Electronic and Structural Properties of Complex Defects in GaAs

A. Janotti and A. Fazzio
Instituto de Física, Universidade de São Paulo,
CxP 66318, 05389-970, São Paulo, SP, Brazil

P. Piquini and R. Mota
Departamento de Física, Universidade Federal de Santa Maria,
97119-900, Santa Maria, RS, Brazil

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The electronic and structural properties of selected complex-defects in GaAs, created during electron or ion irradiation, are studied. An *ab-initio* calculation based on pseudo-potential density-functional theory is used. A supercell with 128 atoms is adopted in Car-Parrinello scheme. For the antistructure pair (As_{Ga} + Ga_{As}), from the total energy calculations, a first donor and a first acceptor levels are observed and a comparison is made with earlier, both theoretical and experimental, results. Two other possible complex defects (V_{As} + As_{Ga} + Ga_i and V_{Ga} + Ga_{As} + As_i) are discussed. It is shown that the first one presents a metastable configuration and the second one is unstable presenting a spontaneous recombination. For all complex defects the formation energies and charge densities are discussed.

I Introduction

Defects in III-V compound semiconductors have been intensively studied, associated mainly to wide technological interest concerning the production of modern devices and integrated circuits. Most of the interesting features of these materials are assumed to be related to deviations from the ideal crystal structure that can appear either as simple defects (vacancy, antisite, intertitial, impurity) or as complex defects (combination of simple defects). The earlier researches were centered mainly on characterization and properties of simple defects. However, with the advances in both theoretical methods and experimental techniques, a deeper understanding of the role of complex defects can now be devised. For GaAs, in particular, due to its attractive physical properties, a great effort has been made in the last few years to the identification and understanding of those defects; nevertheless, a definitive picture is still to be established.

Among the experimental techniques used in the development of III-V semiconductor devices, ion implantation plays a major role for establishing proper n- and p-type conductivity in an initially semi-insulating (si) material, as for Si in si GaAs.[1] Also ion or electron bombardment is often applied to convert a conductive doped layer in a highly resistive one. The electrical isolation obtained in this way is of relevance to enhance the electronic characteristics of semiconductor devices, e.g., the reduction of the backgating effect[2] in GaAs integrated circuits.

The high energies carried by the incoming ions or electrons in the irradiation process can induce many different defects,[3] by energy transfers, during their interaction within the crystal. The resulting electrical isolation is related with the carrier trapping of the defects

arising from irradiation.[4] Although the frequent application of this process in industry, a systematic and complete theoretical study of the related complex-defects has not yet been presented. Of course, the variety of resulting defects makes it a very difficult task to be accomplished.

Our aim in this paper is to report an *ab initio* total energy calculation of the electronic and structural properties of selected complex-defects (Ga_{As}+As_{Ga}, V_{As}+As_{Ga}+Ga_i, V_{Ga}+Ga_{As}+As_i) that can be generated during the irradiation process.

II Details of Calculation

Our calculations have been carried out adopting the supercell approach with 128 atoms. This cell size is expected to represent the defect in the real crystal. The repetition of the cell, in a space-filling mode, satisfies the underlying bulk periodicity, thus no surfaces are introduced. We use the local density approximation, through an *ab initio* nonlocal pseudopotential,[5] including up to l=2. A plane-wave base set expansion up to 10 Ry in kinetic energy is used within the Kleinman-Bylander formulation.[6] The Kohn-Sham equations are solved using the Car-Parrinello scheme.[7] For the Brillouin-zone sampling only the Γ point is used and for the exchange-correlation term we adopt the Ceperley-Alder form, as parametrized by Perdew and Zunger.[8] All studied systems have been relaxed in the directions of the Hellmann-Feynman forces. We allow three neighbor shells around the defects to relax until these forces result lower than 0.005 eV/Å. The remaining forces on the other neighbors are practically negligible.

III Results and Discussion

The first defect to be discussed is the antistructure pair, a nearest-neighbor double antisite, Ga_{As} + As_{Ga}, that can be generated from the GaAs pure crystal by the interchanging of two nearest-neighbor atoms, as seen schematically in Fig. 1(a). As is well known, the pure crystal presents a fully-occupied t_2-level at the top of the valence band and an a_1*-level at the botton of the conduction band. The introduction of this complex-defect reduces the local symmetry from T_d to C_{3v}. This resulting modification in the local crystalline field leads to a splitting of the fully-occupied t_2-level in a a_1-level, resonant in the top of the valence band, plus a fully-occupied e-level in the energy gap. Surprisingly, the unoccupied a_1*-level, with a conduction band character, moves down to the middle of the energy gap.

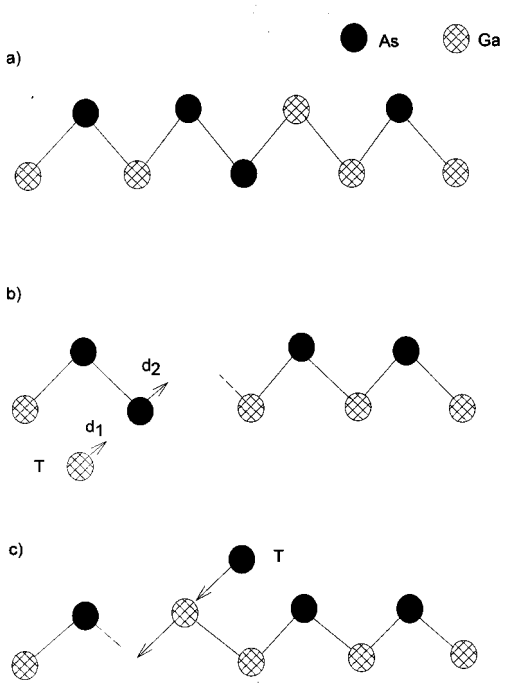

Figure 1. Schematical representation of GaAs in the (110) plane for: (a) antistructure Ga_{As} + As_{Ga}, (b) V_{As} + As_{Ga} + Ga_i, (c) V_{Ga} + Ga_{As} + As_i.

From the Fig. 2(a) and 2(b), we can see the changes in the total charge densities introduced by this antistructure pair in the (110) plane. A comparison between these two figures allow us to see a strong bond between the As atoms, which could be expected from the electronegativity values of the Ga and As atoms. The Fig. 2(c) shows that the wavefunction associated with the double degenerated fully-occupied e-orbital,

that arises in the gap, is localized at the Ga-Ga "wrong structure". For the unoccupied $a_1{}^*$-orbital, we can see from Fig. 2(d) that it is located at the As_{Ga} atom.

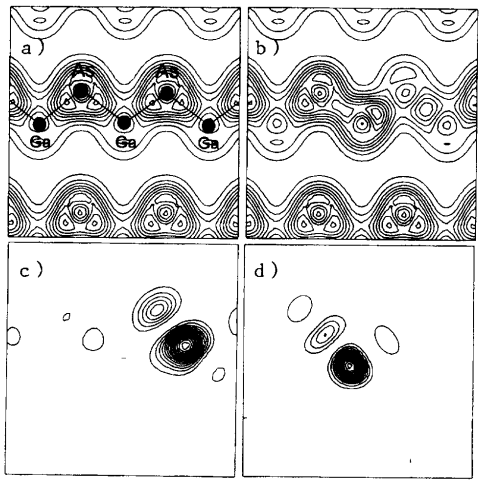

Figure 2. (a) Total charge density for GaAs (0.01 e/au^3), (b) Total charge density for As_{Ga} + Ga_{As} (0.01 e/au^3), (c) Charge density for the highest occupied e-orbital for As_{Ga} + Ga_{As} (0.001 e/au^3), (d) Charge density for the lowest unoccupied $a_1{}^*$-orbital for As_{Ga} + Ga_{As} (0.002 e/au^3). All plots are in <110> plane.

For the negative charge state, the additional electron occupies the $a_1{}^*$-level in the gap. The $a_1{}^*$-orbital, singly occupied, is observed to be close in energy to the fully occupied e-orbital in the energy gap. Although close in energy, it is interesting to notice that these two orbitals are spatially separated, resulting in a weak Coulomb repulsion between them.

The positively charged antistructure pair is obtained by removing an electron from the e-level in the gap, which is the highest fully occupied in the neutral case. This partially occupied e-orbital leads to a ground state with ^{2}E symmetry (bidegenerate), which induces a Jahn-Teller distortion. Then, we expect that this distortion splits the e-level. Our calculation shows that the highest single occupied level, resulting from e-level, is very close to $a_1{}^*$. However, the Aufbau rule for the level occupations makes it very hard for the self consistent field to converge, because, in this configuration, the two close levels alternate energetic positions during the iterative process. We circumvent this problem introducing a ficticious temperature and allowing partial level occupations, while preserving the minimal total energy. This is a very common problem in LDA calculations.[9]

From the total energy calculations, we obtain a first donor level (0/+) and a first acceptor level (0/-), located at 0.29 eV and 0.45 eV above the valence band, respectively. A comparison with Green's function calculation presented by Baraff and Schlüter,[9] shows a good agreement for the first donor level (0.30 eV), while the first acceptor level was not presented by them. It is important to observe that from our calculated values, for these levels, we find a Mott-Hubbard energy U(0) (defined as E(+) + E(-) -2E(0))[10] of 0.16 eV, which is a reasonable value for this kind of s-p impurities. The absence of the first acceptor transition in the Green's function calculation leads to an estimative of U that is higher than 1.0 eV, otherwise an acceptor level should be found by Baraff and Schlüter. This discrepancy comes from the fact that our calculations present one level located in the middle of the gap ($a_1{}^*$), spatially apart from the e-level.

A few experimental results have been used to identify antistructure pairs in GaAs. In particular, an interesting result has been presented by Krambrock and Spaeth[11] using optically detected electron nuclear double resonance (ODENDOR) technique. Their observed results of hyperfine and superhyperfine interaction between the As_{Ga} and its first and second surrounding layers was suggested to be associated with next-nearest-neighbor antistructure pair as a possibility. A nearest-neighbor antistructure pair was not considered as a candidate, in accordance with them, based

mainly on the available theoretical results.[9] Considering that our calculations recover the possibility of the existence of the first and second acceptor transitions, this leads to the necessity of reexaming the interpretation of that experiment properly. Also, it is worth noticing that another possibility is the capture of two electrons by the neutral system (presumably in the a_1^*-level). This would provide a non-paramagnetic state and, in this case, no signal should be observed.

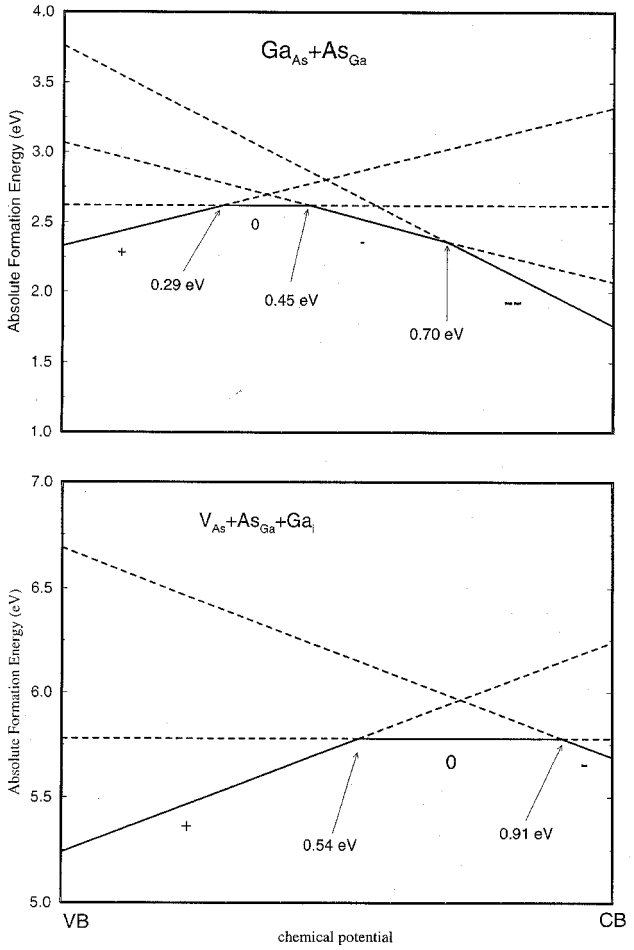

Figure 3. Absolute energies for the reaction: (a) As_{As} + Ga_{Ga} $\longrightarrow$ As_{Ga} + Ga_{As}, (b) As_{As} + Ga_{Ga} $\longrightarrow$ V_{As} + As_{Ga} + Ga_i, as a function of chemical potential.

Let us now consider the formation energy of the antistructure pair. In Fig. 3(a), the formation energy of the reaction As_{As} + Ga_{Ga} $\longrightarrow$ As_{Ga} +Ga_{As} is shown for the three charge states. The required energy to form the neutral antistructure is 2.62 eV. For this defect, without including the atomic relaxation, 2.87 eV was found. For the positive state the corresponding formation energy (taking E_F at the top of the valence band) is found to be 2.33 eV (0/+) and for the negative state 3.07 eV (0/-).

It is remarkable to note that for the chemical potential around the middle gap the negative charge state corresponds to the most stable one. In another words, it is a paramagnetic center with a wave function strongly located on the As in Ga site (As_{Ga}).

Another selected complex defects involve the possible large replacement collision chains obtained in irradiation process. This kind of collision can be associated with the two following alternatives: V_{As} + As_{Ga} + Ga_i or V_{Ga} + Ga_{As} + As_i, which are schematically represented in Fig. 1(b) and 1(c), respectively.

For the first alternative, the starting configuration assumes the Ga atom kept in the tetrahedral interstitial and the As atom kept at the Ga atom position. Fig. 4(a) and 4(b) show the changes in the total charge densities introduced by this defect in the (110) plane. In Fig. 4(b) we can see again a strong As-As bond. Fig. 4(c) shows the a_1-level located at the Ga-As bond. The system was permitted to relax until the Helmann-Feynman forces were lower than 0.005 eV/Å. The As and Ga atoms relax inward with a small displacements (d_1=0.25 Å and d_2=0.16 Å, as seen schematically in Fig. 1(b)) in direction to their original crystal position (<111> direction). Then, this defect corresponds to a metastable configuration with a minimum presenting a barrier of approximately 0.6 eV, as shown schematically in Fig. 4(d). For this defect, the first donor level was obtained to be 0.54 eV, and for the first acceptor the resulting value was 0.91 eV. The formation energy of this reaction in the neutral state is 5.78 eV. For this defect, without including atomic relaxation, this result was found 6.76 eV. The corresponding formation energy the positive case is 5.24 eV and for the negative case it is 6.69 eV, as seen for the three charge states

in Fig. 3(b). Although the formation energies present aparently high values, they are in fact realistic and consistent with the usual implantation processes.

Finally, the last complex defect to be considered corresponds to the second alternative, as described above, and shown in Fig. 1(c), with the starting configuration presenting the As atom kept at the tetrahedral interstitial position and the Ga atom kept at the As site. Considering relaxation, when the ions are left free to move, they return to their original position. This makes it evident that the V_{Ga} + Ga_{As} + As_i defect is unstable, corresponding to a spontaneous recombination. As a consequence, in the isolation process, we should discard it, as participant, in the mechanism of carrier trapping at the defects induced by irradiation associated with the observed change in the resistivity.[4]

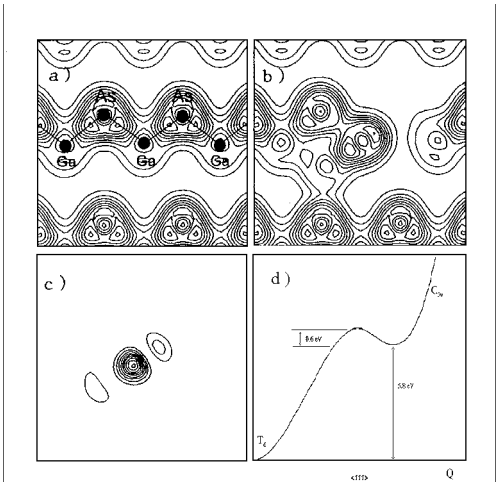

Figure 4. (a) Total charge density for GaAs (0.01 e/au^3), (b)Total charge density for V_{As} + As_{Ga} + Ga_i, (c) Charge density for the highest occupied a_1-orbital (0.002 e/au^3), (d)Schematicaly representation of the displacement of As_{Ga} $\longrightarrow$ As_{As} along the <111> direction.

IV Summary and Conclusions

Summarizing, we have presented an *ab initio* calculation for selected complex-defects in GaAs, based on pseudopotential density-functional theory, for several charge states, adopting a supercell with 128 atoms in Car-Parrinello scheme. All studied systems have been relaxed in the direction of the Helmann-Feynman forces.

For the antistructure pair (As_{Ga} + Ga_{As}), this complex-defect reduces the local symmetry from T_d to C_{3v}. It was shown that the unoccupied a_1*-level moves down to the middle of the energy gap. The changes in the total charge densities, introduced by this complex-defect, have permitted to observe: (i) a strong bond between the As atoms, (ii) the wavefunction associated with the e-orbital is located at the Ga-Ga "wrong structure", and (iii) that the occupied a_1*-orbital is localized at the As_{Ga} atom. For the negative charge state, it is remarkable that the two orbitals (a_1* and e), although close in energy in the gap, are spatially separated, resulting in a weak Coulomb repulsion. For the positive charge state, the distortion associated with the electron removed, splits the e-level, with the highest single occupied level resulting very close to a_1*. From the total energy calculations, a first donor and a first acceptor level are obtained. It was shown that our result for U differs substantially from other earlier calculations. Comparing with experimental results, we have seen that our calculations recover the possibility of the existence of the first level. This possibility had been ruled out, in the interpretation of the experimental results, based on contrasting theoretical calculations, comparing with the conclusions of this paper.

For the V_{As} + As_{Ga} + Ga_i defect, the changes in the total energy result: (i)a strong As-As bond, and (ii) the a_1-level located at the Ga-As bond. This defect corresponds to a metastable configuration. The other studied defect (V_{Ga} + Ga_{As} + As_i) was shown to be unstable, presenting a spontaneous recombination. Consequently, in the isolation process, the first two studied complex defects (As_{Ga} + Ga_{As} and V_{As} + As_{Ga} + Ga_i) should be present and the third one (V_{Ga} + Ga_{As} + As_i) can be discarded as a possible participant.

V Acknowlegments

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