

The interaction of atoms with semiconductor surfaces: the case of Sb on GaAs (110)

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Abstract. A free-parameter LCAO method for chemisorption problems is presented. The method includes many-body effects by means of a local-density potential. The case of Sb on GaAs (110) has been analysed and the results are discussed in the perspective of Schottky barrier formation.

1. Introduction

An important piece of work in the field of chemisorption (March 1986) has been developed using a local density formulation (Lang 1973, Lundquist 1988). Although this program has been successfully applied mainly to simple atoms, only for very simple cases have workers been able to apply it to the analysis of absorbed molecules (Nørskov *et al* 1981). The problem is obviously a time-consuming limitation in the calculation one has to perform for those systems.

The alternative approach to the analysis of the electronic properties of solids is the method of tight binding, or the linear combination of atomic orbitals (LCAO) (Majewsky and Vogl 1986, Sutton *et al* 1988, Doyen 1976). This approach offers an obvious advantage in its computational simplicity and in its appropriate description of the chemical or local environment around an atom. The drawback of this method is its semiempirical description, since some (or many) of the parameters describing the basic Hamiltonian are not obtained from a first-principles approach, but by using some interactions deduced from the physical and chemical trends of different systems (Harrison 1980).

Our work in the past five years has been addressed to developing a free-parameter LCAO method (Goldberg *et al* 1988) that allows us to calculate the electronic properties of solids, in general, and the chemisorption properties of atoms and molecules, in particular. In this paper we present a summary of the method developed in our laboratory, and a discussion of the results obtained for a particular system: Sb deposited on GaAs (110) (Mailhiot *et al* 1985, Bertoni *et al* 1983, Srivastava 1992). This case is related to the field of Schottky barrier formation, a system where the present research is addressed to understanding how the barrier depends on the amount of metal deposited on the semiconductor (Third Int. Conf. on the Formation of Semiconductor Surfaces 1992, Flores and Tejedor 1987, Flores and Ortega 1992).

In section 2 we discuss our LCAO approach and present the method followed to calculate the different parameters defining the LCAO Hamiltonian. In the same section we also discuss our treatment of the many-body effects associated with the electron–electron interaction. We show how these effects can be analysed using a local treatment similar to the one used in LDA. We believe that this approach establishes the link between the usual LDA method and our LCAO approach.

In section 3 we present our results for Sb on GaAs(110) and finally, in section 4, we present our conclusions.

2. LCAO method: general formalism

We introduce our LCAO method by considering a simple diatomic molecule with two levels, 1 and 2, associated with atoms 1 and 2, respectively. In this simple case, the one-electron Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z_1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}_2|} + \frac{Z_1 Z_2}{d} \quad (1)$$

can be expressed in the language of second quantization as follows:

$$\hat{H} = (\epsilon_1 \hat{n}_{1\sigma} + \epsilon_2 \hat{n}_{2\sigma}) + \sum_{\sigma} t (\hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + \hat{c}_{2\sigma}^{\dagger} \hat{c}_{1\sigma}) + \frac{Z_1 Z_2}{d} \quad (2)$$

where the creation and annihilation operators, \hat{c}_i^{\dagger} and \hat{c}_i , are associated with the Löwdin orthogonal basis:

$$\phi_1 = \lambda \psi_1 + \mu \psi_2 \quad \phi_2 = \mu \psi_1 + \lambda \psi_2 \quad (3)$$

where

$$\lambda = \frac{1}{2} \left(\frac{1}{\sqrt{(1+S)}} + \frac{1}{\sqrt{(1-S)}} \right) \quad \mu = \frac{1}{2} \left(\frac{1}{\sqrt{(1+S)}} - \frac{1}{\sqrt{(1-S)}} \right)$$

$S = \langle \psi_1 | \psi_2 \rangle$, and ψ_1, ψ_2 are the atomic wavefunctions associated with the 1 and 2 sites.

In (2), ϵ_i and t are given by

$$\begin{aligned} \epsilon_i &= \epsilon_i^{(0)} + \frac{1}{2} [1 - (1 - S^2)^{-1/2}] (\epsilon_j^{(0)} - \epsilon_i^{(0)}) - S t \\ t &= \frac{1}{(1 - S^2)} [t^{(0)} - \frac{1}{2} S (\epsilon_1^{(0)} + \epsilon_2^{(0)})] \end{aligned} \quad (4)$$

where

$$\begin{aligned} \epsilon_i^{(0)} &= \int \psi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} - \frac{Z_1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}_2|} \right) \psi_i(\mathbf{r}) \, d\mathbf{r} \\ t^{(0)} &= \int \psi_1(\mathbf{r}) \left(-\frac{\nabla^2}{2} - \frac{Z_1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r} - \mathbf{R}_2|} \right) \psi_2(\mathbf{r}) \, d\mathbf{r}. \end{aligned} \quad (5)$$

In our approach, we expand λ and μ up to second order in S , and approximate (4) by

$$\begin{aligned} \epsilon_i &= \epsilon_i^{(0)} + \frac{1}{4} S^2 (\epsilon_j^{(0)} - \epsilon_i^{(0)}) - S t \\ t &= t^{(0)} - \frac{1}{2} S (\epsilon_1^{(0)} + \epsilon_2^{(0)}). \end{aligned} \quad (6)$$

A further step can be made by relating t to the Bardeen tunnelling current t^B (Goldberg *et al* 1988, García-Vidal *et al* 1991, Flores *et al* 1988):

$$t^B = \frac{\hbar}{2m} \int (\psi_1 \nabla \psi_2 - \psi_2 \nabla \psi_1) \mathbf{n} \, ds. \quad (7)$$

Hamiltonian (2) and equations (5) and (6) define our LCAO-method for the simple diatomic molecule we are considering. Notice how the overlap S between wavefunctions ψ_i and ψ_j renormalize the diagonal levels, introducing a kind of repulsive energy between the two atomic wavefunctions.

Many-body terms are introduced in Hamiltonian (1) by the electron-electron interaction $\frac{1}{2} \sum_{i,j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$. This term can be written in the same Löwdin basis introduced above. Using the expression of λ and μ up to second order in S , one can prove that the total Hamiltonian (electron-electron interaction included) is as follows:

$$\begin{aligned} \hat{H} = & \sum_{\sigma} E_1^{\sigma} \hat{n}_{1\sigma} + \sum_{\sigma} E_2^{\sigma} \hat{n}_{2\sigma} + \sum_{\sigma} T^{\sigma} (\hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + \hat{c}_{2\sigma}^{\dagger} \hat{c}_{1\sigma}) + U_1^{(0)} \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \\ & + U_2^{(0)} \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} + \sum_{\sigma} [J^{(0)} \hat{n}_{1\sigma} \hat{n}_{2\bar{\sigma}} + (J^{(0)} - J_x^{(0)} + J^{(0)} S^2) \hat{n}_{1\sigma} \hat{n}_{2\sigma}] + \frac{Z_1 Z_2}{d} \end{aligned} \quad (8)$$

where $U_i^{(0)}$ and $J^{(0)}$ are the intra- and inter-atomic Coulomb interactions associated with the atomic orbitals, ψ_i , $J_x^{(0)}$ the exchange interaction between ψ_i and ψ_j , and $J^{(0)} S^2$ a correction to the exchange interaction introduced by the wavefunction overlap; T can also be related to the Bardeen tunnelling current (7), and E_i^{σ} to the atomic levels corrected by the wavefunction overlap (6).

In a more general case, we can introduce the following Hamiltonian:

$$\begin{aligned} \hat{H} = & \sum_{i,\sigma} E_i^{\sigma} \hat{n}_{i\sigma} + \sum_{\sigma,(i,j)} T_{ij}^{\sigma} (\hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^{\dagger} \hat{c}_{i\sigma}) + \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \\ & + \frac{1}{2} \sum_{i,j \neq i,\sigma} [J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}} + (J_{ij}^{(0)} - J_{x,ij}^{(0)} + J_{ij}^{(0)} S_{ij}^2) \hat{n}_{i\sigma} \hat{n}_{j\sigma}] + \frac{Z_1 Z_2}{d} \end{aligned} \quad (9)$$

where the different operators \hat{c}_i^{\dagger} and \hat{c}_i are associated with the Löwdin wavefunctions ϕ_i . Equation (9) defines the total Hamiltonian as the superposition of the different Hamiltonians defined, as in (8), for each pair of atomic orbitals.

2.1. Local density approximation to the many-body terms

Hamiltonian (9) defines our model for the chemisorption problem. Let us now discuss how the many-body terms are analysed in our approach. These terms are rewritten as follows:

$$\hat{H}^{mb} = \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum_{i,j \neq i,\sigma} (J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma}) \quad (10)$$

with an obvious definition for $\tilde{J}_{ij}^{(0)}$; then, the total Hamiltonian takes the form

$$\hat{H} = \hat{H}^{oc} + \hat{H}^{mb} + \frac{Z_1 Z_2}{d} \quad (11)$$

where \hat{H}^{oe} represents the one-electron terms, $\sum_{i\sigma} E_i^\sigma \hat{n}_{i\sigma} + \sum_{\sigma,(i,j)} T_{ij}^\sigma (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})$ of (9). In our approach, we reduce Hamiltonian (11) to the effective one-electron Hamiltonian

$$\hat{H}_{\text{eff}} = \hat{H}^{oe} + \sum_{i,\sigma} V_{i,H}^\sigma \hat{n}_{i\sigma} + \sum_{i,\sigma} V_{xc,i}^\sigma \hat{n}_{i\sigma} + \frac{Z_1 Z_2}{d} \quad (12)$$

where

$$V_{i,H}^\sigma = U_i^{(0)} n_{i\bar{\sigma}} + \sum_{j \neq i} (J_{ij}^{(0)} n_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} n_{j\sigma}) \quad (13)$$

and $V_{xc,i}^\sigma$ is a local potential that includes in the $i\sigma$ site the exchange and correlation effects.

The critical point in our formulation is the extension of Hohenberg and Kohn theorem to our LCAO method; thus we can prove that

$$V_{xc,i}^\sigma = \frac{\partial E_{xc}[n_{i\sigma}]}{\partial n_{i\sigma}} \quad (14)$$

where $E_{xc}[n_{i\sigma}]$ is the total exchange and correlation energy that only depends on the orbital occupation numbers, $n_{i\sigma}$.

The exchange contribution to $E_{xc}[n_{i\sigma}]$ can be obtained from (10) using the Hartree-Fock approximation to this Hamiltonian. This yields

$$E_x[n_{i\sigma}] = -\frac{1}{2} \sum_{j \neq i, \sigma} \tilde{J}_{ij}^{(0)} \langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \rangle \langle \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma} \rangle \quad (15)$$

where $\langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \rangle$ defines the i - j bond order. One can prove that, if the exchange hole of our $i\sigma$ electron is localized in the first nearest neighbours of the given i site, (14) takes the form (García-Vidal *et al* 1991)

$$E_x[n_{i\sigma}] = -\frac{1}{2} \sum_{i,\sigma} \tilde{J}_i^{(0)} \langle \hat{n}_{i\sigma} \rangle (1 - \langle \hat{n}_{i\sigma} \rangle) \quad (16)$$

where $\tilde{J}_i^{(0)}$ is the $\tilde{J}_{ij}^{(0)}$ interaction between the i - j orbitals in the first nearest neighbours. In the more general case, we can write

$$E_x[n_{i\sigma}] = -\frac{1}{2} \sum_{i,\sigma} \tilde{J}_i^{(0)} \alpha[n_{i\sigma}] \langle \hat{n}_{i\sigma} \rangle (1 - \langle \hat{n}_{i\sigma} \rangle) \quad (17)$$

where $\alpha[n_{i\sigma}]$ is a factor that is almost constant in the range $0.15 \simeq n_{i\sigma} \simeq 0.50$, and behaves as $n_{i\sigma}^{1/3}$ for $n_{i\sigma}$ smaller than 0.15 (α is symmetric with respect to the mid occupancy, 0.5). Equation (17) yields the exchange potential:

$$V_x = \frac{dE_x[n_{i\sigma}]}{dn_{i\sigma}}. \quad (18)$$

Electron correlation effects can be introduced by considering the fluctuations that appear around the occupation numbers, $n_{i\sigma}$. These fluctuations are measured by the quantity

$\langle \hat{n}_{i\sigma}^2 \rangle - \langle \hat{n}_{i\sigma} \rangle^2 = n_{i\sigma}(1 - n_{i\sigma})$, which can be related to the exchange energy given by (16) when the exchange hole is localized in the first nearest neighbours. The correlation energy can be approximated by

$$E_c[n_{i\sigma}] = -\frac{1}{2} \sum_{i,\sigma} \bar{J}_i^{(0)} \langle \hat{n}_{i\sigma} \rangle (1 - \langle \hat{n}_{i\sigma} \rangle) \quad (19)$$

if we also assume that the correlation hole is localized in the first nearest neighbours. Equations (16) and (19) suggest a simple relationship between E_x and E_c ; thus, by taking into account the dynamical processes that reduce E_c by around 25%, we write the correlation effects as follows:

$$E_c = \frac{3}{4} E_x \quad E_{xc} = \frac{7}{4} E_x. \quad (20)$$

We should comment that this approximation neglects the intrasite correlation energy, which can be important for very electronegative atoms (O, Cl, etc) or atoms with localized shells (d or f bonds). From (20) we define the exchange and correlation potential:

$$V_{xc,i}^\sigma = \frac{7}{4} \frac{dE_x}{dn_{i\sigma}} \quad (21)$$

and the effective Hamiltonian (12). This Hamiltonian is the basis of our calculation that yields $n_{i\sigma}$ self-consistently. Once $n_{i\sigma}$ is obtained we can calculate the total electron energy by adding to the electron energy of the effective Hamiltonian the following contribution:

$$-\frac{1}{2} \sum_{i,\sigma} V_{i,H}^\sigma n_{i\sigma} + E_{xc}[n_{i\sigma}] - \sum_{i,\sigma} V_{xc,i}^\sigma n_{i\sigma}. \quad (22)$$

The first term avoids double counting in the Hartree energy, and the second and third terms yield the total exchange and correlation energy after cancelling the contribution coming from the $V_{xc,i}^\sigma$ potential.

3. Results and discussion

We have applied the previous approach to the calculation of the adsorption of Sb on GaAs(110). In our approach, the method has been used to calculate the interaction between Sb and the semiconductor surface. In other words, the clean semiconductor surface has been calculated using the parameters of Vogl *et al* (1983); in a further step, our method has been applied to the calculation of Sb interacting with the GaAs(110) surface. We should also mention that, in the calculations presented here, the semiconductor surface is assumed to be unrelaxed; this is a reasonable approximation since it is well known (Srivastava 1992) that, under Sb deposition, the GaAs(110) surface relaxes to an almost ideal geometry.

We have analysed different geometries and coverages. Figure 1(a) shows the semiconductor surface and the different adsorption sites we have analysed for a 1/2 coverage ($\theta = 1$ corresponds to two atoms per semiconductor unit cell). Our calculations show that the long-bridge position (C in figure 1) yields the most favourable chemisorption energy; figure 2 shows this chemisorption energy per unit cell as a function of the distance between

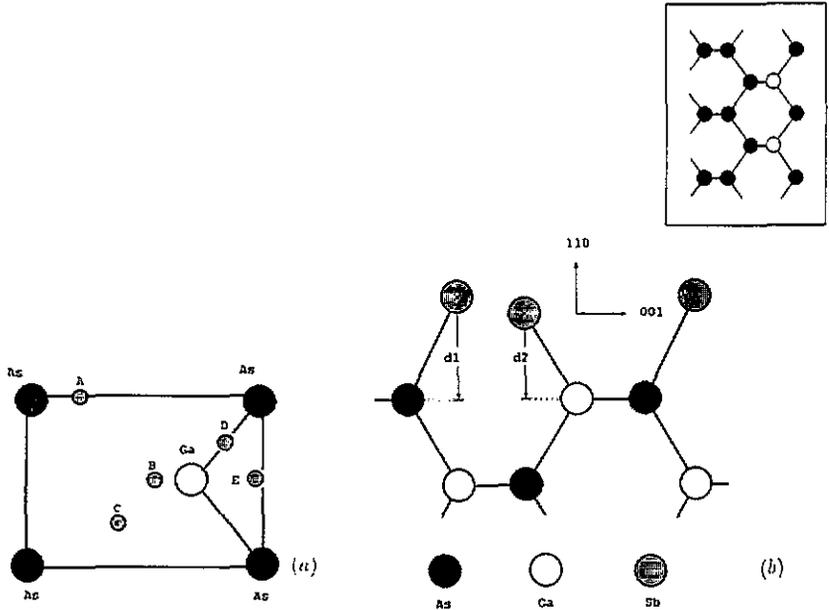


Figure 1. (a) GaAs(110) surface showing the different sites we have considered for the Sb adsorption. The C site yields the most favourable position for $\theta = 1/2$. (b) Sb adsorption sites for an Sb monolayer ($\theta = 1$).

the Sb layer and the last semiconductor layer. Notice that the maximum chemisorption energy is 1.3 eV; this quantity is more than 1 eV larger than the values obtained for Sb absorbed on either As or Ga. Figure 3 shows the chemisorption energy per unit cell for a monolayer, $\theta = 1$, of Sb as a function of the distances between the two Sb atoms and the last semiconductor layer (see figure 1(b)). This figure corresponds to the geometrical configuration we have found to give the maximum chemisorption energy: this is the case for which the two Sb atoms per unit cell are bonded to As and Ga as shown in figure 1(b). It is remarkable that one Sb atom per unit cell appears bonded to Ga and As, at the same time, by occupying the long-bridge position, while two Sb atoms per unit cell prefer to be bonded one to Ga, the other to As. This is a result similar to the one found for Al (Ortega *et al* 1992): in this case too, a single Al atom prefers the long-bridge position, while two atoms are located on the ideal continuation of the GaAs crystal.

Let us also comment that the minimum of energy found in figure 3, ≈ 2.3 eV per Sb atom, corresponds to different distances of the two Sb atoms to the semiconductor layer. The Sb–Ga distance is found to be ≈ 0.3 Å smaller than the Sb–As distance, in good agreement with recent results (Srivastava 1992). (Notice that in our calculation we neglect the small surface relaxation).

In order to understand how previous results are related to the Schottky barrier formation, we show in figure 4 the local density of states on the last semiconductor layer for the minimum energy of the two coverages: $\theta = 1/2$ and $\theta = 1$. For $\theta = 1/2$, figure 4(b) shows an Sb-induced surface band located around the middle of the semiconductor gap; for $\theta = 1$, figure 4(c) shows, however, an energy gap limited by two Sb-induced surface bands (the arrows shown in figure 4(c)). These results can be understood in the following way: for $\theta = 1/2$, there is an odd number of electrons per unit cell and a metal-like density of

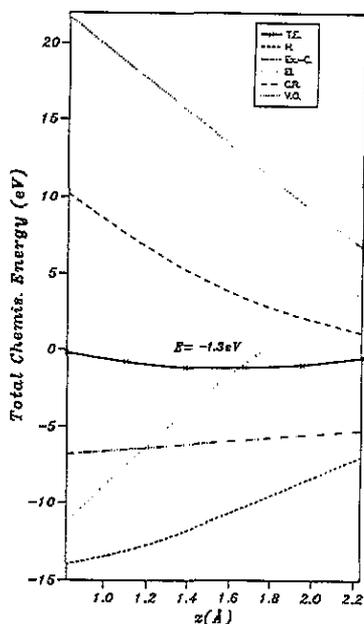


Figure 2. Chemisorption energy for Sb (C site of figure 1(a)) as a function of the distance between the Sb layer and the last semiconductor layer. We also show the different contributions to the total chemisorption energy. TE: total chemisorption energy. H: hybridization energy. Ex-C: exchange and correlation energy. El: electrostatic energy. CR: repulsion between the core levels and the valence electrons. VO: repulsive energy (kinetic energy) between valence electrons.

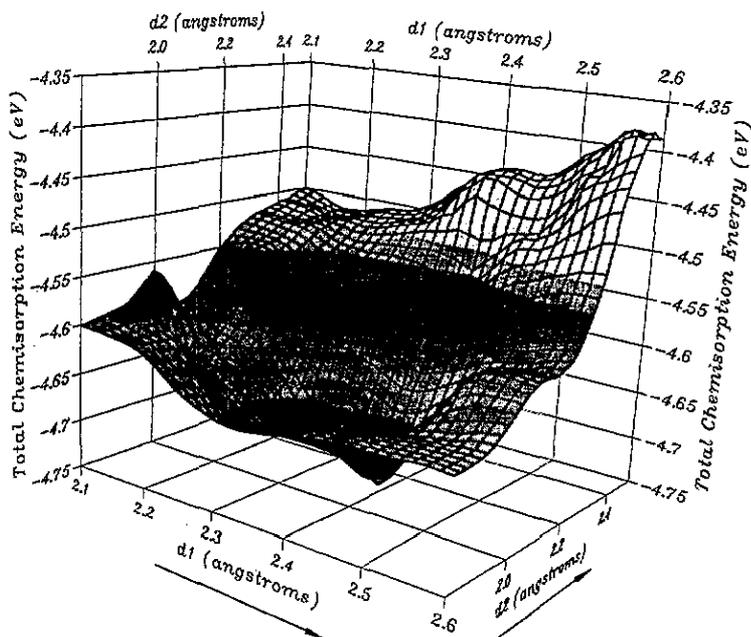


Figure 3. Chemisorption energy per unit cell (two Sb atoms) as a function of the distances d_1 and d_2 shown in figure 1(b).

states must appear with the Fermi level in the middle of a surface band (unless correlation effects open an energy gap (Flores and Ortega 1992)); for $\theta = 1$, the number of electrons per unit cell is even, and the strong bonding between Sb and the semiconductor dangling bonds (as the one between the Sb atoms) yield a semiconductor-like structure of the surface, like the one found in figure 4(c).

Although, for half a monolayer, the Fermi level is pinned by the Sb-induced surface band, the energy position of this surface band is very much dependent on the site of the

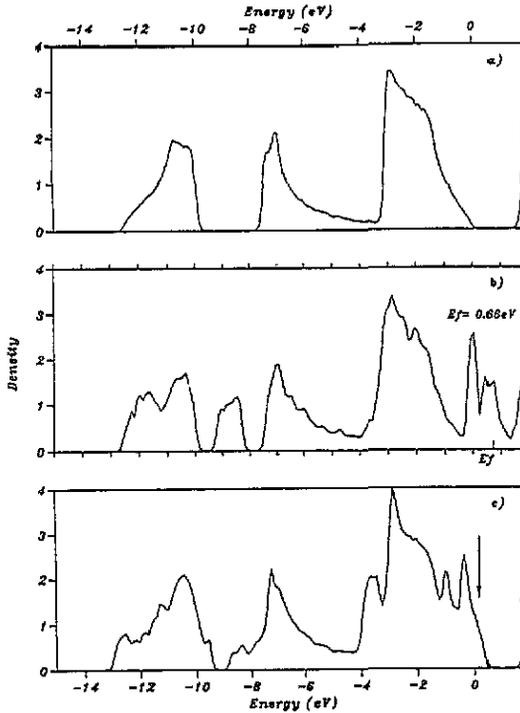


Figure 4. Total for different Sb coverages: (a) clean GaAs (110) surface; (b) $\theta = 1/2$; (c) $\theta = 1$.

absorbed Sb. For the long-bridge position we find $E_F = 0.66$ eV; however, for the As and Ga sites we find $E_F = 1.4$ eV and 0.6 eV, respectively. As discussed elsewhere (Flores and Tejedor 1987, Flores and Ortega 1992) the Fermi levels found for the different geometries fluctuate around the semiconductor charge neutrality level.

From all the previous results, we can get the following picture about the Schottky barrier formation upon the deposition of Sb on GaAs(110). For very low coverages, one can expect to find isolated atoms located in the long-bridge position of the semiconductor unit cell. As far as the coverage increases a little, we can expect, however, to see small clusters or Sb islands on the semiconductor surface. This is due to the strong attraction that we deduce to exist between Sb atoms. Thus, for half a monolayer, the adsorption energy per unit cell is $\simeq 1.3$ eV, while for a monolayer the energy per unit cell increases to 4.7 eV, 2.1 eV more than the adsorption energy of two Sb atoms for the half-monolayer case.

Considering the results we have found for the monolayer case, one can deduce that, for small islands or surface clusters, the Fermi level will not be pinned by any Sb-induced surface states, unless some new states associated with the islands edges were to appear. These edge states have been seen by Feenstra and Martensson (1988). We can speculate about the origin of these states, by noticing that for half-monolayer we find different surface bands in the semiconductor energy gap depending on the Sb adsorption site: these surface states are related to the unsaturated dangling bonds of either As or Ga. This suggests that near the island edges we can find some states associated with the dangling bonds of the unrelaxed semiconductor surface (the Sb atoms suppress almost completely the semiconductor relaxation). The As-like surface band (found for unsaturated As dangling bonds) has been found around 0.7 eV above the valence band top, its position, below the Ga-like surface band, suggesting that it could be responsible of the edge states pinning the Fermi energy for coverages below an Sb monolayer.

We should stress, however, that for a full monolayer no Sb-induced surface band can be expected to pin the Fermi energy in the semiconductor gap. The Schottky barrier formation should appear for a higher Sb coverage. As discussed (Ortega *et al* 1992) in the case of Al, a second monolayer would close the energy gap found for a monolayer, and the Fermi level should be pinned by an Sb-induced surface band, this effect completely forming the Schottky barrier.

4. Conclusions

In this paper we have presented a summary of the LCAO approach developed in our laboratory to analyse chemisorption problems. The method allows us, in a first step, to determine the different parameters associated with the diagonal and the off-diagonal terms of the Hamiltonian. In a further step, many-body terms are also introduced and analysed using a local density approximation: this means that, as in an LDA approach, many-body effects are introduced by means a diagonal potential, $V_{xc,i}^{\sigma}$ acting on each orbital of our system. The method yields the occupation number, $n_{i\sigma}$, for each orbital and allows us to calculate the total energy of the system.

We have applied this approach to the case of Sb chemisorbed on GaAs (110). We have analysed how Sb is chemisorbed as a function of its coverage, and have found that for very low coverages the Sb atoms tend to be adsorbed on the long-bridge position of the GaAs unit cell. As the coverage increases, the Sb atoms attract each other strongly and form the rows shown in figure 1(b) and found previously by other authors (Mailhiet *et al* 1985, Bertoni *et al* 1983, Srivastava 1992, Feenstra and Martensson 1988).

Finally, we discuss how these chemisorption properties are related to Schottky barrier formation. In particular, we argue that the barrier can be completely formed only when more than one Sb monolayer is deposited on the semiconductor. The island edge states, found by Feenstra and Martensson (1988) at coverages smaller than one, are argued to be As-like states associated with the non-saturated As dangling bonds located at the island edges.

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