

First Principles Calculation of Substitutional Oxygen and Oxygen-Hydrogen Complex in Gallium Arsenide

Walter M. Orellana * and A. C. Ferraz.

Departamento de Física dos Materiais

Instituto de Física, Universidade de São Paulo

C.P. 66318, 05315-970 São Paulo-SP, BRAZIL

Received February 2, 1997

We report first-principles investigation of the electronic structure, atomic geometry and formation energy of the isolated substitutional oxygen impurity (O_{As}) and the oxygen-hydrogen pair complex (O_{As} -H) in GaAs. Our results for O_{As} in neutral charge state, show an on-site defect with an A_1 midgap level occupied with one electron. The O_{As}^{-2} charge state shows an off-center displacement of 0.7 Å on the $\langle 111 \rangle$ direction associated to a JT distortion. The calculated formation energy reveal a negative-U behavior for the doubly negative charge state. For the neutral complex O_{As} -H, we calculated the total energy and atomic configuration for seven different positions of hydrogen atom with oxygen in the same substitutional site. The lowest energy configuration obtained from our calculations has hydrogen near a bond-center site of O_{As} -Ga bond, with O_{As} -H bond length of 1.88 Å and H-Ga of 1.54 Å. The angle between these bonds is found to be 160°. The hydrogen passivation of the impurity level is observed.

I. Introduction

Localized vibrational modes spectroscopy (LVM)^[1,2] shows that O_{As} is an off-center electrically active defect, displaced from the regular substitutional position, in the $\langle 100 \rangle$ direction, and can exist in three charge states, with the middle one being unstable, *i.e.*, an U-negative behavior is observed. *Ab initio* total-energy pseudopotential calculations remain restricted due to the difficulty of describing correctly the first-row elements with an appropriate plane-wave basis set. In the case of oxygen, the 2*p* orbital is very strong, needing a large basis set in order to achieve the convergence, which is computationally costly.

In the present paper we study the electronic structure, atomic geometry and energetics of the isolated substitutional oxygen impurity in GaAs with first-principles total-energy calculation, using a soft pseudopotential. Also we study the interaction of the oxygen impurity with an interstitial hydrogen atom. It is well known that hydrogen interacts strongly with

dopants in crystalline semiconductors; in fact oxygen and hydrogen atoms are common residual impurities in III-V compounds grown by the liquid-encapsulated Czochralski (LEC) crystal-growth method^[3]. We have investigated the electronic properties and atomic configuration of this center in order to understand the mechanisms that govern the impurity incorporation.

II. Computational Details

Our calculation are based on density-functional theory (DFT) in the local density approximation (LDA)^[4], using the iterative method suggested by Car-Parrinello^[5]. The atoms are described by soft norm-conserving pseudopotential generated by the scheme of Troullier-Martins^[6] and transformed into the separable form of Kleinmann-Bylander^[7]. The wave-functions are expanded in a plane-wave basis set with a kinetic energy cutoff up to 48 Ry. We employ a *bcc* supercell containing 32 atoms, relaxing up to two atomic shells

*Contact Author: WM Orellana E-mail: wmomunoz@if.usp.br

around the impurity. The optimized atomic geometry is obtained using a damped dynamics approach considering the Hellmann-Feynman forces on each atom being smaller than $0.01 \text{ eV}/\text{\AA}$. Two special k points^[8] are employed to sample the primitive Brillouin zone. The dispersion of the impurity level due to the supercell approach was estimated to be 0.1 eV . For testing the convergence of the total energy as a function of the plane-wave basis set, we performed total energy calculations for the oxygen and water molecules with the same cutoff energy considered in this work. The calculated bond length for O_2 was found to be 1.24 \AA and for H_2O , 0.97 \AA . These results are in good agreement with the experimental values (1.21 \AA and 0.96 \AA respectively), thus we conclude that our plane-wave basis set can reproduce the main characteristics of the oxygen atom.

The formation energy of a defect determines whether this can actually be formed and which are the relevant competing processes in thermodynamic equilibrium. That can be estimated by the relative abundance of the constituent atoms (Ga, As and O) in the environment in which the crystal is grown, where this abundance is described by the chemical potentials: μ_{Ga} , μ_{As} and μ_O . Thus the formation energy for the substitutional O_{As} in the charge state q can be written as^[9]:

$$E_f(O_{As}^q) = E_t(O_{As}^q) - n_{Ga}\mu_{Ga} - n_{As}\mu_{As} - \mu_O + q\mu_e,$$

where $E_t(O_{As}^q)$ is the total energy derived from a supercell calculation, n_{Ga} (n_{As}) are the number of Ga (As) atoms in the cell and μ_e is the electronic chemical potential (position of the Fermi level). The Ga and As chemical potentials are not independent variables, since their are constrained by the equation: $\mu_{Ga} + \mu_{As} = \mu_{GaAs(bulk)}$. On the other hand, the Ga and As chemical potentials vary over a range given by the heat of formation of GaAs, where the upper limits are given by its respective bulk phases. To establish an upper limit to the chemical potential of the impurity, it is necessary to consider other possible phases that resemble the interaction of the impurity with the constituent host atoms. For the case of oxygen, a strict constraint for μ_O is given by the formation of gallium oxide, Ga_2O_3 .

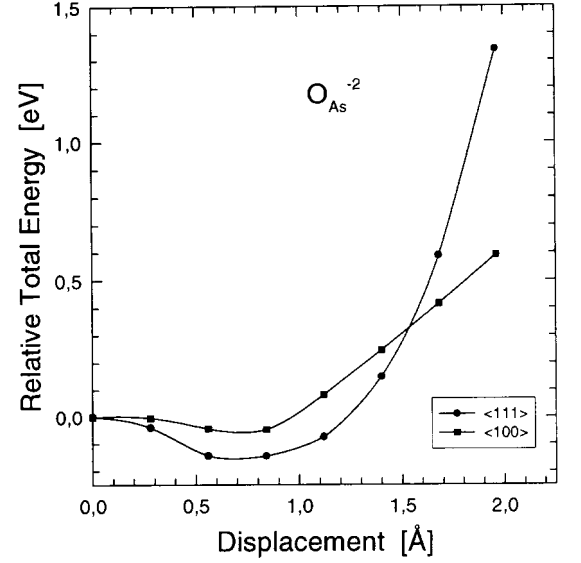


Figure 1. Relative total energy as a function of the oxygen displacement in the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions for the doubly negative O_{As} defect in GaAs. The zero energy refers to the energy at the substitutional position.

III. Results and Discussion

A. Oxygen in GaAs

Our results for O_{As} in the neutral charge state show an A_1 midgap level occupied with one electron, and no oxygen displacement from the arsenic site was observed. There is an inward relaxation of the four gallium nearest-neighbors, directly related to the small size of the oxygen atom. The O-Ga bond length is 12% smaller than the Ga-As bulk bond length (2.43 \AA) while the bond length between the first and seconds nearest-neighbors is 2.5% longer. This relaxation is accompanied by an energy gain of 1.1 eV . For the single negative charge state we also found an on-site defect. Considering that the off-center displacement is experimentally seen in this charge state, we calculated the energy surface as a function of the oxygen displacement in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, no other energy minimum distinct from the on-site position was found. These results were confirmed in a calculation with 60 Ry cutoff energy on a 16 atom supercell. For O_{As}^{-2} system we found an off-center displacement of the oxygen atom about 0.7 \AA in the $\langle 111 \rangle$ direction, lowering by 0.14 eV the energy with respect to the on-site position, as shown in Fig. 1. Since the upper occupied level (T_2) is degenerate, we observed a Jahn-Teller distortion. A displacement in the $\langle 100 \rangle$ direction is also observed, but appears as an energetically less favorable situation. We also find that the on-site posi-

tion is metastable. Table 1 shows the bond length for the four nearest-neighbors Ga atoms and the relaxation energy for the different charge states.

Table 1. Change of defect geometry with charge state for O_{As} in GaAs. d_i is the distance of the nearest-neighbors Ga atoms from the oxygen impurity and ΔE is the energy gain due to the atomic relaxation. The distances are given in \AA and the energies in eV.

Defect	d_1	d_2	d_3	d_4	ΔE
O_{As}^{+1}	2.19	2.17	2.18	2.19	0.78
O_{As}^0	2.15	2.13	2.15	2.15	1.10
O_{As}^{-1}	2.13	2.10	2.12	2.12	1.46
O_{As}^{-2}	1.98	2.72	1.98	1.98	1.50
O_{As}^{-3}	1.97	2.73	1.97	1.97	1.98

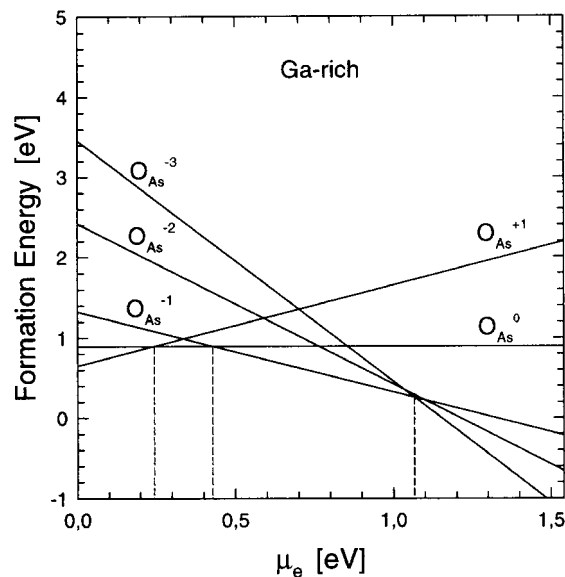


Figure 2. Formation energy of the five charge states of the O_{As} impurity in GaAs, as a function of the position of the Fermi level (μ_e) for the Ga-rich condition. The dashed lines indicate the position of the transition levels [(0/+)=0.24 eV, (-/0)=0.43 eV and (-3/-)=1.07 eV]. The O_{As}^{-2} state is unstable.

In Fig. 2, we show the formation energy of the O_{As} impurity in GaAs for the extreme Ga-rich condition, which is the most favorable situation for the incorporation of X_{As} defects. From these results we conclude that this center can exist in five charge states (from +1 to -3). The doubly negative state is unstable showing a negative-U behavior which is in agreement with experimental results^[2]. Under p-type conditions, the positive and neutral charge states dominate, while under n-type conditions the triply negative dominates. The single negative appears as the most favorable state around the midgap.

B. O-H Complex in GaAs

In order to determine the minimum-energy structure of the neutral O_{As} -H complex, we examine several configurations for the H atom as shown in Fig. 3. We considered the oxygen atom in the on-site position (O_{As}) and the hydrogen atom occupying seven high symmetry positions, including the bond center (BC), antibonding to the O atom (AB-O), antibonding to the Ga atom (AB-Ga), tetrahedral (Td), hexagonal (Hex), in the $\langle 100 \rangle$ direction (C1) and in the center of a rhombus formed by the O-Ga-As bonds (C2).

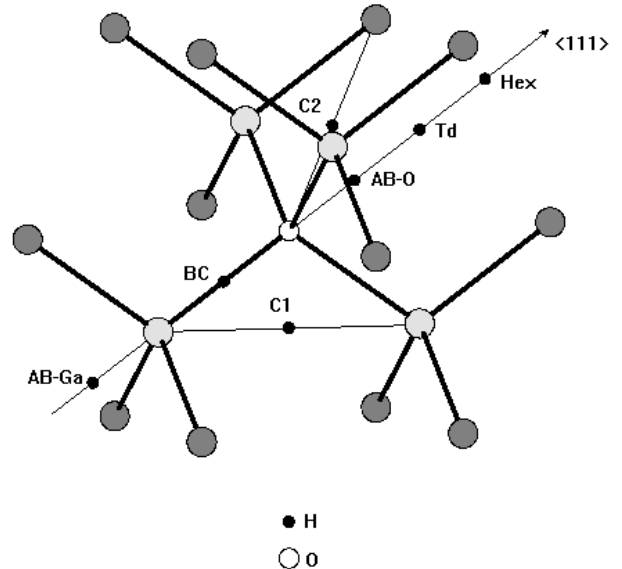


Figure 3. Different interstitial sites for the hydrogen atom used as a starting configuration for study the formation of the complex O_{As} -H in GaAs.

Our results show that the lowest-energy configuration for the different hydrogen interstitial sites corresponds to some kind of bond centered position, with the H atom weakly bonded to both oxygen and gallium atoms, as can be seen in Fig. 4. The O-H-Ga bonds form an angle of 160° . This angle looks greater in the Fig. 4 because its plane is normal to the plane of the figure. The O-H and H-Ga bond length are found to be 1.88 \AA and 1.54 \AA , respectively. This configuration was obtained from the C2 starting position. We also found the same energy starting from the C1 configuration, but the geometry is slightly different: in this case

the O-H and H-Ga bond length are found to be 2.19 Å and 1.67 Å, respectively, and the corresponding angle is 100°.

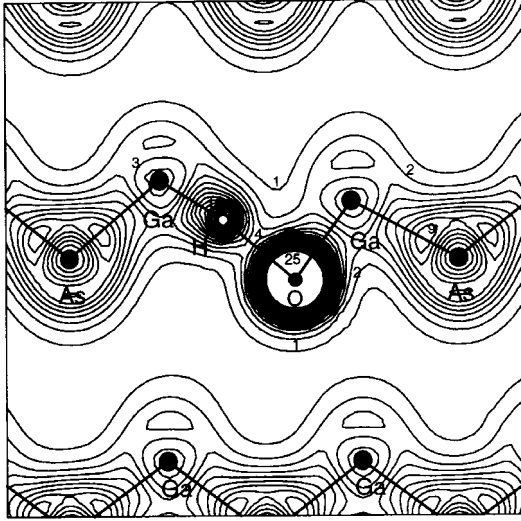


Figure 4. Contour plot of the total valence charge density in the $[1\bar{1}0]$ plane for the minimum energy configuration of the O_{As} -H complex in GaAs. The units are in $2.25 eV/\text{Å}^3$.

For the BC configuration we found a straight-line bond-centered H atom, strongly bonded to oxygen. The O-H bond length is found to be 1.05 Å, slightly larger than the calculated value for water molecule (0.97 Å). For the AB-O configuration we also found the same strong O-H bond, with the same bond length. The oxygen atom does not break any of its four Ga-O bonds, remaining fivefold coordinated. This center has the highest energy among the H-bonded system (1.36 eV). In the AB-Ga configuration the Ga and H atoms relax ~ 1 Å from each other. This result show an effective break of the O-Ga bond and the formation of a Ga-H bond, leaving the O atom threefold coordinated. For the Td configuration the H atom has a similar behavior observed in the C1 and C2, *i.e.*, it tends to occupy a bond-centered position between H and Ga atoms, consequently the energy for this center is small compared with C2 (0.16 eV). The O-H-Ga angle is found to be 83°. Finally for the Hex configuration the H atom does not bond with any atom, remaining in its interstitial position.

From our results we observed the formation of two types of bonds involving the hydrogen and oxygen atoms in the lattice. The first is a strong O-H bond, that resemble a dimer OH, wich is formed when these two atoms are left close each other (~ 1 Å). The total energy of this system shows that the strong O-H bond is difficult to be formed. The second type is a *bridging*

Ga-H-O bond, with the H atom weakly bonded. This configuration is energetically favorable and show that the formation of the O_{As} -H complex can be understood as a H atom arriving to a O_{As} defect, in a process of hydrogenation. The electronic structure of the stable configuration show that the one electron midgap level induced by the O_{As} defect, enter into the valence band when the H atom is incorporated. Meanwhile the lowest empty level, initially in the bottom of the conduction band, goes down ~ 0.2 eV into the gap. It is important to note that the passivation is only observed for the minimum-energy configuration.

IV. Conclusions

We have studied from first principles calculations the energetics of O_{As} and the complex pair O_{As} -H in GaAs. For the O_{As} impurity we found stable structures for four charge states and a U-negative behavior. For the O_{As} -H complex the minimum energy configuration was found with the H atom occupying a displaced bond centered position between Ga and O atoms. The incorporation of the H atom produces the passivation of the midgap level.

Acknowledgements

One of us (W.M.O.) thanks Professor A. Fazzio for many valuable discussions. We thank CNPq and FAPESP for financial support and CENAPAD-SP, LNCC-RJ and LCCA-USP for computational support.

References

1. M. Skowronski, Mater.Sci. Forum **83-87**, 377 (1992); Phys. Rev. **B 46**, 9476 (1992).
2. H. Ch. Alt, Phys. Rev. Lett. **65**, 3421 (1990).
3. B. Clerjoud, D. Coté and C. Naud, Phys. Rev. Lett. **58**, 1755 (1987).
4. P. Hohenberg and W.Kohn, Phys. Rev. **B 136**, 864 (1964). W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
5. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
6. N. Troullier and J. M. Martins, Phys. Rev. **B 43**, 1993 (1991).
7. L. Kleinmann and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
8. H. J. Monkhorst and J. D. Pack, Phys. Rev. **B 13**, 5188 (1976).
9. S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).