PHYSICAL REVIEW B VOLUME 48, NUMBER 12 15 SEPTEMBER 1993-II

Hydrogen passivation of carbon-doped gallium arsenide

A. Amore Bonapasta
Consiglio Nazionale delle Ricerche (CNR), Istituto Chimica dei Materiali (ICMAT), Via Salaria Km 29,
500–Casella Postale 10, 00016 Monterotondo Scalo, Italy

(Received 14 December 1992; revised manuscript received 23 April 1993)

The stability of a C atom at the cationic and anionic sites in GaAs and the hydrogen passivation of the C dopant activity have been investigated by performing first-principles total-energy calculations within the pseudopotential-density-functional-theory framework. In these calculations it is found that the C atom has almost the same stability at the gallium and at the arsenic sites. It is suggested that the preferred incorporation of C at the As site is due to phenomena occurring at the grown surface of GaAs. The H atom forms stable complexes with both the C acceptor (C_{As}) and the C donor (C_{Ga}). The H-C_{As} and H-C_{Ga} complexes show the same structural features despite previous theoretical results. They are both characterized by a stable configuration where the H atom is located at the bond-centered site by a strong H-C interaction and by negligible interactions of H with the host atoms. Present results give theoretical evidence of the hydrogen passivation of C donors and acceptors. Moreover, they suggest that hydrogen may form strong bonds with carbon and passivate its dopant activity even in other III-V semiconductors.

I. INTRODUCTION

Recently, there has been considerable interest on carbon doping of III-V semiconductors.[1–5] A diffusion coefficient much smaller than that of Be (the acceptor of choice for GaAs in conventional molecular-beam epitaxy), a high solubility, and a high doping efficiency (hole concentrations in excess of $1\text{x}10^{20}$ cm^{-3}) render carbon indeed an excellent candidate for high doping of GaAs. Furthermore, carbon is an unintentional dopant of GaAs grown by gas source molecular-beam epitaxy or chemical-beam epitaxy, due to the decomposition of the organometallic compounds (e.g., trimethylgallium).[6]

Carbon, like the isovalent silicon, may show amphoteric properties in III-V semiconductors. A carbon atom may indeed occupy a site on the group-III sublattice, thus giving rise to a donor behavior, or on the group-V sublattice, thus giving rise to an acceptor behavior. However, while silicon may behave as an acceptor or a donor in a given III-V material (e.g., GaAs), carbon is generally known as an acceptor in GaAs and $Al_xGa_{1-x}As$,[2,4] as a donor in InAs and $In_xGa_{1-x}As$.[7] A compensating behavior has been also observed in $In_xGa_{1-x}As$.[7]

The interaction of atomic hydrogen with native defects and impurities in semiconductors has been widely investigated both experimentally and theoretically.[8,9] It is now well established that the introduction of H atoms in semiconductors causes the loss of electrical activity of a variety of shallow donors and acceptors. In general, this phenomenon has been explained in terms of the amphoteric behavior of the hydrogen atom and of the formation of complexes involving hydrogen and dopant atoms. Hydrogen introduced in a semiconductor gives indeed rise to a donor level in *p-type* materials and to an acceptor level in *n-type* ones, thus leading to the electrical compensation of the dopants. Moreover, the diffusing H ions (H^+ or H^-) pair with ionized dopants thus forming neutral complexes where the presence of the hydrogen in the close proximity of the dopant significantly modifies its electronic energy state. The formation of the hydrogen-dopant complexes plays an important role in the loss of the electrical activity of the dopant. The overall process has been therefore termed neutralization or passivation by opposition to the simpler compensation mechanism where the dopant atom remains isolated. The hydrogen passivation of the dopant activity has quite interesting applications in carbon-doped III-V materials. As an example, the formation of stable hydrogen-carbon complexes can be used to neutralize the dopant activity only in selected regions of a given sample. This capability and the good qualities of the C dopant have been utilized in the technological processes of realization of various electronic devices.[10] Furthermore, the hydrogenation process may be used to neutralize the electrical effects due to unintentional carbon incorporation.

The hydrogen passivation of carbon-doped *p-type* GaAs has not been extensively investigated so far. Recently, far-infrared[11–13] and Raman[14] spectroscopy studies have given support to the formation of a hydrogen-carbon complex in GaAs and suggestions about its structure. The same studies have provided the vibrational energy values of the H local modes. Two theoretical studies have been also published;[15,16] both focused on the interaction of hydrogen with the carbon acceptor. The former has provided preliminary results on the structure of the H-C complex and the characteristics of the H-C bond. In this study, the equilibrium geometries of different complex configurations and the vibrational energies of the H local modes have been calculated by using atomic pseudopotentials and plane-wave basis sets in the local-density-functional framework (PPLDF).[17,18] The latter study has given the structure of the H-C complexes, a detailed analysis of the H local modes, and preliminary results on the structure of the complex formed by hydrogen and a carbon donor. In this study, the calculations have been performed by using Gaussian-orbital basis sets in a local-density-functional cluster (LDFC) approach.[16]

In the present study, PPLDF calculations have been performed to achieve a clear understanding of the interaction of hydrogen with both the carbon acceptors and donors as well as a theoretical evidence of the neutralization of the dopant activity. Some features of the carbon incorporation in GaAs have been also investigated. In particular, the stability of a carbon atom located at a gallium site (C_{Ga}) and at an arsenic site (C_{As}) has been studied in order to clarify the tendency of the C atom to occupy the latter site. The results achieved indicate that the location of a C atom at an As site is not energetically favored with respect to its location at a Ga site. The disagreement between theoretical and experimental findings has been discussed. It has been also suggested that the incorporation of a C atom at the cationic or anionic sites is controlled by other effects, such as phenomena occurring at the grown surface.

The structural properties of the C_X-H (X=Ga,As) complexes, i.e., the complexes formed by hydrogen, a carbon dopant, and their nearest arsenic or gallium atoms, have been carefully investigated together with the changes induced by the formation of the complexes on the defect levels in the energy gap. The results achieved have shown that the H-C_{As} and H-C_{Ga} complexes have the same stable configuration and are both characterized by a strong H-C interaction. It is worth noticing that these findings are somewhat unexpected because quite different from those obtained in the case of the isovalent Si dopant[19–21] and in partial disagreement with the LDFC results.[16] Present results have also established that hydrogen neutralizes the dopant activity of both the carbon acceptors and donors.

The results concerning the geometries and the electronic structure of the H-C complexes suggest that hydrogen may strongly interact with carbon and passivate its dopant activity even in other III-V materials. It is expected, therefore, that the present results have a general usefulness in the understanding of the hydrogen passivation of C-doped, III-V semiconductors.

The stability of the H-C complexes, a crucial feature in the technological processes based on the hydrogen passivation of the C dopant,[10] has been also investigated.

II. METHODS

The equilibrium geometries of the complexes formed by a C atom or a H-C pair with their nearest-neighbor Ga and As atoms have been investigated by performing total-energy and -force calculations in the PPLDF framework. In particular, the H atom has been located at different high-symmetry sites of a supercell whose structure has been fully relaxed. The pseudo-wave-functions have been expanded in plane-wave basis sets with kinetic-energy cutoffs ranging from 12 to 16 Ry. The vibrational energies of the H local modes have been evaluated in the harmonic approximation by fitting the total-energy values to a parabola. Convergence tests have been performed by comparing the results obtained for supercells of 8, 16, and 32 atoms. The technical details are similar to those of Ref. 22.

For what concerns the passivation phenomenon, the investigation of the defect levels in the energy gap is crucial in order to make clear the electrical neutralization of the dopant activity. However, such an investigation may be performed only at a qualitative level in the PPLDF framework. Defect levels showing no dispersion for an isolated impurity form indeed a band, when using finite-size supercells, because of the interactions between impurities in neighboring cells. A more important limit of the local-density (LD) treatments concerns the position of the electronic levels in the energy gap. It is well known, indeed, that LD predicts conduction bands and hence conduction-band-related energy levels to be too low. Notwithstanding, the PPLDF method may provide useful results about the existence and the nature of defect levels. It has indeed predicted a H-induced donor level in crystalline silicon (*c*-Si),[23] which agrees with the observation of H^+ species in boron-doped silicon.[24] In *c*-GaAs, shallow and deep H-related levels in the gap have been evaluated,[25,26] in agreement with experimental measurements.[26] In phosphorus-doped *c*-Si, a defect level has been evaluated about 0.2 eV below the bottom of the conduction band.[27] Although this level does not account for the shallow character of the P dopant because of the above-mentioned LD limits, it is located in the upper half of the band gap in agreement with the donor character of phosphorus. Moreover, the P defect level disappears when a H-Si-P complex is formed, thus proving the electrical neutralization of the P atom.[27]

In the present work, a kinetic energy cutoff of 16 Ry has given a direct energy gap equal to 1.4 eV in the 32-atom supercell (to be compared with the experimental value of 1.52 eV).[28] This supercell size has also given a band structure for the C-doped GaAs which strongly resembles that of pure GaAs. The position of a defect level in the energy gap has been evaluated by taking a weighted average of the related electronic eigenvalues over several high symmetry points in the Brillouin zone. The position and the dispersion of an electron level have been tested against the supercell size by comparing the results obtained with 16- and 32-atom supercells. In the C_{Ga} case, the dispersion of the donor level in the gap was ~ 1.1 and 0.4 eV for 16- and 32-atom cells, respectively. In the C_{As} case, no defect levels have been observed in the gap. This is likely due to the closeness of the shallow acceptor level to the top of the valence band. It has been therefore impossible to establish the electrical neutralization of the C acceptor through a direct analysis of the electronic levels in the energy gap. This problem has been overcome by analyzing the distribution of the valence charge density and of the electronic charge density $|\Psi_{n,\mathbf{k}}|^2$, determined by the wave functions $\Psi_{n,\mathbf{k}}$ related to the defect level and to the states at the top of the valence band, as discussed in the following sections.

A Gaussian broadening scheme[29] has been used to deal with the Fermi surface whenever the unit cell contained an odd number of electrons.

III. RESULTS AND DISCUSSION

A. C stability at the Ga and As sites

Carbon is generally incorporated at the anionic site in GaAs. The carbon incorporation may be affected by a different stability of the C atom at the Ga and As sites. In order to investigate this point, the structures of two supercells of GaAs containing a carbon acceptor and a carbon donor, respectively, have been fully relaxed. The equilibrium geometries of the supercell structures show that the As (Ga) atoms nearest neighbor of the C_{Ga} (C_{As}) one move symmetrically toward the dopant site. The optimized C_{Ga}-As and C_{As}-Ga bond lengths are 2.20 and 2.10 Å, respectively, to be compared with a Ga-As bond length of 2.43 Å (theoretical value). It is worth noticing that a contraction of the lattice constant $\Delta a/a = 1.3 \times 10^{-3}$ has been experimentally observed in C-doped GaAs (GaAs:C) for a doping level of 7.2 $\times 10^{19}$ cm^{-3}.[1,2] This value may be compared with an estimate of 4.0 $\times 10^{-3}$ made by using the above C_{As}-Ga bond length. The stability of a C_{Ga} atom has been evaluated by calculating the dissociation energy of the complex formed by the C atom and by its nearest-neighbor As atoms. The dissociation of this complex leads to the formation of a gallium vacancy (V_{Ga}) plus an interstitial C atom (C_i), as represented by the following reaction:

$$(C_{Ga})_{complex} \longrightarrow V_{Ga} + C_i .$$

The structures of two supercells containing a V_{Ga} vacancy and a C_i atom located at a tetrahedral site (see Fig. 1) have been therefore relaxed in order to evaluate their minimum energies. The dissociation energy E_d has been then estimated as the energy difference between the initial and the final states of the reaction:

$$E_d = E(C_i) + E(V_{Ga}) - E(C_{Ga}) - E(\mathrm{GaAs})$$

where $E(C_i)$ is the total energy of a 32-atom supercell of GaAs containing a C_i atom, $E(V_{Ga})$ is the total energy of a supercell of the same size containing a gallium vacancy, and so on. Similarly, the stability of the C acceptor has been evaluated by considering the complex formed by a C_{As} atom and by its nearest-neighbor Ga atoms, whose dissociation leads to the formation of an arsenic vacancy (V_{As}) and of an interstitial C atom. Dissociation energies of 12.4 eV and 12.0 eV have been found for the donor and the acceptor cases, respectively, by using this procedure. The same quantities, roughly estimated by the sum of the dissociation energies of four C-As or C-Ga molecular bonds,[30] are equal to 10.9 eV and 9.9 eV, respectively. The slight difference between the stabilities of a C atom located at the Ga site and at the As one should favor an amphoteric behavior of the C dopant. The present results cannot explain, therefore, the preference given by the C atom to the As site. The disagreement between theoretical and experimental results needs some comments. The convergence of the present total-energy calculations has been carefully checked and the evaluated dissociation energies for the complexes with carbon seem reasonable. Notwithstanding, further calculations could be required in order to determine the relative stability of the C_{As} and C_{Ga} impurities. As an example, present investigations take into account neither dynamical aspects of the C_{As} and C_{Ga} complex dissociation, such as effects of energy barriers opposing to the dissociation process nor a possible influence of intrinsic point defects (e.g., arsenic and gallium vacancies) on the stability of C donors and acceptors. The C incorporation might be also affected by phenomena occurring at the grown surfaces. A qualitative explanation of the C incorporation in GaAs, as well as in InAs (where carbon is incorporated at the cationic site) and $In_xGa_{1-x}As$, may indeed be attempted by comparing the strenghts of the molecular C-Ga, C-In, and C-As bonds, whose dissociation energies are 63 Kcal/mol,[30] 49 Kcal/mol,[30] and 57 Kcal/mol,[31] respectively. C and Ga atoms may form bonds stabler than the C-As ones on the grown surface of GaAs, thus favoring the C incorporation at the As site. Similarly, the formation of C-As bonds stabler than the C-In ones may account for the C donor behavior in InAs and for C autocompensation in $In_xGa_{1-x}As$. The relevance of surface phenomena in the C incorporation should be supported by accurate theoretical investigations, which are, however, behind the scope of the present study. Finally, it may be worth noticing that a localized vibrational mode line at 563 cm^{-1} has been recently observed in carbon-doped GaAs, which might be due to the C donors or to a transverse mode of the H-C_{As} pairs.[13]

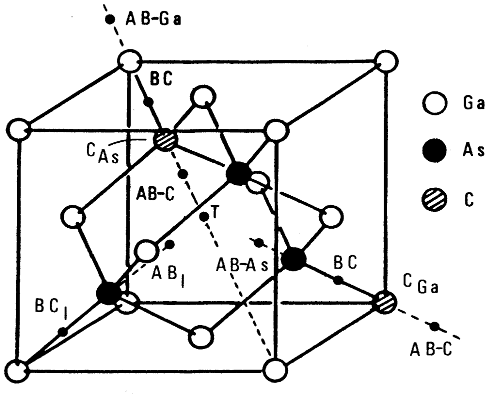

FIG. 1. Locations of a C donor (C_{Ga}) and a C acceptor (C_{As}) in GaAs and high-symmetry interstitial sites for the hydrogen atom studied in the present work. BC is the bond-centered site, AB-C is the antibonding site on the carbon side, and AB-Ga and AB-As are the antibonding sites on the gallium side and on the arsenic side, respectively. The same hydrogen sites may be considered in the Si dopant case (i.e., when the Si atom replaces the C one). A tetrahedral site T is also reported in the figure together with the BC_I and the AB_I sites, which are H equilibrium sites in intrinsic GaAs (see the text).

B. Structural properties of the C_X-H complexes (X=Ga,As)

In order to determine the stable structure of the C_{As}-H and C_{Ga}-H complexes, different complex configurations have been investigated by locating a H atom at the interstitial sites of Fig. 1 and by fully relaxing the geometry of the corresponding supercells. In the acceptor case, this procedure results in a stable bond-centered site (BC) configuration, in a metastable antibonding site on the carbon side (AB-C) configuration 0.6 eV higher in energy, and in an unstable AB-Ga configuration. These configurations all show an *on-line* geometry where the atoms in the complex, i.e., the H atom and the atoms of a C_{As}-Ga bond, are located along a [111] bond axis. The structural details of these configurations are reported in Table I together with the vibrational frequencies of the H local modes. Present results nicely agree with those of far-infrared and Raman spectroscopy studies,[11,12,14] which find a stable BC configuration for the C_{As}-H complex and give a value of 2635.13 cm^{-1} for the H stretching mode frequency. A satisfactory agreement is found with the LDFC results,[16] which are also reported in Table I. In the BC configuration, where the H atom is located between the atoms of a C_{As}-Ga bond, the C-H interaction is stronger than the Ga-H one. The calculated C-H and Ga-H bond lengths are indeed, respectively, 10% and 27% greater than those estimated by using the atomic covalent radii[32] (i.e., 1.09 Å for the C-H bond and 1.58 Å for the Ga-H one). The formation of a strong C-H bond is further confirmed by the vibrational energy value of the H stretching mode and by a contour plot of the electron charge density in the (110) plane; see Fig. 2(a). The value of the H stretching mode approaches within a 10% that measured in the methane molecule (2914 cm^{-1}).[33] The density plot of Fig. 2(a) shows a concentration of the electron charge around the C-H pair, which indicates that the chemical binding in the complex is mainly characterized by a two-center interaction. All these results indicate that the H atom has a negligible interaction with the Ga atom whereas it is strongly attached to the lobe of an sp^3 orbital of the C atom.

Both the PPLDF and the LDFC methods give significant values for the frequencies of the H bending modes (see Table I), which, however, have not been observed by far-infrared measurements.[11,12] In the LDFC study,[16] the invisibility of these modes has been attributed to a too small effective charge.

TABLE I. Equilibrium geometries for different configurations of the C_{As}-H complex (C acceptor case) and vibrational energies of the H local modes. For the H atom located at the BC, AB-C, and AB-Ga sites (see Fig. 1) the complex configurations are stable, metastable, and unstable, respectively. Some results obtained by using the LDFC method (see the text) are reported in the last row of the table. Atomic displacements from the unrelaxed positions have a positive sign whenever the atom moves outward in the [111] direction. Bond lengths and atomic displacements are given in angstroms, vibrational frequency values in cm^{-1}.

Site	ΔGa	ΔC	C-H	Ga-H	C-Ga	ν_s	ν_b
BC	0.46	0.30	1.20	2.00	3.20	2781	724
AB-C	-0.09	0.34	1.20	3.87	2.68	2825	872
AB-Ga	-0.44	0.07	3.83	1.77	2.06		
BC[a]			1.13	2.20	3.33	2605	730

[a] Reference 16.

The configurations of the complex formed by hydrogen and the carbon acceptor may be compared with those of the complex formed by hydrogen and the isovalent silicon acceptor in GaAs.[19] For silicon, like for carbon, the BC configuration is the stable one, the AB-Si configuration is metastable and the AB-Ga configuration is unstable. In the BC configuration, however, the strengths of the H-Si and H-Ga bonds are comparable. The H-Si and the H-Ga bond lengths, which are equal to 1.55 Å and 1.70 Å, respectively, are indeed 4% and 7% longer than the corresponding estimates made by using the atomic covalent radii[32] (i.e., 1.49 Å for the Si-H bond and 1.58 Å for the Ga-H one). The BC configuration is therefore characterized by a three-center interaction in the Si case, by a two-center one in the C case.

In the C donor case, like in the acceptor one, the BC, the AB-C, and the AB-As configurations are the stable, the metastable, and the unstable ones, respectively. The

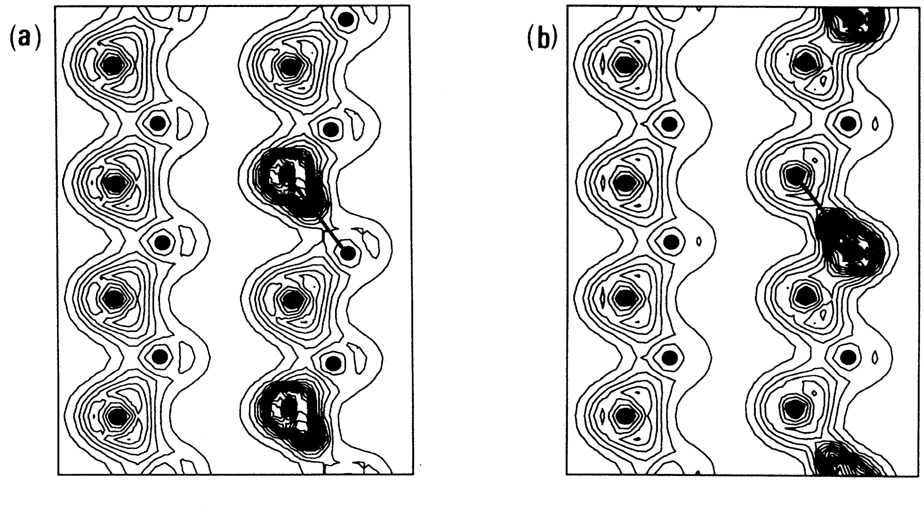

FIG. 2. Contour plots in the (110) plane of the valence charge density for the BC configuration of the H-C complexes: (a) H-C_{As} complex, (b) H-C_{Ga} complex. The atomic positions are indicated by solid circles of different size corresponding, from the largest to the smallest, to As, Ga, C, and H atoms, respectively.

structural details of the configurations of the C_{Ga}-H complex are given in Table II. The stability of the BC configuration is somewhat surprising. A different configuration, the AB-C one, is indeed indicated as the stable one by the LDFC study.[16] Moreover, the AB-Si configuration (see Fig. 1) is the stable one for the complex formed by hydrogen and the Si donor in GaAs.[19] A careful analysis of the geometries of the AB-Si and AB-C configurations (see Table II) may account for this different behavior of the C and Si donors. In the AB-Si configuration, the Si atom moves from the As atom located along the H-Si bond axis toward the H atom, becoming almost coplanar with its three nearest-neighbor As atoms. However, the *on-axis* As atom follows the Si one thus indicating a slight bonding Si-As interaction. In this geometry, the Si atom has therefore a partial fivefold coordination, as in the amorphous silicon case,[34,35] which may stabilize the AB-Si configuration. In the AB-C configuration, instead, the *on-axis* As atom goes away from the C one in agreement with the fact that the C atom does not sustain fivefold coordinations.

The BC configuration of the C_{Ga}-H complex presents the same structural features as the C_{As}-H complex. The C-H and the H-As bond length values are indeed, respectively, 10% and 30% greater than those estimated by the atomic covalent radii (i.e., 1.09 Å for the C-H bond and 1.50 Å for the As-H one), thus indicating that the H-C interaction is stronger than the As-H one. The C-H bond length and the H stretching mode frequency have values close to those found for the C_{As}-H complex. A contour plot of the electron charge density, see Fig. 2(b), shows that the charge density has its largest values around the C-H pair, as in the acceptor case [see Fig. 2(a)]. The stable complexes formed by carbon acceptors and donors with hydrogen are therefore both characterized by a strong H-C interaction.

TABLE II. The equilibrium geometries for the different configurations of the C_{Ga}-H complex (C donor case) and the vibrational energies of the H local modes are reported in the first three rows of the table (X=C). For the H atom located at the BC, AB-C, and AB-As sites (see Fig. 1) the complex configurations are stable, metastable, and unstable, respectively. Some results given by the LDFC method for the same complex (X=C, see the text) are reported in the fourth row of the table. The geometry of the stable configuration of the Si_{Ga}-H complex (X=Si, see the text) is given in the last row. Atomic displacements from the unrelaxed positions have a positive sign whenever the atom moves outward in the [111] direction. Bond lengths and atomic displacements are given in angstroms, vibrational frequency values in cm^{-1}.

Site	ΔAs	ΔX	X-H	As-H	X-As	ν_s	ν_b
BC	0.38	0.35	1.21	1.95	3.16	2760	930
AB-C	0.14	0.74	1.21	4.52	3.31	2743	944
AB-As	-0.08	0.12	4.34	1.86	2.48		
AB-C[a]			1.08	4.24	3.16		
AB-Si[b]	-0.26	0.51	1.63		2.67	1590	790

[a] Reference 16.

[b] Reference 19.

Although a carbon donor behavior has not been observed in GaAs, the results here obtained by investigating the structural properties of the C_{Ga}-H complex are quite interesting. These results, together with those obtained for the C_{As}-H complex, show indeed that the strength of the C-H bond and the atomic arrangement of the C-H complexes are somewhat *intrinsic* characteristics of the H-C interaction. Therefore, the formation of H-C complexes having these characteristics is expected even in other III-V materials, e.g., in InAs, where the formation of a C_{In}-H complex with the H atom located at the BC site may be predicted.

C. Dissociation energies of the C_X-H complexes (X=Ga,As)

The stability of the H-C complexes plays a key role in the technological processes based on the hydrogen passivation of carbon.[10] The thermal stability of several dopant-hydrogen complexes in GaAs has been recently investigated by performing experiments of thermal annealing in presence of an electric field.[36,37] This technique avoids the reassociation of the H ions and the ionized dopants produced by the dissociation of the hydrogen-dopant complexes. However, these experiments measure an energy which corresponds to the binding energy of the hydrogen-dopant pair plus the H-migration energy. It is therefore quite interesting to compare these experimental results with theoretical estimates of the dissociation energies of the H-C complexes. These quantities have been estimated here as the energy difference between the initial and the final state of the reactions:

$$(\text{Ga-H-C}_{\text{As}}) \longrightarrow \text{Ga-C}_{\text{As}} + \text{H}^0,$$

$$(\text{As-H-C}_{\text{Ga}}) \longrightarrow \text{As-C}_{\text{Ga}} + \text{H}^0,$$

where it is supposed that the formation of the H ions follows the release of a neutral H atom by the complex. The H atom is located in its minimum-energy site in GaAs.[25]

The related dissociation energies are, respectively,

$$E_d = E(\text{Ga-C}_{\text{As}}) + E(\text{H}^0) - E(\text{Ga-H-C}_{\text{As}}) - E(\text{GaAs}),$$

$$E'_d = E(\text{As-C}_{\text{Ga}}) + E(\text{H}^0) - E(\text{As-H-C}_{\text{Ga}}) - E(\text{GaAs}),$$

where, e.g., $E(\text{Ga-C}_{\text{As}})$ is the total energy of a 32-atom supercell containing a C_{As} acceptor.

The calculated dissociation energies are 1.85 eV and 1.60 eV for the complexes formed by the C acceptor and the C donor, respectively. These values are reported in Table III together with experimental findings[36] and values calculated, by using the PPLDF method, for the Si-H complexes.[19] The dissociation energies of the C-H and the Si-H bonds in methane and silane molecules[30] are also reported in the same table. The theoretical values are always greater than their experimental counterparts and lower than the values measured for molecules. In the case of the C and Si acceptors, where the same stable configuration has been found for the complexes formed with hydrogen, the theoretical results give a dissociation

TABLE III. Theoretical and experimental dissociation energies of the H-C and H-Si complexes in their stable configurations (see the text). The dissociation energies of the H-C and the H-Si bonds in methane and silane molecules are given in the last column. The dissociation energy values are given in eV.

Complex	H site	E_d (Theor.)	E_d (Expt.)	E_d (molec.)
H-C_{As}	BC	1.85	1.35[b]	4.3[c]
H-C_{Ga}	BC	1.60		
H-Si_{As}	BC	1.75[a]	1.45[b]	3.3[c]
H-Si_{Ga}	AB	2.20[a]	1.25[b]	

[a] Reference 19.

[b] Reference 36.

[c] Reference 30.

energy of the H-C complex slightly higher than that of the H-Si one, in agreement with a H-C stretching mode frequency ~500 cm^{-1} higher than that found for the H-Si pair[19] and with the different strength of the H-C and the H-Si molecular bonds. For the same complexes, the experimental dissociation energy values are close as the theoretical ones; however, they indicate the H-Si bond as the stabler one. In the case of the C and Si donors, theory gives quite different dissociation energies for the H-C and the H-Si complexes which have, however, different configurations. The theoretical dissociation energy of the H-Si complex is significantly larger than the experimental one. In conclusion, the PPLDF methods show a tendency to overestimate the binding energies of both the H-C and H-Si complexes. Moreover, theory and experiment indicate that the stability of the H-C complexes is comparable with that of the H-X complexes formed by the most utilized dopants in GaAs (X= Sn, Se, Zn, Be, Cd), whose experimental dissociation energies range between 1.15 and 1.52 eV.[36]

D. Hydrogen passivation of the C dopant

In GaAs, a hydrogen atom induces a donor level in the band gap when placed in a bond-center site (BC_I in Fig. 1), a deep acceptor level when located in the stable antibonding site (AB_I in Fig. 1).[25] In C-doped GaAs, H may therefore compensate a shallow donor level, as well as a shallow acceptor one, by leading to the formation of H^+ or H^- ions and of charged dopant atoms. The electrical neutralization of the dopant activity is realized when the pairing between the mobile H ions and the ionized dopants is accompanied by the disappearance of the defect levels in the gap or by the evolution of the same levels from shallow to deep levels. The electrical neutralization of the C dopant in GaAs has not been theoretically established yet. The LDFC calculations[16] have indeed given an energy gap cleared of levels for both the C acceptor and the C donor, even in absence of hydrogen. This result does not allow us to relate the disappearance of the levels in the gap to the effects of the hydrogen-dopant interaction.

In the present work, the passivation of the C dopant has been investigated by analyzing the location of the defect levels in the energy gap and the electronic charge density distributions related to these levels, before and after the formation of the H-C complexes. In the absence of H, a C donor induces a level in the energy gap about 0.25 eV below the bottom of the conduction band. This level is in the upper half of the energy gap, but it does not account for the shallow character of the C donor level because of the intrinsic limits of the local-density approach discussed in a preceding section. The defect level disappears when the H atom is located at the stable BC site to form the H-C_{Ga} complex, thus indicating the C passivation. In the C acceptor case, instead, no defect levels have been identified in the energy gap. Thus, the dopant passivation cannot be established through a direct analysis of the electron energy levels. Notwithstanding, an evidence of the C passivation has been obtained by analyzing the distribution of the valence charge density and of the charge densities $|\Psi_{n,\mathbf{k}}|^2$, produced by the electronic wave functions $\Psi_{n,\mathbf{k}}$ related to the levels near the top of the valence band.[38] In absence of hydrogen, a valence charge density plot, see Fig. 3(a), shows a concentration of the electronic charge around the C atom. A plot of the $|\Psi_{n,\mathbf{k}}|^2$ function corresponding to

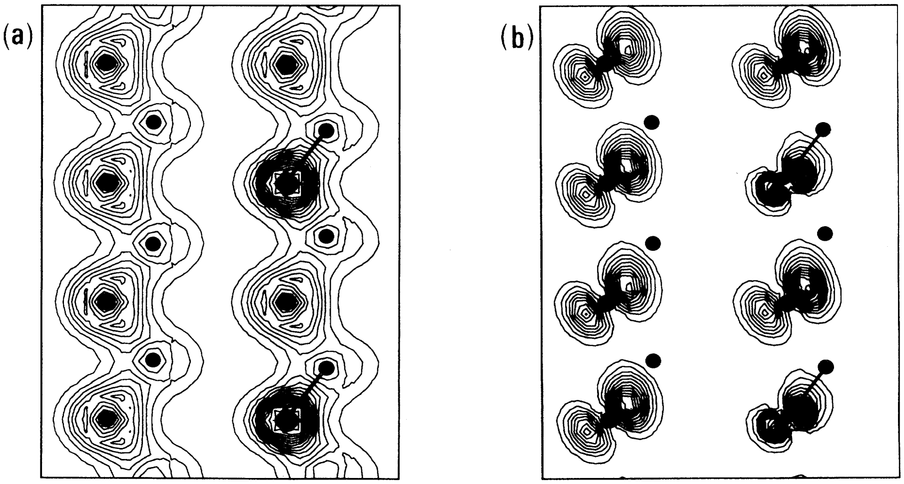

FIG. 3. Contour plots, in the (110) plane, of electronic charge densities corresponding to a C acceptor (in absence of hydrogen): (a) valence charge density; (b) charge density given by the $|\Psi_{n,\mathbf{k}}|^2$ function corresponding to the level at the top of the valence band. The atomic positions are indicated by solid circles of different size corresponding, from the largest to the smallest, to As, Ga, C and H atoms, respectively.

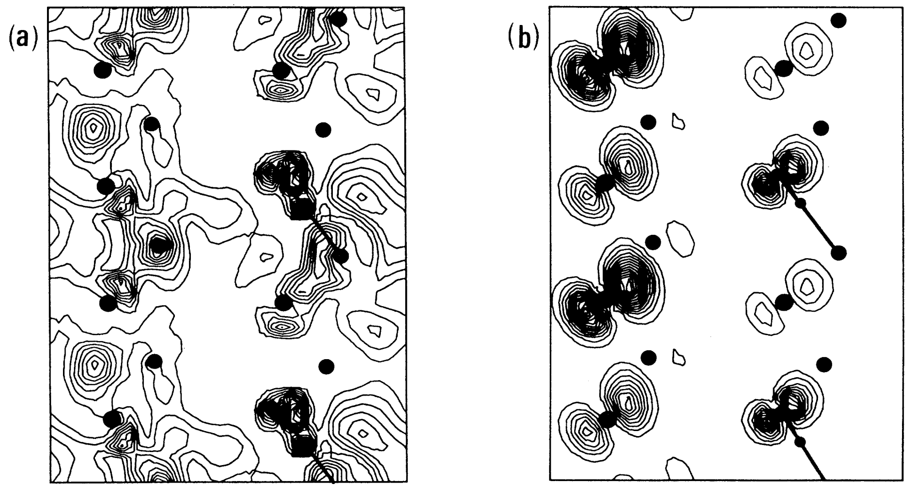

FIG. 4. Contour plots, in the (110) plane, of the charge density corresponding to $|\Psi_{n,\mathbf{k}}|^2$ functions for the BC configuration of the H-C_{As} complex (see the text): (a) charge density corresponding to an electron level in the valence band; (b) charge density corresponding to an electron level at the top of the valence band. The atomic positions are indicated by solid circles of different size corresponding, from the largest to the smallest, to As, Ga, C, and H atoms, respectively.

the level at the top of the valence band, see Fig. 3(b), shows that this level is related to the p orbitals of the C and As atoms. When hydrogen is located at the BC site to form the H-C_{As} complex, the level at the top of the valence band is related to the p orbitals of the As and C atoms, see Fig. 4(b), once more. Moreover, an electronic level whose wave function piles up electronic charge around the H-C pair, see Fig. 4(a) and compare with Fig. 2(a), is found deep in the valence band. This level is clearly related to the formation of the H-C bond. The main characteristics of the electronic structure of the H-C_{As} complex can therefore be described as follows. The charge density plot of Fig. 4(b) shows the p orbitals of the As atoms and one of the three equivalent sp^3 orbitals of carbon involved in the formation of stable C-Ga bonds. The fourth sp^3 orbital of carbon is involved in the formation of the H-C_{As} bond. This bond is quite strong, as indicated by the fact that the electron level related to the density plot of Fig. 4(a) is deep in the valence band. The sp^3 orbitals of C are therefore all involved in the formation of stable bonds. Moreover, the charge distributions shown in Figs. 2(a) and 4(a) indicate that the formation of the H-C_{As} bond is accompanied by a significant concentration of electron charge on the C atom. The chemical valence of the C atom is therefore fulfilled and the lacking of electron charge, which characterizes the C acceptor, is well neutralized thus establishing the passivation of the C dopant.

A similar analysis has been performed in the C donor case. When the H-C_{Ga} complex is formed, a level is found in the valence band whose wave function piles up electronic charge around the H-C pair; see Fig. 5(a) and compare with Fig. 2(b). This level is clearly related to the chemical bond formed by pairing the unpaired electron of the C atom (which occupies the donor level) with that of the H atom. Figure 5(b) shows a plot of the electronic charge density relative to the top level of the valence band, which is quite similar to that of Fig. 4(b). The former level is lower in energy than the latter one, thus further confirming the C donor passivation. The excess of the electronic charge characterizing the C donor is therefore neutralized by the formation of the H-C bond.

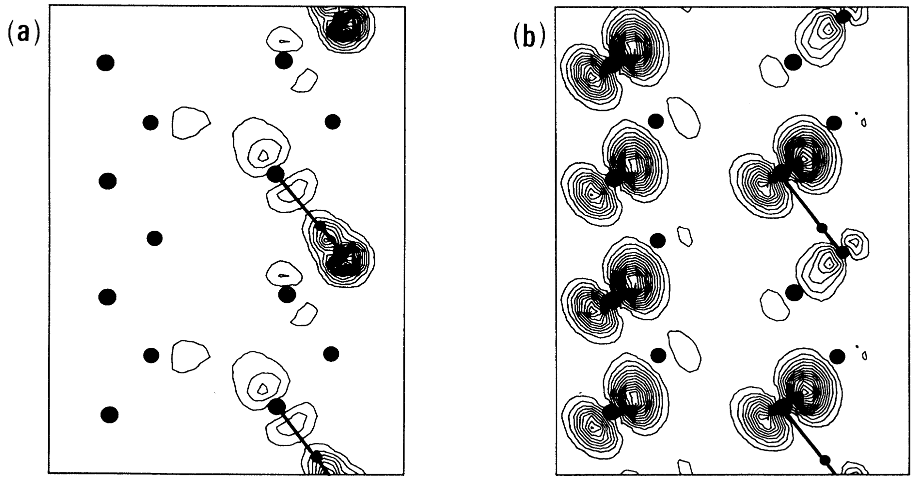

FIG. 5. Contour plots, in the (110) plane, of the charge density corresponding to $|\Psi_{n,\mathbf{k}}|^2$ functions for the BC configuration of the H-C_{Ga} complex (see the text): (a) charge density corresponding to an electron level in the valence band; (b) charge density corresponding to an electron level at the top of the valence band. The atomic positions are indicated by solid circles of different size corresponding, from the largest to the smallest, to As, Ga, C, and H atoms, respectively.

IV. CONCLUSIONS

The carbon incorporation in GaAs and the hydrogen passivation of the carbon dopant activity have been investigated in the PPLDF framework. The total-energy calculations have shown that the location of the C atom at the Ga site is not energetically favored with respect to that at the As site. The preferred incorporation of C at the anionic site in GaAs is in disagreement with this result. It has been suggested that this might be due to phenomena occurring at the grown surfaces, which have been discussed at a qualitative level. For what concerns the interaction of hydrogen with the carbon dopant, both the C acceptor and the C donor form stable H-C complexes where the H atom is located at the BC site, give rise to a strong H-C interaction, and lose their electrical activity when the H-C complexes are formed. In particular, the strong H-C interaction modifies significantly the chemical bonding of the C atom by neutralizing the lacking of electronic charge in the acceptor case and the excess of electronic charge in the donor one. The features of the H-C interaction also suggest that, in other III-V semiconductors doped with carbon, hydrogen may form the same complexes and passivate the dopant activity as in GaAs.

The dissociation energies of the H-C complexes, a key parameter for several technological processes, have been also evaluated. Present estimates indicate that the stability of the H-C complexes is comparable with that of the most used dopants in GaAs.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge P. Giannozzi for very helpful discussions.

---

[1] T.H. Chiu, J.E. Cunningham, J.A. Ditzenberger, and W.Y. Jan, Appl. Phys. Lett. **57**, 171 (1990).

[2] T.H. Chiu, J.E. Cunningham, J.A. Ditzenberger, and W.Y. Jan, J. Cryst. Growth **111**, 274 (1991).

[3] J. Nagle, R.J. Malik, and D. Gershoni, J. Cryst. Growth **111**, 264 (1991).

[4] W.E. Hoke, P.J. Lemonias, P.S. Lyman, H.T. Hendriks, D. Weir, and P. Colombo, J. Cryst. Growth **111**, 269 (1991).

[5] P.M. Enquist, Appl. Phys. Lett. **57**, 2348 (1990).

[6] M. Gotoda, S. Maruno, Y. Morishita, Y. Nomura, H. Ogata, K. Kuramoto, and H. Kuroki, J. Cryst. Growth **100**, 5 (1990).

[7] M. Kamp, R. Contini, K. Werner, H. Heinecke, M. Weyers, H. Luth, and P. Balk, J. Cryst. Growth **95**, 154 (1989).

[8] *Hydrogen in Semiconductors: Bulk and Surface Properties, Proceedings of the 6th Trieste Semiconductor Symposium, Trieste, 1990*, edited by M. Stutzmann and J. Chevallier (Elsevier, Amsterdam, 1991).

[9] *Hydrogen in Semiconductors*, edited by J.I. Pankove and N.M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, San Diego, 1991).

[10] Pr.E. Constant, *Proceedings of the 6th Trieste Semiconductor Symposium, Trieste, 1990* (Ref. 8), p. 397.

[11] B. Pajot, B. Clerjaud, and J. Chevallier, *Proceedings of the 6th Trieste Semiconductor Symposium, Trieste, 1990* (Ref. 8), p. 371.

[12] B. Clerjaud, F. Gendron, M. Krause, and W. Ulrichi, Phys. Rev. Lett. **65**, 1800 (1990).

[13] K. Woodhouse, R.C. Newman, R. Nicklin, R.R. Bradley, and M.J.L. Sangster, J. Cryst. Growth **120**, 323 (1992).

[14] J. Wagner, M. Maier, Th. Lauterbach, K.H. Bachem, A. Fischer, K. Ploog, G. Morsch, and M. Kamp, Phys. Rev. B **45**, 9120 (1992).

[15] A. Amore Bonapasta, G. Simeone, and M.R. Bruni, in *Materials for Photonic Devices, Proceedings of the 1st Italian Workshop, Taormina, 1991*, edited by A. D'Andrea, R. Del Sole, and A. Lapiccirella (World Scientific, Singapore, 1991), p. 243.

[16] R. Jones and S. Oberg, Phys. Rev. B **44**, 3673 (1991).

[17] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[18] R.M. Martin, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, edited by J.T. Devreese and P. Van Camp (Plenum, New York, 1985).

[19] L. Pavesi and P. Giannozzi, Phys. Rev. B **43**, 2446 (1991).

[20] B. Pajot, R.C. Newman, R. Murray, A. Jalil, J. Chevallier, and R. Azoulay, Phys. Rev. B **37**, 4188 (1988).

[21] J. Chevallier, B. Pajot, A. Jalil, R. Mostefaoui, R. Rahbi, and M.C. Boissy, in *Defects in Electronics Materials*, edited by M. Stavola, S.J. Pearton, and G. Davies, MRS Symposia Proceedings No. 104 (Materials Research Society, Pittsburgh, 1988), p. 337.

[22] A. Amore Bonapasta, M. Capizzi, and P. Giannozzi, Phys. Rev. B **42**, 3175 (1990).

[23] C.G. Van de Walle, P.J.H. Denteneer, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).

[24] N.M. Johnson and C. Herring, Mater. Sci. Forum. **38-41**, 961 (1989).

[25] L. Pavesi, P. Giannozzi, and F.K. Reinhart, Phys. Rev. B **42**, 1864 (1990).

[26] M. Capizzi, C. Coluzza, V. Emiliani, P. Frankl, A. Frova, F. Sarto, A. Amore Bonapasta, Z. Sobiesierski, and R.N. Sacks, J. Appl. Phys. **72**, 1454 (1992).

[27] A. Amore Bonapasta, Phys. Rev. B **46**, 10 119 (1992).

[28] The pseudopotentials here used are nonrelativistic. This compensates for the tendency of LDA to produce too small energy gaps.

[29] C.L. Fu and K.M. Ho, Phys. Rev. B **28**, 5480 (1983).

[30] *Handbook of Chemistry and Physics*, 71st ed., edited by D.R. Lide (CRC, Boca Raton, FL, 1990).

[31] F. Hartley and S. Patai, *The Chemistry of the Metal-Carbon Bond* (Wiley, New York, 1982), pp. 53–71.

[32] The values of the covalent radii, in angstroms, are 0.32 (H), 0.77 (C), 1.26 (Ga), 1.18 (As), and 1.17 (Si). See J.C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 21.

[33] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II* (Van Nostrand Reinhold, New York, 1945), p. 167.

[34] R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988).

[35] A. Amore Bonapasta (unpublished).

[36] S.J. Pearton, C.R. Abernathy, and J. Lopata, Appl. Phys. Lett. **59**, 3571 (1991).

[37] T. Zundel and J. Weber, Phys. Rev. B **39**, 13 549 (1989).

[38] The plots of the charge density $|\Psi_{n,\mathbf{k}}|^2$ shown in the figures have been obtained by using 16-atom supercells. Tests performed by using 32-atom supercells have given quite similar charge-density distributions.