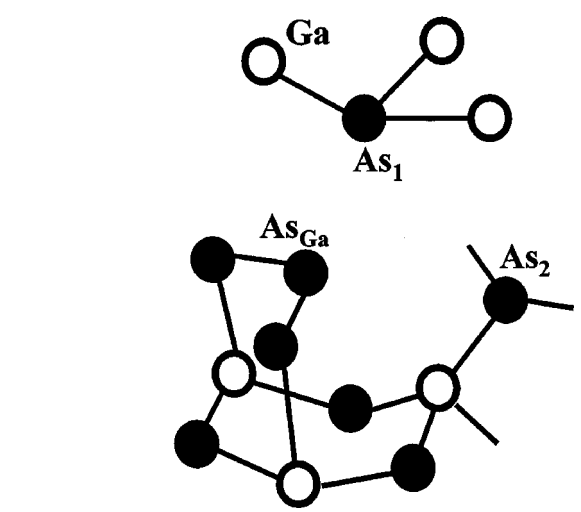

FIG. 2. An alternative low energy structure for the -2 charged state of the As-antisite defect in GaAs is shown. This structure is degenerate with that shown in Fig. 1 for the -2 state.

In connection with the two different structures for negatively charged $\mathrm{As_{Ga}}$ in GaAs, it is worthwhile to note that optically detected ENDOR experiments in electron irradiated n-type InP have shown that the corresponding $\mathrm{P_{In}}$ defect occurs in at least two different perturbed configurations differing from the T_d-symmteric on-site geometry.[28] We have performed similar first-principles calculations for InP and find that the two types of structures for the -2 charged state of the As antisite in GaAs also occur for the P antisite in InP with similar energies. The atomic relaxations and bonding in InP for the two structures are different in detail from those in GaAs but the symmetries remain unchanged.

Enhanced p-type photoconductivity at low temperatures (around 40 K) is observed after the photoquenching of the normal state of EL2 in GaAs samples grown by the liquid encapsulated Czochralski (LEC) method but not in horizontal Bridgman grown samples. LEC grown samples contain a large concentration of boron impurities and there is speculation that they form complexes that are involved in enhanced photoconductivity.[14] We have examined the effect of B on the properties of the EL2 defect in GaAs and find a nearest-neighbor $\mathrm{As_{Ga}}$-$\mathrm{B_{As}}$ antisite pair can provide an explanation for enhanced photoconductivity. In the normal state of this paired defect, the two antisites compensate each other and form a neutral center. The antisite pair has a metastable state similar in structure to EL2M (shown in Fig. 1 but with $\mathrm{As_2}$ replaced by B) in which it is an effective-mass double acceptor. It is most likely this state that is responsible for the enhanced photoconductivity in LEC grown GaAs. The compensation of the donor electrons of the As antisite by B in the neutral state of the complex makes the optical response of the antisite different than that in a normal EL2 center.

In summary, we find that the As-antisite defect in GaAs is an amphoteric defect that can compensate both shallow acceptors and shallow donors in GaAs. The antisite can exist in previously well known $EL2^0$, $EL2^+$, $EL2^{2+}$, and $EL2M^0$, as well as in $EL2M^+$, $EL2M^-$, and two different $EL2M^{2-}$ states. The existence of additional electronic levels associated with the various configurations and charge states of the As antisite opens the door to the explanation of the optical properties of the metastable state and of various defect levels (e.g., EL3, EL6, EL5, and EL14) that are known to be associated with the antisite but which have remained inexplicable so far.[29–31] For example, the EL6 electron trap defect[29] most probably corresponds to a negatively charged state of the As-antisite defect.[32] The results obtained here are also relevant to a description of the properties of the P-antisite defect in InP.[28]

[1] A. Mitonneau and A. Mircea, Solid State Commun. **30**, 157 (1970).

[2] G. Vincent, D. Bois, and A. Chantre, J. Appl. Phys. **53**, 3643 (1982).

[3] M. O. Manasreh, D. W. Fischer, and W. C. Mitchel, Phys. Status Solidi B **39**, 3239 (1989).

[4] P. Omling, E. R. Weber, and L. Samuelson, Phys. Rev. B **33**, 5880 (1986).

[5] M. O. Manasreh and D. W. Fischer, Phys. Rev. B **40**, 11 756 (1989).

[6] J. Jiménez, P. Hernandez, J. A. de Saja, and J. Bonnafé, J. Appl. Phys. **57**, 5290 (1985).

[7] M. Kaminska, M. Skowronski, and W. Kuszko, Phys. Rev. Lett. **55**, 2204 (1985).

[8] M. K. Nissen, A. Villemaire, and M. L. W. Thewalt, Phys. Rev. Lett. **67**, 112 (1991).

[9] P. Trautman and J. M. Baranowski, Phys. Rev. Lett. **69**, 664 (1992).

[10] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).

[11] J. Dabrowski and M. Scheffler, Phys. Rev. B **40**, 10391 (1989); Phys. Rev. Lett. **60**, 2183 (1988).

[12] F. Wirbeleit and J. R. Niklas, Mater. Sci. Forum **258–263**, 987 (1997).

[13] B. K. Meyer, D. M. Hoffmann, J. R. Niklas, and J.-M. Spaeth, Phys. Rev. B **36**, 1332 (1987).

[14] W. C. Mitchel and J. Jiménez, J. Appl. Phys. **75**, 3060 (1994).

[15] A. Alvárez, J. Jiménez, M. Chafai, J. Bonnafé, and M. A. Gonzalez, J. Appl. Phys. **73**, 5004 (1993).

[16] J. Jiménez, P. Hernandez, J. A. de Saja, and J. Bonnafé, Phys. Rev. B **35**, 3832 (1987).

[17] A. Fukuyama, Y. Morooka, Y. Akashi, K. Yoshino, K. Maeda, and T. Ikari, J. Appl. Phys. **81**, 7567 (1997).

[18] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[19] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[20] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[21] An energy difference between 0.03 and 0.04 eV is found for 64- and 32-atom cell calculations. The magnitudes of Helmann-Feynman forces were optimized to the greatest extent possible in order to obtain an accurate estimate of this small energy difference.

[22] The Ga vacancy is an acceptor defect and its charge ranges from -1 to -3.

[23] K. Krambrock, B. K. Meyer, and J.-M. Spaeth, Phys. Rev. **39**, 1973 (1989).

[24] The notation adopted here assigns EL2 to the tetrahedrally symmetric configuration of the antisite and EL2M to the state with large lattice relaxation. In the neutral and positively charged states, EL2 is more stable than EL2M, whereas in *n*-type GaAs, the negatively charged EL2M states are lower in energy than EL2.

[25] J. Lagowski, H. C. Gatos, J. M. Parsey, K. Wada, M. Kaminska, and W. Walukiewicz, Appl. Phys. Lett. **40**, 342 (1982).

[26] The atomic coordinates for the structure are symmetric under $x \leftrightarrow y$ interchange.

[27] The antisite moves from $(000)a$ to $(-0.13,-0.13,-0.02)a$, where a is cubic lattice constant of 5.65 Å.

[28] H. J. Sun, H. P. Gislason, C. F. Rong, and G. D. Watkins, Phys. Rev. B **48**, 17 092 (1993).

[29] Z.-Q. Fang, T. E. Schlesinger, and A. G. Milnes, J. Appl. Phys. **61**, 5047 (1987).

[30] U. V. Desnica, D. I. Desnica, and B. Santic, Appl. Phys. Lett. **58**, 278 (1991).

[31] K. Yokota, H. Kuchii, K. Nakamura, M. Sakaguchi, H. Takano, and Y. Ando, J. Appl. Phys. **88**, 5017 (2000).

[32] M. Stavola, M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **30**, 832 (1984); M. Levinson, M. Stavola, J. L. Benton, and L. C. Kimerling, *ibid.* **28**, 5848 (1983).