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# Hydrogen passivation of *EL*2 defects and $H_2^*$-like complex formation in gallium arsenide

A. Amore Bonapasta
*Consiglio Nazionale delle Ricerche, Istituto di Chimica del Materiali, Via Salaria Kilometer 29,5, Casella Postale 10, 00016 Monterotondo Scalo, Italy*

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A complex formed by one As antisite ($As_{Ga}$), one As, and two H atoms is proposed, in GaAs, which is reminiscent of the $H_2^*$ defect in crystalline Si and properly accounts for the hydrogen neutralization of the *EL*2 deep donor activity. It is noticeably stable, in agreement with experimental results. The geometry and electronic structure of this complex present interesting connections with those of the isolated As antisite which clarify the *EL*2 passivation mechanism.

The *EL*2 defect is the dominant deep defect in undoped GaAs, where it gives rise to a midgap donor level responsible for the GaAs semi-insulating properties. This defect is characterized by a well-known metastability which has attracted much attention from semiconductor researchers. It can be optically bleached, for $T < 140$ K, and regenerated by annealing (for a review of the *EL*2 properties, see Refs. 1 and 2). The *EL*2 defect shows a double donor behavior that is related to the presence of the two unshared electrons of an isolated As antisite ($As_{Ga}$) — i.e., an As atom on a Ga site (see Fig. 1). Exposure to hydrogen plasma neutralizes the *EL*2 donor activity.[3,4] This is explained by the formation of stable H-As bonds which involves the unshared $As_{Ga}$ electrons and leads to the disappearance of the electronic levels from the energy gap.[3] This assumption is quite reasonable being well known that H atoms neutralize the electrical activity of a variety of shallow and deep dopants by forming stable complexes.[5] Moreover, in hydrogenated *n*-type GaAs, an annealing at 450 °C completely restores the electrical activity of shallow centers, only partially that of *EL*2, thus indicating that H is more strongly bonded to the latter centers.[4]

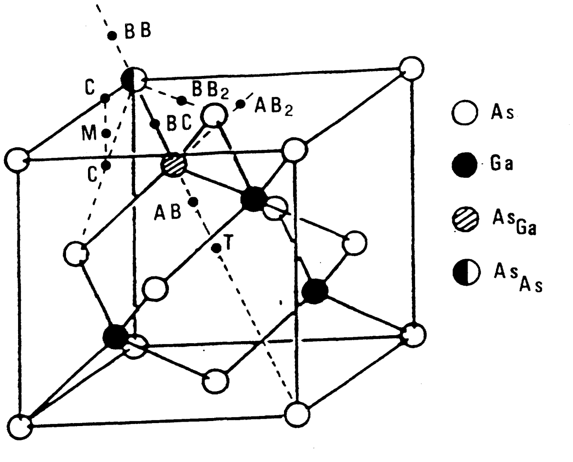

FIG. 1. Locations of an isolated As antisite ($As_{Ga}$) in GaAs and of the interstitial hydrogen sites close to the $As_{Ga}$ atom studied in the present work. The high-symmetry sites BC (bond centered), AB and $AB_2$ (antibonding sites on the $As_{Ga}$ side), BB and $BB_2$ (antibonding sites on the side of an As atom nearest neighbor of the $As_{Ga}$), and *T* (tetrahedral site) are reported in the figure together with the low-symmetry sites *C* (midway between two As atoms) and *M* (midway between two *C* sites). $As_{As}$ represents the As atom nearest neighbor of $As_{Ga}$ aligned with the $As_{Ga}$ and the AB site.

In this paper, a configuration is proposed for the H-$As_{Ga}$ complex, see Fig. 2, which is reminiscent of the $H_2^*$ defect in crystalline silicon (*c*-Si) (Ref. 6) and in crystalline GaAs (*c*-GaAs).[7] This complex is formed by two H, one As ($As_{As}$ in Fig. 2) and one $As_{Ga}$ atoms located along the same [111] axis and it will be hereafter referred to as $As_{Ga}$-$H_2^*$. It is *stable*, while the $H_2^*$ complexes in *c*-Si and *c*-GaAs are metastable. The $H_{AB}$ atom, where the $H_{AB}$ represents a H atom at the AB site (see Figs. 1 and 2), is bonded to the As antisite, the $As_{As}$-$As_{Ga}$ bond is broken, the $H_{BC}$ atom (see Figs. 1 and 2) saturates the $As_{As}$ dangling bond and has a weak bonding interaction with the $As_{Ga}$ atom which increases the stability of the complex and contributes to the neutralization of the *EL*2 activity. Interesting connections have been found

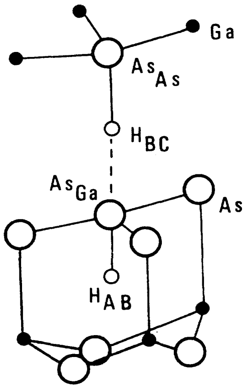

FIG. 2. Equilibrium geometry of the $As_{Ga}$-$H_2^*$ complex (see the text). The positions of the As, Ga, and H atoms are indicated by large open, small solid, and small open circles, respectively. The $As_{As}$-$As_{Ga}$-As bond angle in the figure is close to 90.0°.

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between the structural and electronic properties of the proposed complex and those of the isolated $As_{Ga}$, which clarify the *EL*2 passivation mechanism.

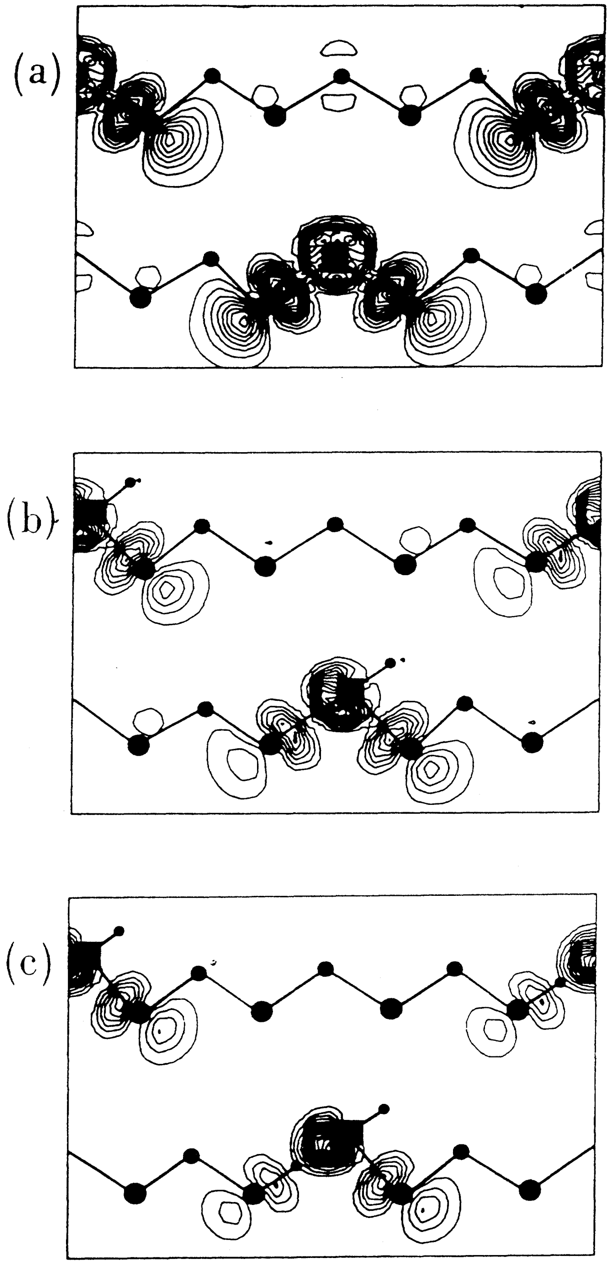

FIG. 3. Contour plots in the (110) plane of the electronic charge density ($|\Psi_{n,\mathbf{k}}|^2$) for the highest occupied state relative to (a) the isolated $As_{Ga}$ center, (b) the $As_{Ga}$-$H_{AB}$ complex, and (c) the $As_{Ga}$-$H_2^*$ complex (see the text). The atomic positions are indicated by a solid square corresponding to $As_{Ga}$ and by solid circles of different size corresponding, from the largest to the smallest, to the As, Ga, and H atoms, respectively.

The equilibrium geometries of different H-$As_{Ga}$ complexes have been investigated by performing *ab initio* total energy and force calculations in the local-density functional framework.[8,9] The geometry of supercells containing one or two H atoms and one $As_{Ga}$ atom has been fully relaxed by minimizing the Hellmann-Feynman forces on the atoms.[10] The exchange-correlation functional of Ceperley-Alder[11] has been used together with norm-conserving pseudopotentials[12] and plane-wave basis sets; **k**-space integration has been performed with the use of the special-points technique.[13] Convergence tests have been performed by using plane-wave cutoffs ranging from 12 to 16 Ry, supercells of 8, 16, and 32 atoms and **k**-point meshes equivalent to the (4,4,4) and (8,8,8) Monkhorst-Pack meshes in the zinc-blende unit cell. In the following, satisfactorily converged total energy and atomic force values have been achieved by using 32-atom supercells, the (4,4,4) **k**-point mesh and a cutoff of 12 Ry. A rough estimate of the defect level position in the gap has been obtained by taking a weighted average of the electronic eigenvalues over several high-symmetry points in the Brillouin zone. In the $As_{Ga}$-$H_2^*$ complex case, the occupancy levels relative to the defect state have been also calculated by following the approach of Baraff *et al.*[14]

First, an isolated $As_{Ga}$ has been investigated. The optimized geometry of this center shows a $T_d$ symmetry, with As-$As_{Ga}$ bonds lengths equal to 2.55 Å (the calculated Ga-As bond length is 2.43 Å). This center has a filled level in the energy gap, whose electronic eigenvalue is 0.6 eV above the top of the valence band ($E_{VB}$). The corresponding wave function [see Fig. 3(a)] is antibonding with respect to the central $As_{Ga}$ and its four As neighbors, in agreement with previous theoretical results.[1]

The formation of a H-$As_{Ga}$ complex has been then investigated by locating a H atom at the *high-symmetry* bond centered (BC) and antibonding (AB) sites and at the *low-symmetry* *M* and *C* sites shown in Fig. 1 and by relaxing the supercell geometries. The *M* and *C* sites have been chosen because they form almost a grid around the As antisite. The $H_{AB}$-$As_{Ga}$ configuration is stable, the $H_{BC}$-$As_{Ga}$ configuration is metastable, the $H_M$-$As_{Ga}$ and $H_C$-$As_{Ga}$ ones are unstable, as for pure GaAs.[15] It is worth noticing that the H atom moves from the unstable *M* and *C* sites without finding metastable, low-symmetry (or no-symmetry) sites around the As antisite. The structural details of the $H_{AB}$-$As_{Ga}$ configuration are given in Table I. The $As_{Ga}$ atom moves toward the AB site by stretching and weakening the $As_{As}$-$As_{Ga}$ bond (see Fig. 1) and forms a quite strong H-As bond, as indicated by the value of the $H_{AB}$-$As_{Ga}$ bond length (1.63 Å) and by the contour plot of the electron charge density shown in Fig. 4(a). The electrons involved in this bond occupy a level in the valence band, while a filled and a half-filled level are found in the energy gap whose electronic eigenvalues are located at $E_{VB}+0.12$ eV and $E_{VB}+0.4$ eV, respectively. The lowest level in the gap is related to the stretched $As_{Ga}$-$As_{As}$ bond, the highest one arises from the defect state of the isolated $As_{Ga}$, see Fig. 3(b). The weakening of the $As_{As}$-$As_{Ga}$ bond and a charge transfer from the $As_{Ga}$ atom to the $H_{AB}$ one reduce the antibonding character of the wave function related to the highest level [see Fig. 3(b) and compare with Fig. 3(a)], in agreement with the shift of the elec-

TABLE I. Bond lengths and atomic displacements for the stable configurations of the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ complex (first row) and of the proposed $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ complex (second row), see the text. $\mathrm{H_{BC}}$ and $\mathrm{H_{AB}}$ represent a H atom located at the BC and AB sites (see Fig. 1), respectively. $\mathrm{As_{As}}$ represents the As atom near the $\mathrm{As_{Ga}}$ and located along the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ bond axis (see Figs. 1 and 2). Atomic displacements ($\Delta X$) from the perfect GaAs lattice positions have a positive sign whenever the atoms of the $\mathrm{As_{Ga}}$-$\mathrm{As_{As}}$ bond move outward along the [111] direction. All values are given in angstroms.

| $\Delta\mathrm{As_{Ga}}$ | $\Delta\mathrm{As_{As}}$ | $\mathrm{As_{Ga}}$-$\mathrm{H_{AB}}$ | $\mathrm{As_{As}}$-$\mathrm{H_{BC}}$ | $\mathrm{As_{Ga}}$-$\mathrm{H_{BC}}$ | $\mathrm{As_{Ga}}$-$\mathrm{As_{As}}$ |
|---|---|---|---|---|---|
| 0.56 | -0.16 | 1.63 | | | 2.83 |
| 0.71 | 0.27 | 1.56 | 1.61 | 1.80 | 3.41 |

tronic eigenvalue from $E_{\mathrm{VB}}+0.6$ eV to $E_{\mathrm{VB}}+0.4$ eV.

The formation of complexes containing two H atoms has been finally investigated by taking into account that, in *c*-GaAs, a H atom behaves as a donor when located at the BC site of a Ga-As bond, as an acceptor when located at the AB site on the As side of the same bond.[15] All the possible configurations involving two H atoms located at the antibonding sites close to the $\mathrm{As_{Ga}}$ atom (e.g., *AB* and $AB_2$ in Fig. 1) or close to an As atom nearest neighbor of the $\mathrm{As_{Ga}}$ (e.g., *BB* and $BB_2$ in Fig. 1) have been, therefore, considered in order to form a complex where the double donor $\mathrm{As_{Ga}}$ could be compensated by the presence of two "acceptor" H atoms. However, they are all metastable with respect to the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ configuration. A second H atom has been also located at *off-axis* positions next to the *M* and *C* sites. The relaxation procedure has confirmed the instability of these sites by showing that the H atom moves from the off-axis positions toward the BC site, thus leading to the stable $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ configuration. It is worth noticing that, in the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ complex, the presence of a stretched, weakened $\mathrm{As_{Ga}}$-$\mathrm{As_{As}}$ bond favors indeed the insertion of a further H atom at the bond centered position (see Fig. 1). The stable configuration of the di-hydrogen complex is, therefore, characterized by the presence of an acceptor-like H atom at the AB site and of a H atom at the BC site. However, the latter H *does not behave* as a donor. This is shown by the structural details of the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ configuration, see Table I. The $\mathrm{As_{Ga}}$ atom is close to the plane formed by its three nearest neighbor As atoms and forms the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ bond. The $\mathrm{As_{Ga}}$-$\mathrm{As_{As}}$ bond is broken and the $\mathrm{H_{BC}}$ atom simply *saturates* the $\mathrm{As_{As}}$ dangling bond, thus forming a strong $\mathrm{H_{BC}}$-$\mathrm{As_{As}}$ bond instead of the three-center bond characterizing the H donor behavior.[7] This picture is confirmed by the sizeable piling up of the electron charge density along the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ and the $\mathrm{H_{BC}}$-$\mathrm{As_{As}}$ bonds, see Fig. 4(b) (similar charge density distributions are found in the $\mathrm{H}_2^*$ complexes[6,7]). A small but appreciable charge density piling up between the $\mathrm{H_{BC}}$ and the $\mathrm{As_{Ga}}$ atoms [see Fig. 4(b)] suggests an additional, weak bonding interaction between these atoms which favors an $sp^2$ hybridization of the $\mathrm{As_{Ga}}$ atom (see Fig. 2) and stabilizes the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ complex. In fact, this complex is 0.6 eV lower in energy than a $\mathrm{H}_2$ molecule located at a *T* site (see Fig. 1), while the $\mathrm{H}_2^*$ defect is metastable.[6,7] The noticeable stability of the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ complex is confirmed by the dissociation energies ($E_d$) of the two H-As bonds which have been estimated by considering the formation of the $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ or the $\mathrm{H_{BC}}$-$\mathrm{As_{Ga}}$ complexes plus an interstitial H atom at its stable site. In fact, the $E_d$ values for the $\mathrm{H_{BC}}$-$\mathrm{As_{As}}$ and $\mathrm{H_{AB}}$-$\mathrm{As_{Ga}}$ bonds (2.3 eV and 2.8 eV, respectively) are significantly greater than that evaluated for the $\mathrm{H_{AB}}$-As bond in GaAs, 1.46 eV,[15] or measured for several bonds formed by shallow dopants and hydrogen in GaAs.[16] The $E_d$ value corresponding to the breaking of both the H-As bonds, 3.5 eV, further confirms the peculiar stability of the proposed complex, which agrees with the experimental observation that the thermal recovery of the hydrogenated *EL*2 centers needs temperatures higher than those required for the recovery of hydrogenated shallow impurities.[4]

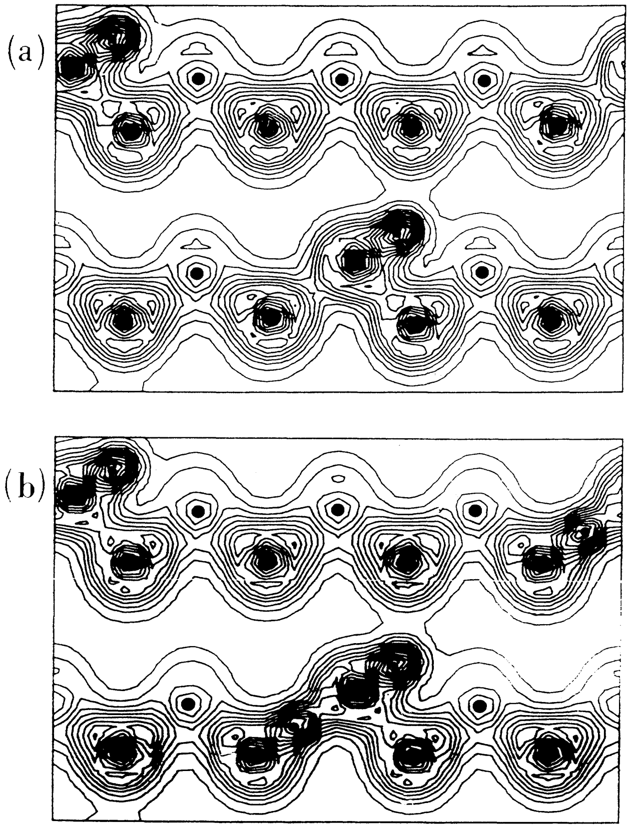

FIG. 4. Contour plots in the (110) plane of electronic charge density for the stable configuration of (a) the $\mathrm{As_{Ga}}$-$\mathrm{H_{AB}}$ complex and (b) the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ complex (see the text). The atomic positions are indicated by a solid square corresponding to $\mathrm{As_{Ga}}$ and by solid circles of different size corresponding, from the largest to the smallest, to the As, Ga, and H atoms, respectively.

The electronic structure of the $\mathrm{As_{Ga}}$-$\mathrm{H}_2^*$ complex is characterized by two filled levels in the valence band corresponding to the stable H-As bonds and by a filled level degenerate with the top of the valence band, thus accounting for the passivation of the *EL*2 activity. The wave function related to the last level, see Fig. 3(c), is distinguished by a reduced antibonding character with respect to that of Fig. 3(b), due to the breaking of the $As_{Ga}$-$As_{As}$ bond, and by an *sp*-orbital contribution from the $As_{Ga}$ atom which piles up electronic charge between the H and the As antisite, thus accounting for the above weak $H_{BC}$-$As_{Ga}$ bonding interaction. The occupancy levels relative to the highest electronic level confirm the passivation of the As antisite. The state relative to the doubly occupied level is indeed more stable than that corresponding to the singly (or zero-) occupied one, when the Fermi level is located at the top of the valence band.

It may appear surprising that the formation of a di-hydrogen complex containing only one "acceptor" $H_{AB}$ atom leads to the $As_{Ga}$ passivation. However, some relationships between the properties of the isolated $As_{Ga}$ and those of the $As_{Ga}$-$H_2^*$ complex can account for this result. The isolated $As_{Ga}$ reaches its metastable site through a displacement of 1.4 Å along the [111] direction, far from the $As_{As}$ atom and toward the AB site of Fig. 1.[1,17] The barrier opposing this motion shows a maximum for an $As_{Ga}$ displacement of the order of 0.6 Å.[1,17] At the barrier maximum, the defect level of the $As_{Ga}$ is lowered in energy. It disappears from the energy gap when the $As_{Ga}$ is located at its metastable site, i.e., the *EL*2 donor activity is *neutralized* even in absence of H atoms.[17] In detail, in the barrier region, a charge transfer takes place from the $As_{Ga}$ to the $As_{As}$ atom through two quasidegenerate levels in the energy gap which localize the two unpaired electrons, one on each of these two atoms.[1] The electronic eigenvalues related to these levels are lowered by about 0.3 eV (present estimate) with respect to that of the $As_{Ga}$ defect state, when relaxation effects are taken into accounts. This lowering can be accounted for by a reduction of the antibonding character of the defect state due to the breaking of the $As_{Ga}$-$As_{As}$ bond and by a partial charge transfer from the $As_{Ga}$ to the $As_{As}$ atom. When the $As_{Ga}$ reaches its metastable site, the quasidegenerate levels evolve in a level deep into the valence band which localizes both the electrons on the $As_{As}$ atom.[1,17] The defect level of an isolated $As_{Ga}$ is, therefore, stabilized by a charge transfer related to the motion of the $As_{Ga}$ atom from the stable to the metastable position. In the $As_{Ga}$-$H_2^*$ complex, six electrons must be taken into account: the two electrons of the broken $As_{Ga}$-$As_{As}$ bond, the two electrons introduced by the H atoms and the two electrons of the $As_{Ga}$ defect level. Four electrons are involved in the formation of the two strong $H_{AB}$-$As_{Ga}$ and $H_{BC}$-$As_{As}$ bonds thus filling two electronic levels deep in the valence band. Two more electrons fill a level related to the defect level of the $As_{Ga}$ [see Fig. 3(c)]. However, in the di-hydrogen complex, the displacement of the $As_{Ga}$ atom (0.71 Å) is even *larger* than that in the barrier configuration and a lowering of the $As_{Ga}$ defect state occurs because the $As_{Ga}$-$As_{As}$ bond is broken (thus reducing the antibonding character of this state) and a partial charge transfer takes place from the $As_{Ga}$ to the $H_{BC}$ atom [see Fig. 3(c)]. The displaced $As_{Ga}$ tends indeed to lose one electron as at the barrier configuration, thus resulting in a more stable defect level. A charge transfer is also induced by the presence of the acceptor $H_{AB}$ atom thus further stabilizing the defect state and leading to its disappearance from the energy gap.

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