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Impurity levels induced by a C impurity in GaAs

Luiza M. R. Scolfaro, R. Pintanel, V. M. S. Gomes, J. R. Leite, and A. S. Chaves*
Instituto de Física da Universidade de São Paulo, Caixa Postal 20516, Código de Endereçamento 01498, São Paulo, Brazil

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We have used the Watson-sphere-terminated molecular-cluster model within the framework of the multiple-scattering $X\alpha$ theory to carry out electronic-structure calculations of a carbon substitutional impurity in GaAs. The activation energy of the C_{As} impurity level is calculated as a function of inward symmetrical displacements of the nearest-neighbor Ga atoms. The center is found to be a shallow acceptor, and it is shown that an inward relaxation of the Ga atoms is expected. Unlike other group-IV elements, such as Si and Ge, carbon replacing Ga in GaAs is found to be a deep center.

I. INTRODUCTION

The molecular-beam-epitaxy (MBE) process has been an efficient and intensively used technique for growing thin GaAs (Refs. 1 and 2) and $Al_xGa_{1-x}As$ layers[3] and superlattices consisting of alternate layers of GaAs and $Al_xGa_{1-x}As$ compound semiconductors.[4–7] Despite all the efforts to assure the highest possible purity for the samples it is generally accepted that undoped GaAs (grown with an elemental arsenic source) is slightly *p*-type and the main residual impurity is thought to be carbon.[1] The possible origins of this contamination are the residual gas species hydrocarbons[1] and carbon monoxide[3] in the MBE systems. Previous studies[8] in the preparation of GaAs in graphite boats showed that the sample could contain as much as 8×10^{16} atoms cm^{-3} of carbon.

Recent photoluminescence (PL) experiments performed on high-quality GaAs (Refs. 1–3) and GaAs related new materials[4,7,9] show emission bands which can possibly be related with the shallow acceptor activity of the carbon impurity at the As site. In recent PL studies of vapor phase epitaxial GaAs a transition related to a residual shallow donor, which was thought previously to be carbon at a Ga site, was found (X_3 center).[10] Though this has been a controversial subject, these studies indicate that the X_3 residual donor is more likely to be associated with Ge and not to carbon. It has been suggested that carbon and Ge shallow donors may have ionization energies very close to each other which should explain the difficulties found to determine the chemical identity of the X_3 center.

Despite the role that carbon seems to play as a residual contaminant in bulk GaAs and MBE grown new materials, to our knowledge no rigorous self-consistent electronic-state calculations have been performed for this element as an impurity in GaAs. In this paper we study the ground-state electronic properties of carbon impurities replacing As and Ga in GaAs. The aim of the work is to proceed a step towards understanding the physical properties of carbon as a possible residual of impurity in GaAs related new materials.

The calculations reported in this paper were carried out by use of the Watson-sphere-terminated molecular-cluster model within the framework of the self-consistent-field multiple-scattering (MS) $X\alpha$ theory. This model has been applied successfully to the study of defects and impurities in elemental group-IV (Refs. 11–13) and compound III-V (Refs. 14 and 15) tetrahedrally coordinated semiconductors.

The cluster model used here consists of a central atom surrounded by four nearest neighbors and twelve next-nearest neighbors in a tetrahedral configuration compatible with the undistorted GaAs lattice geometry. Two basic atomic configurations have been used, one for carbon replacing the As atom (1C 4Ga 12As) and the other for carbon replacing the Ga atom (1C 4As 12Ga). The model as it has been applied to study impurity levels in GaAs is described in Ref. 15, therefore no further details will be provided here.

II. RESULTS

A. C_{As} center

Contrary to other elements of group IV, such as Si and Ge which are known to replace both Ga or As depending on the growth conditions, becoming donor or acceptor centers, respectively, it is currently accepted that carbon replaces As in a GaAs lattice becoming a shallow acceptor impurity.[2,8] An activation energy of 26 meV has been reported for the ground state of this center.[4,16] Recently, direct evidence that substitutional carbon in GaAs is predominantly on the As sublattice has been provided from Fourier transform infrared (FTIR) absorption spectroscopy measurements of the carbon associated localized vibrational modes.[17]

The self-consistent energy spectrum of the cluster (1C 4Ga 12As) simulating the electronic structure of the GaAs:C_{As} system is shown in Fig. 1. The results for the "perfect" cluster (1As 4Ga 12As) simulating the main features of the energy bands of a perfect GaAs crystal is also shown.[15] Since it is always instructive to picture a substitutional impurity as one atom captured by a single vacancy we are also including in the figure the energy spectrum of the (V 4Ga 12As) cluster, where the central atom was removed in order to simulate the electronic structure of the GaAs:V_{As} center.[15]

According to the results shown in Fig. 1, the main effect of removing an As atom from the lattice is the ap-

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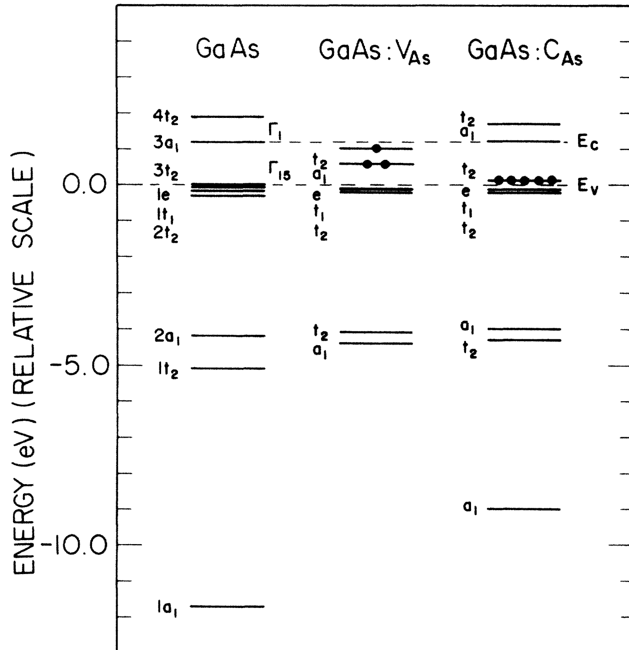

FIG. 1. Energy spectra of the cluster (1As 4Ga 12As), (V 4Ga 12As), and (1C 4Ga 12As) simulating the electronic structure of GaAs, As vacancy, and C_{As} substitutional impurity, respectively. The top of the valence band, $3t_2$, was placed at the zero of energy. The dashed lines indicate the gap and the solid circles denote the electron occupancies of the gap levels. The antibonding a_1 and t_2 states for the V_{As} center, not shown in the figure, lie far above in the conduction band.

pearance of two deep levels a_1 and t_2 within the band gap. They are originated from the broken sp^3 bonds between the central As atom and the four Ga nearest neighbors. Since five valence electrons were removed from the cluster, the vacancy impurity t_2 level has five holes, therefore the center is able to act as a deep acceptor. When carbon is placed at the vacancy site we see clearly that the sp^3 central bonds are remade and the a_1 and the t_2 levels are pulled down to the valence band. In order to stress this conclusion we show in Table I the charge distribution for the gap levels of the As vacancy and carbon impurity. The entries show that when the As vacancy is created some charge is transferred from the central region to the second shell of As atoms, reinforcing the back bonds. The sp^3 hybridization between carbon and the Ga neighbors pull this charge back to the central region. The charge normalized to one electron in the central sphere (radius 2.17 a.u.) for the t_2 gap state increases from 1% for the vacancy to 38% for the carbon impurity.

We have shown that carbon replacing As at an undistorted GaAs lattice leads to a threefold degenerate t_2 level just above the top of the valence band, at $E_v+0.12$ eV. Since four valence electrons are added to the vacancy by carbon, this level has five electrons or a single hole able to accept one electron. The partial occupancy of the t_2 level indicates that the center may undergo Jahn-Teller (JT) lattice distortions which lower the impurity local symmetry. However, there are indications that these effects are small or even absent. Successful interpretation of the localized vibrational modes induced by carbon in GaAs has been made by assuming a tetrahedral (T_d) symmetry for the C_{As} center.[17,18] The fact that the activation energy found by us for the center is larger than the measured value may raise some doubts about the adequacy of our finite cluster model to describe shallow acceptor states. However, the same model leads to an activation energy for the ground acceptor state of boron impurity in silicon in very good agreement with the experimental value.[11] Moreover, according to the previous applications of the model to study Se impurity replacing an As atom in a GaAs lattice, no charge was found within the central region of the cluster for the impurity gap state.[19] This behavior of a typical shallow impurity state, which is reproduced by the cluster model, is quite different from the carbon related acceptor state behavior observed here.

The considerations made above allow us to assume that carbon impurity replacing As at an ideal GaAs lattice is not a stable center. The occurrence of lattice relaxations around the impurity is expected. This assumption is further supported by the quite large difference between the covalent radii (R) of carbon and As. Furthermore, these species have different electronegativities (χ). By comparing the values, $R(\mathrm{C})=0.77$ Å, $R(\mathrm{As})=1.20$ Å, and $\chi(\mathrm{C})=2.5$ and $\chi(\mathrm{As})=2.0$ (Pauling's scale values), we conclude that an inward relaxation will occur, with the nearest neighbor Ga atoms moving towards the carbon impurity.

In order to simulate the lattice relaxation around the carbon impurity we carry out self-consistent calculations for various atomic configurations of the (1C 4Ga 12As). In each configuration the four Ga neighbors were displaced symmetrically (T_d) around the carbon impurity.

TABLE I. Charge distribution normalized to one electron for the gap states of the As and Ga vacancies and C impurity in GaAs. The states are labeled as in Figs. 1 and 3.

Defect	State	Central region	First shell	Second shell	Interatomic region
V_{As}[a]	a_1	0.07	0.12	0.63	0.17
	t_2	0.01	0.14	0.70	0.15
C_{As}	t_2	0.38	0.08	0.39	0.15
V_{Ga}[a]	t_2	0.05	0.45	0.25	0.25
C_{Ga}	a_1	0.04	0.21	0.52	0.23

[a]Reference 15.

The remaining 12As atoms were kept fixed at their ideal positions. In order to retain the standard "muffin-tin" approximation for the molecular potential[15] the atomic spheres radii of carbon and the nearest-neighbor Ga atoms were appropriately changed. Figure 2 summarizes the main feature of our calculations. The carbon acceptor binding energy is shown as a function of the Ga displacements. As the four Ga atoms move towards the carbon impurity the t_2 gap level moves down in energy. The experimental value for the activation energy of the center, indicated by an empty circle in Fig. 2, corresponds to a displacement of 0.14 Å for the Ga atoms. It is worthwhile to mention that the results shown in Fig. 2 refer to the energy difference between the t_2 gap level and the valence edge E_v. In other words, we are neglecting the electron relaxation effects. We have verified by using the Slater transition-state method that a slightly higher value for the binding energy is obtained when these effects are considered in the calculations. Of course, we are not at a position to determine the stable atomic configuration of the center because different muffin-tin geometries are used for the clusters. Therefore, the results depicted in Fig. 2 have to be considered as an indication that an inward relaxation of the Ga atoms is likely.

Recently, a cluster Bethe lattice treatment was made by Kleinert[18] to describe the results of high-resolution FTIR absorption measurements of localized vibrational modes of an isolated carbon impurity replacing As in GaAs. The author was able to achieve a good frequency fit for the four observed peaks by scaling the C-Ga and Ga-As (carbon first and second neighbors) force constants to the GaAs bulk values. The calculations show that there is a stressing of the C-Ga and a weakening of the Ga-As force constants. These results reinforce our conclusions that an inward relaxation occurs for the C_{As} center.

B. C_{Ga} center

Carbon replacing Ga in GaAs has not been detected experimentally although suggestions have been made that is likely to be a shallow donor as are Si and Ge.[10] Though it seems to be currently accepted that carbon replacing Ga in GaAs plays a minor role in determining the physical properties of GaAs and GaAs related new materials, there are strong evidences that this center is also important.

The results of our investigations of carbon replacing the cationic host atom in GaAs are shown in Fig. 3. The self-consistent MS-$X\alpha$ energy spectra of the clusters (1Ga 4As 12Ga), (V 4As 12Ga) and (1C 4As 12Ga) are depicted in order to simulate the electronic structure of the GaAs perfect crystal,[15] Ga vacancy,[15] and C_{Ga} systems, respectively. The results show that the removal of a Ga atom from the lattice leads to a deep threefold degenerate t_2 level within the band gap. Since three valence electrons were removed from the cluster, this level is partially occupied by three holes and therefore the Ga vacancy is a deep acceptor center. The electrical, optical, and magnetic properties of the center are then related to the broken sp^3 chemical bonds which give rise to the a_1 and t_2 impurity levels, the former appearing as a resonance just below the top of the valence band and the latter lying within the band gap. When carbon is placed at the vacancy site the sp^3 bonds are remade and the a_1 and t_2 vacancy states are pulled down towards the valence band. The

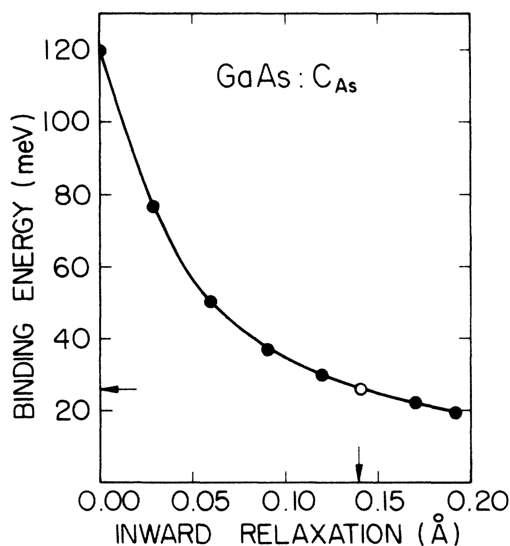

FIG. 2. Binding energy of the t_2 acceptor level of C_{As} in GaAs as a function of the Ga nearest-neighbor displacements (inward relaxation). The origin of the displacement is taken at the normal Ga site surrounding the impurity. The carbon atom is at 2.45 Å from the origin. The open circle, indicated in the scales by the arrows, denotes the experimental value for the activation energy of the center.

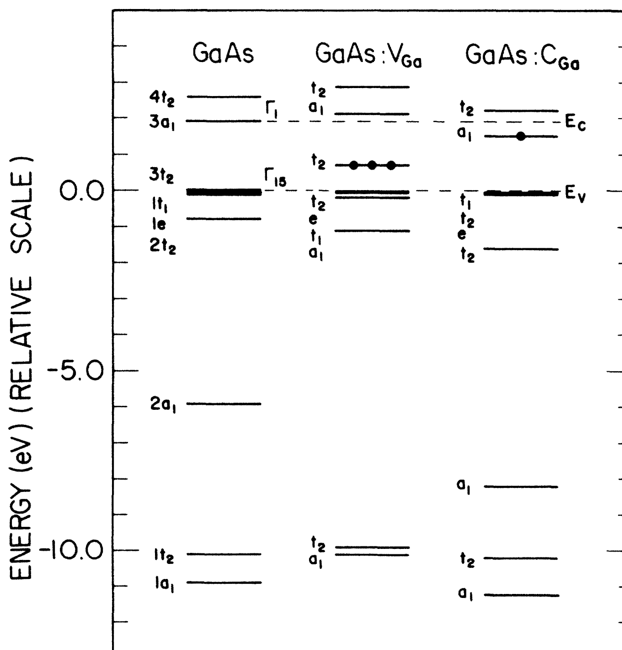

FIG. 3. Energy spectra of the clusters (1Ga 4As 12Ga), (V 4As 12Ga), and (1C 4As 12Ga) simulating the electronic structure of GaAs, Ga vacancy, and C_{Ga} substitutional impurity, respectively. The reference for the energy, the meaning of the dashed lines and solid circles are the same as in Fig. 1.

antibonding a_1 and t_2 states, which were placed at the conduction band for the vacancy, also decrease in energy. The a_1 merges into the band gap and the t_2 remains as a resonance in the conduction band. Therefore, carbon replacing Ga in a GaAs lattice leads to a nondegenerate level a_1, occupied by one electron, placed below the conduction band edge, at $E_c - 0.4$ eV.

The main feature of the present calculations is the conclusion that C_{Ga} is a deep center. Additional support to this finding is provided by the entries displayed in Table I. There the charge distribution associated with the gap states for the Ga vacancy and C_{Ga} center are shown. The C_{Ga} a_1 impurity state has 21% of the charge concentrated on the first shell of As atoms. For a typical shallow donor such as Se replacing As in GaAs, previous cluster calculations lead to less than 5% of charge on the first shell of neighbors for the a_1 impurity state.[19] The calculations indicate that the C_{Ga} impurity is not an active JT center. However, the system may display lattice relaxations, or lower its symmetry,[20] due to the large difference between the covalent radii and electronegativities of carbon and Ga [$R(\mathrm{Ga}) = 1.26$ Å, $\chi(\mathrm{Ga}) = 1.6$]. We expect that an inward relaxation will decrease the total energy of the center lowering the energy of the a_1 impurity gap state which will become deeper within the band gap.

There are two other evidences from theoretical studies that C_{Ga} is a deep center in GaAs. The application of an empirical Koster-Slater model within the framework of an orthogonalized-tight-binding-function basis leads, for this center, to an a_1 state placed at about 1 eV below the bottom of the conduction band.[21] Recently, C_{Ga} in GaP was the object of an investigation by the use of a self-consistent pseudopotential Green's function method.[22] A deep a_1 state in the gap at $E_c - 1.3$ eV is reported. Carbon is also not known to occupy Ga sites in GaP and by analogy with Si_{Ga} it would be expected to act like a shallow donor at this site.[23]

III. CONCLUSIONS

We have calculated the ground-state acceptor binding energy of carbon replacing an As atom in GaAs using the MS-$X\alpha$ molecular cluster model. The results indicate that the experimental value for the binding energy of the center can be obtained by allowing an inward symmetrical relaxation of the first neighbor Ga atoms. This result yields the first theoretical indication that carbon can be a possible source of the shallow acceptor activities currently seen in GaAs and GaAs related new materials.

The same theoretical model was used to carry out electronic calculations of the carbon impurity replacing Ga in GaAs. A nondegenerate level, occupied by one electron, at 0.4 eV below the bottom of the conduction band was found. This indicates that C_{Ga} is not a shallow level impurity. Therefore, the presence of carbon as a residual shallow donor in high-quality GaAs can be ruled out on the grounds that, unlike Si_{Ga} and Ge_{Ga}, the C_{Ga} center is deep.

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*Permanent address: Departamento de Física, Instituto de Ciências Exatas (ICEx), Universidade Federal de Minas Gerais (UFMG), Caixa Postal 702, 30000 Belo Horizonte, Minas Gerais, Brazil.

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