

Chemisorption of Metals or Electronegative Atoms on GaAs

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Abstract

An ab-initio LCAO method is used to calculate the electronic properties of metals (Li, Na, K and Al), H and electronegative atoms (Cl and O) chemisorbed on GaAs (110). Results for different coverages are presented. The adsorption geometry, the corresponding chemisorption energy, the local density of states and the transfer of charge are obtained for each case. A discussion of the similarities and differences between the different cases is presented.

1. Introduction

The chemisorption properties of different atoms on semiconductor surfaces is a subject of great interest on many areas. Electropositive (or metallic) atoms chemisorb on semiconductors to form a Schottky barrier [1]: the formation and properties of this barrier are intimately related to the chemical bond between the metal ad-atoms and the semiconductor [2]. More electronegative atoms (the components of semi-conductors) are deposited epitaxially to grow superlattices or specific man-made structures [3]: the mechanism of growth also depends crucially on the chemisorption interaction between the ad-atoms and the semiconductor. Very electronegative atoms, O, Cl, etc., can be deposited on semiconductors [4] to form oxides or other compounds in order to passivate or control the interface properties of semiconductors.

All these areas are closely related. Thus, it has been suggested [5] that by depositing a metal monolayer between two semiconductors, one can control the heterojunction band-offset. Likewise, by depositing very electronegative atoms at the interface of a Schottky junction, the barrier and other electronic properties can be dramatically modified [4].

The evolution in the field of semiconductor interfaces has shown that many macroscopic properties of different junctions are intimately related to the chemical bonds formed at the interface. This perspective has prompted many different groups to analyze the properties of different chemisorbed species and its relation with other properties: barriers, reconstructions etc. [6–8].

The aim of the work presented in this paper is closely related to this point of view. For many years, we have been working on semiconductor junctions using approaches related mainly to the physical properties of the interface [9]. The evidence collected in the last few years [10–12] has convinced us that the details of these physical properties are mainly determined by the chemical bond at the interface. One example will show this point more clearly: the Schottky barrier and the band-offset of semiconductor junctions have been shown to be deeply related to the concept of the charge neutrality level (CNL) of the semiconductor [13].

Detailed calculations have shown, however, that the CNL can change at a semiconductor junction due to the different chemical bonds formed at the semiconductor interface. The semiconductor CNL is a function of each specific interface, its actual value (the extrinsic CNL) fluctuating around the intrinsic CNL [14].

In this paper, we present a discussion of the chemisorption properties of different atoms, ranging from very electropositive (alkali atoms) to very electronegative (Cl and O). Our aim has been to analyze the evolution of the chemisorption properties of different atoms on GaAs (110), as a function of the ad-atom electronegativity. The interface electronic properties, the chemisorption energy, the chemisorption sites and other related properties have been analyzed for Li, Na, K, Al, H, Cl and O.

In our approach, we follow a free-parameter LCAO-method that yields the chemisorption properties of the interface as a function of the properties of the atomic ingredients of the system. In Section 2 we present a summary of the method that has been fully presented elsewhere [15]. In Sections 3, 4 and 5 our results for different chemisorbed species on GaAs are discussed. Finally, in Section 6 we present our conclusions.

2. Model and method of calculation

The electronic structure of GaAs is described using a LCAO-model with the sp^3s^* hybrids and the interactions discussed by Vogl *et al.* [16]. The interaction between the adsorbate-atoms and between the adsorbate and the substrate is analyzed by means of a LCAO method [15] that gives a prescription to calculate the hopping elements between the different orbitals as well as the one body and the many body contributions to the total energy of the chemisorption system. A full discussion of this free-parameter method is presented elsewhere [15]: here, we only quote its main characteristics.

First of all, let us mention that the hopping integrals, T_{ij} , between two orbitals ψ_i and ψ_j (taken as the atomic orbitals of two atoms) are related to the Bardeen tunneling current, T_{ij}^B by the eqns.:

$$T_{ij} = \gamma T_{ij}^B \quad (1)$$

$$T_{ij}^B = \frac{\hbar}{2m} \int (\psi_i \bar{\nabla} \psi_j - \psi_j \bar{\nabla} \psi_i) \bar{n} \, ds \quad (2)$$

where γ is typically around 1.3–1.5, a parameter that can be calculated exactly [15].

The overlap between different orbitals, $S_{ij} = \langle \psi_i | \psi_j \rangle$, introduces a contribution to the total energy that is found to be well described by the following correction to the

diagonal level, δE_i , of a given orbital ψ_i :

$$\delta E_i = - \sum_{j \neq i} S_{ij} T_{ij} + \frac{1}{4} \sum_{j \neq i} S_{ij}^2 (E_i - E_j) \quad (3)$$

where E_i and E_j are the mean levels of the i and j orbitals.

Many-body contributions are introduced by means of the following terms in the total Hamiltonian:

$$\begin{aligned} \hat{H}^{m.b.} = & \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum_{i \neq j, \sigma} J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}} \\ & + \frac{1}{2} \sum_{i \neq j, \sigma} \bar{J}_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma} \end{aligned} \quad (4)$$

where $U_i^{(0)}$ and $J_{ij}^{(0)}$ are the intraorbital and interorbital bare coulomb interactions, respectively, and $\bar{J}_{ij}^{(0)}$ an effective [15] interorbital coulomb interaction given by:

$$\bar{J}_{ij}^{(0)} = J_{ij}^{(0)}(1 + S_{ij}^2) - J_{x,ij}^{(0)} \quad (5)$$

where $J_{x,ij}^{(0)}$ is the exchange integral between the i and j orbitals having the same spin.

The terms given by eq. (4) are treated using a many-body approximation equivalent to the one given by Slater for a free electron gas. This means using a mean field approximation supplemented by a Slater-like potential, $V_{xc,i\sigma} \equiv V_{x,i\sigma} + V_{c,i\sigma}$. Thus, we replace Hamiltonian (4) by the following mean-field Hamiltonian:

$$\begin{aligned} \hat{H}_{eff}^{m.b.} = & \sum_i U_i^{(0)} \hat{n}_{i\sigma} \langle \hat{n}_{i\sigma} \rangle + \sum_{j \neq i, \sigma} J_{ij}^{(0)} \hat{n}_{i\sigma} \langle \hat{n}_{j\bar{\sigma}} \rangle \\ & + \sum_{j \neq i, \sigma} \bar{J}_{ij}^{(0)} \hat{n}_{i\sigma} \langle \hat{n}_{j\sigma} \rangle + \sum_{i\sigma} V_{x,i\sigma} \hat{n}_{i\sigma} + \sum_{i\sigma} V_{c,i\sigma} \hat{n}_{i\sigma} \end{aligned} \quad (6)$$

plus some constant terms cancelling the double counting in the electron-electron interaction. $V_{x,i\sigma}$ is related to the exchange pair distribution function $g_\sigma(i, j)$, and is given by the eqn.:

$$V_{x,i\sigma} = - \sum_{j \neq i} \bar{J}_{ij}^{(0)} g_\sigma(i, j) \quad (7)$$

where $g_\sigma(i, j)$ is defined by:

$$\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \langle c_{j\sigma}^\dagger c_{i\sigma} \rangle = \langle \hat{n}_{i\sigma} \rangle g_\sigma(i, j) \quad (8)$$

$V_{c,i\sigma}$ is related to the correlation effects associated with the i σ -orbital. Basically, $V_{c,i\sigma}$ is $(1 - \langle \hat{n}_{i\sigma} \rangle)$ times the Coulomb-hole selfinteraction the i σ electron induces in itself through the electron gas; notice that the factor $(1 - \langle \hat{n}_{i\sigma} \rangle) \langle \hat{n}_{i\sigma} \rangle = \langle \hat{n}_{i\sigma}^2 \rangle - \langle \hat{n}_{i\sigma} \rangle^2$ measures the electron fluctuations in the $i\sigma$ -level (details about $V_{c,i\sigma}$ will be published elsewhere). This procedure yields the adequate potential that takes into account both the intra-atomic and the inter-atomic correlation effects. Intra-atomic correlation effects appear to be very important for Cl and O.

In our actual calculation we have solved the LCAO mean field Hamiltonian using conventional Green-function techniques [17]. Moreover, selfconsistency in the charges is achieved by relating the induced potential (as given by the many-body Hamiltonian) to the charges induced in each orbital.

3. Metals on GaAs (110)

The (110) surface of GaAs is one of the most thoroughly studied semiconductor surfaces [18]. Fig. 1 shows the zig-zag chains of alternate Ga and As atoms present on the

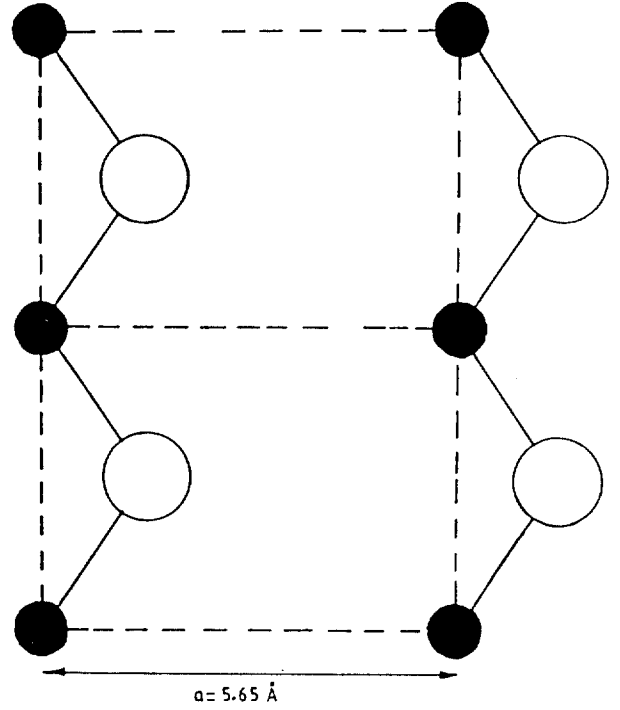


Fig. 1. The (110) ideal surface of GaAs (top view)

ideal (110) surface. Filled (As) and empty (Ga) dangling bonds appear when the surface is formed. The surface relaxes with the As atoms moving out of the surface and the Ga atoms moving towards the bulk so that the dangling bond states are removed from the semiconductor energy gap (~ 1.5 eV). The deposition of low coverages of metallic atoms has been found to remove the semiconductor surface relaxation [19, 20]. However, the deposition of hydrogen on GaAs (110) has been calculated not only to remove the surface relaxation, but also to induce some counter-relaxation [21]. In this paper we assume, for simplicity, that the different atoms are chemisorbed on the ideal surface.

The deposition of metallic atoms on GaAs (110) has been extensively studied in the last years, trying to elucidate the process of formation of the metal-semiconductor interface. This implies understanding the chemisorption properties of the first metal atoms deposited on the semiconductor surface. With this goal in mind, we study in this section the cases of alkali metals and aluminum on GaAs (110).

A Alkali metals

The early stages of the metal-semiconductor interface formation for the case of alkali atoms on GaAs (110) have been discussed in detail elsewhere [8, 11, 12, 20, 22]. Here, we focus on the main results found for the chemisorption of Li, Na and K on GaAs (110).

Table I shows the results obtained for the equilibrium distance and its corresponding chemisorption energy for a coverage of $\theta = \frac{1}{4}$. (In this paper we consider $\theta = 1$ - a monolayer (ML) - as the coverage corresponding to one adsorbate per atom on the semiconductor surface, i.e. 8.9×10^{14} atoms/cm²). The most favourable position is, in all cases, on the Ga-dangling bond, although we find only small differences, ~ 0.1 - 0.2 eV, with other chemisorption places (like the As-dangling bond). Alkali atoms are the most electropositive ones; they show a big atomic size and

Table I. Chemisorption energy, E_q , and chemisorption distance, d , for the deposition of $\frac{1}{4}$ ML of alkali metals on GaAs (110). Chemisorption energies are referred to the ideal surface

	Li	Na	K
E_q	1.75 eV	1.85 eV	1.90 eV
d	2.8 Å	2.8 Å	3.1 Å

their chemisorption properties are not very much dependent on the particular adsorption site on the semiconductor surface. Also, they tend to repel each other (if the semiconductor relaxation is neglected [22]) for coverages lower than the first physical monolayer (the one in direct contact with the substrate; $\theta \sim \frac{1}{2}$ in this case). The chemisorption energies that we obtain for $\theta = \frac{1}{2}$ are lower by ~ 0.3 eV than those shown in Table I for $\theta = \frac{1}{4}$. (On the other hand, we can use the $\theta = \frac{1}{4}$ results to estimate the chemisorption energy of a single alkali atom on GaAs (110), by subtracting the dipole-dipole interaction: the chemisorption energies that we obtain in this way increase by ~ 0.3 eV the results of Table I.) The transfer of charge from the alkali atoms to the semiconductor is $\sim 0.3e^-$ for $\theta = \frac{1}{2}$ and $\sim 0.5e^-$ for $\theta = \frac{1}{4}$.

Due to the big atomic size of alkali atoms, the Fermi energy at the interface, E_F , is not very sensitive to the particular geometry of chemisorption of the alkali atom, and is pinned close to the midgap of the semiconductor [13] when the first physical monolayer is deposited. In their most favourable geometry (on the Ga-dangling bond) we obtain $E_F^K = 0.7$ eV, $E_F^{Na} = 0.66$ eV and $E_F^{Li} = 0.6$ eV, respectively. (Fermi levels are referred to the semiconductor valence band maximum (VBM) throughout the paper).

Figure 2 summarizes the process associated with the alkali metal chemisorption on GaAs (110). Due to their atomic size, the alkali atoms have a similar interaction with both dangling bonds (in Fig. 2, t represents the hopping interaction between the atomic orbitals of the adsorbate and those of the substrate). This interaction is not a strong one ($t \sim 1$ eV), so that both states are slightly displaced to higher binding energies without changing very much its character (the empty dangling bond, which was initially 70% Ga-character, after its interaction with $\frac{1}{2}$ ML of alkali atoms is still 45% Ga-like and only 15% Alkali-like). However, one electron is "transferred" to the "Ga-dangling bond" and the Fermi level is pinned near the semiconductor CNL. All these results present a good agreement with the experimental evidence [12].

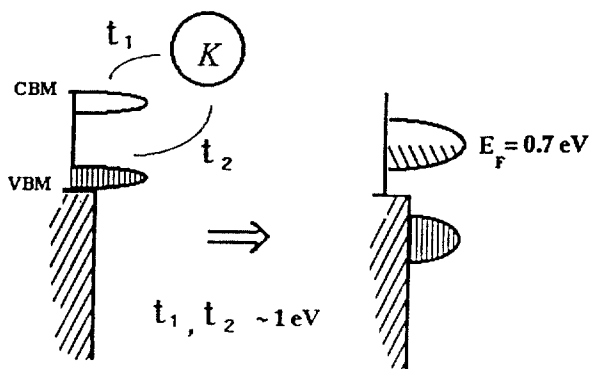


Fig. 2. Alkali metal chemisorption on GaAs (110)

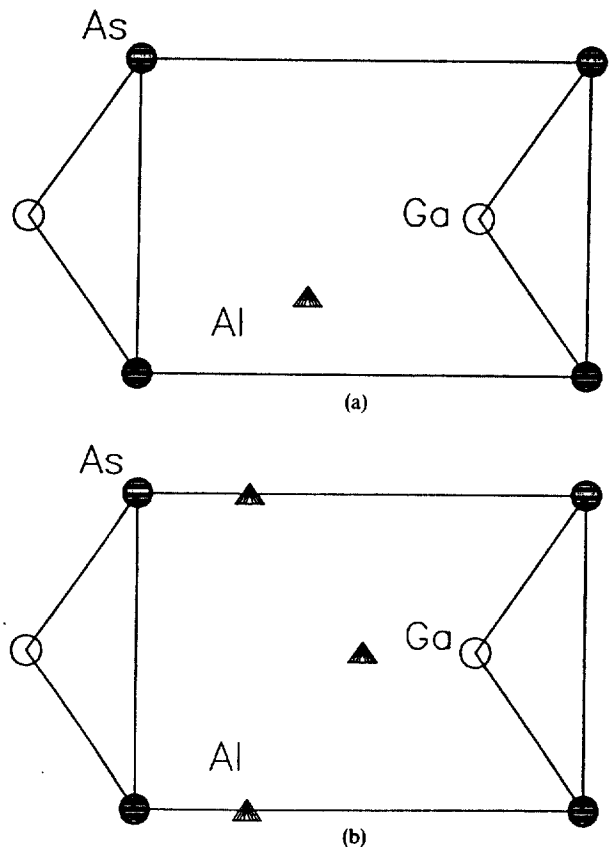


Fig. 3. Chemisorption geometries for Al on GaAs (110). (a) $\theta = \frac{1}{2}$. (b) $\theta = 1$

B Aluminum

Figure 3 shows the most favourable geometries found for the Al chemisorption on GaAs (110) for the cases $\theta = \frac{1}{2}$ and $\theta = 1$. For very low coverages Al-atoms are bonded simultaneously [23] to As and Ga, occupying the mid-point of the largest bridge distance between the cation and the anion [Fig. 3(a)], with a chemisorption energy of $E_q = 2.1$ eV (chemisorption energies are given with respect to the ideal surface). However, Al-atoms "attract" each other on the GaAs (110) surface, and they tend to be bonded at nearest Ga- and As-dangling bonds [Fig. 3(b)]. The chemisorption energy per aluminum atom that we obtain in this second case is $E_q = 2.7$ eV. These results are in good agreement with a local density approximation (LDA) calculation by Ihm and Joannopoulos [24]. The distance between Al-atoms in this configuration [Fig. 3(b)], $d(\text{Al-Al}) = 2.45$ Å, is quite short (comparing with $d(\text{Al-Al}) = 2.83$ Å in bulk Al) and would usually imply a repulsive interaction between Al-atoms. However, the energy gained by saturating both dangling bonds surmounts that repulsion and there is a net attraction. This case is in contrast with the otherwise similar case of In on GaAs (110): the In-atoms are appreciably larger and they cannot adopt the geometry shown in [Fig. 3(b)].

It is interesting to notice that this geometry for the deposition of Al on GaAs (110) (the natural continuation of the semiconductor surface) yields a density of states at the interface that presents an energy gap ~ 1.2 eV in good agreement with recent scanning tunneling microscopy (STM) [25] and photoemission [23] experiments. The deposition of a second Al-layer closes that gap [23]; then, the Schottky barrier is formed and the Fermi level is pinned near the CNL by the

density of interface states induced by the metal in the semiconductor energy gap.

4. Hydrogen on GaAs (110)

There have been several studies on the adsorption of hydrogen on GaAs (110). Experimental results [26–28] show that H chemisorbs on both As and Ga atoms. Also, molecular hydrogen was found not to adsorb on cleaved GaAs (110) [29]. Theoretical [21, 30] results based on the Local Density Approximation (LDA) give very close values for the chemisorption energy on both Ga- and As-dangling bonds, and a counterrelaxation of the semiconductor surface when H is chemisorbed on it [21].

Figure 4 illustrates the chemisorption of H on one or the other dangling bond; these are the most favourable geometries that we have found for $\theta = \frac{1}{2}$. Both chemisorption energies are obtained to be quite similar, E_q (on As) ~ 2.7 eV, E_q (on Ga) ~ 2.5 eV. The distance between the H-atom and the nearest semiconductor atom is in both cases ~ 1.8 Å.

As shown in Fig. 4, the hopping interaction, t , between the H-orbital and the nearest semiconductor dangling bond is around 3 eV, and its interaction with the other atoms in the semiconductor surface is very small. When H is chemisorbed on As [Fig. 4(a)] one electron is “transferred” to the Ga-dangling bond, while the H and the As bond levels form bonding and anti-bonding orbitals. On the other hand, when H is chemisorbed on Ga [Fig. 4(b)] the bonding combination of H and Ga takes one electron from the As-dangling bond, which is then half-filled.

When both dangling bonds are saturated with H-atoms for a ML coverage ($\theta = 1$), we obtain a chemisorption energy $E_q = 2.15$ eV per adsorbate, and a gap ~ 1.4 eV in the local density of states (LDOS) appearing at the Fermi energy.

Our results show that the main characteristic of the H-chemisorption on GaAs (110) is the formation of strong

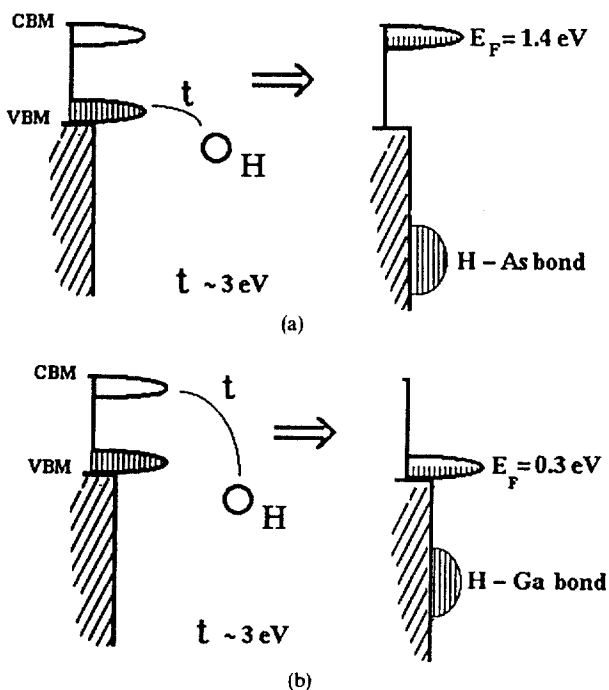


Fig. 4. Chemisorption of H on GaAs (110). (a) H chemisorbed on the As-dangling bond. (b) H chemisorbed on the Ga-dangling bond

bonds between H and the semiconductor dangling bonds. The strength of these bonds is, however, very similar, these results explaining that H tends to chemisorb on both As and Ga atoms.

5. Electronegative atoms on GaAs (110)

The chemisorption of Cl on GaAs is very similar to that of H (in both cases only one electron of the adsorbate is involved in the chemisorptive bond), and Fig. 4 is also appropriate for this case. However, the chemisorption energy of Cl-atoms on the Ga-dangling bond, E_q (on Ga) ~ 2.6 eV ($\theta = \frac{1}{2}$) is greater than its counterpart on the As-dangling bond, E_q (on As) = 2.0 eV. The distances of chemisorption between Cl and the nearest semiconductor atom are again quite similar on both cases, ~ 2.2 Å (see Fig. 5).

The deposition of a coverage of $\theta = \frac{1}{2}$ Cl-atoms on the Ga-dangling bonds yields a Fermi energy of $E_F = 0.48$ eV, strongly pinning the Fermi energy at the interface. This Fermi energy is not changed when we reduce the coverage to $\theta = \frac{1}{4}$. Troost *et al.* [31] have found that in the initial stages of Chlorine deposition on GaAs (110) the Fermi level is pinned at $E_F \sim 0.1$ – 0.2 eV. When the deposition is increased, the Fermi level moves to a value of $E_F = 0.55$ eV. We think that this pinning position is connected with the deposition of $\theta \sim \frac{1}{2}$ Cl-atoms on Ga-dangling bonds and that the initial Fermi level position is related to a low deposition of Cl-atoms on Ga, when the relaxation of the surface has not been completely removed. We have checked this last point by calculating the case of $\theta = \frac{1}{4}$ in which the Cl atoms are chemisorbed on alternate Ga-dangling bonds and all the other atoms of the semiconductor surface are placed on the positions of the relaxed surface: this geometry yields $E_F = 0.25$ eV (see Fig. 6).

It has been argued, on the basis of the results of core-level photoemission experiments [32] that Cl, when deposited on GaAs (110), chemisorbs on the As-atoms. In those experiments, when Cl is deposited, the As-3d core-level is shifted by 0.82 eV to higher binding energies, while the Ga-3d level remains almost unchanged. However, when Cl is chemisorbed on Ga, our results for the transfer of charge at the

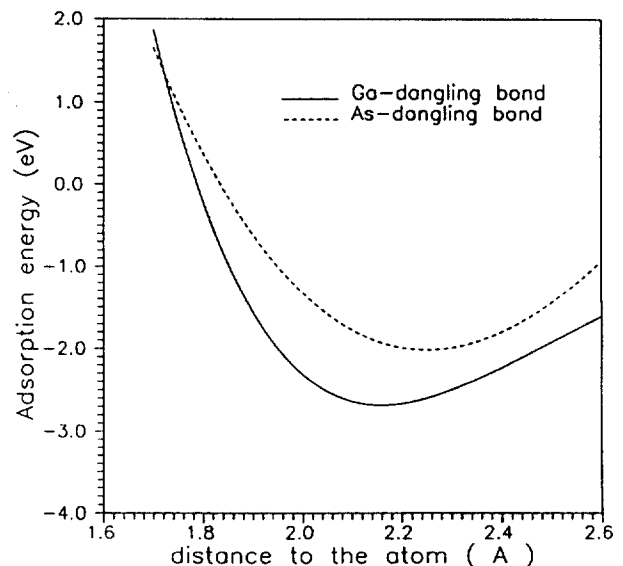


Fig. 5. Adsorption energy as a function of the distance between Cl and As or Ga, for the chemisorption of Cl on the As or the Ga-dangling bond. ($\theta = \frac{1}{2}$)

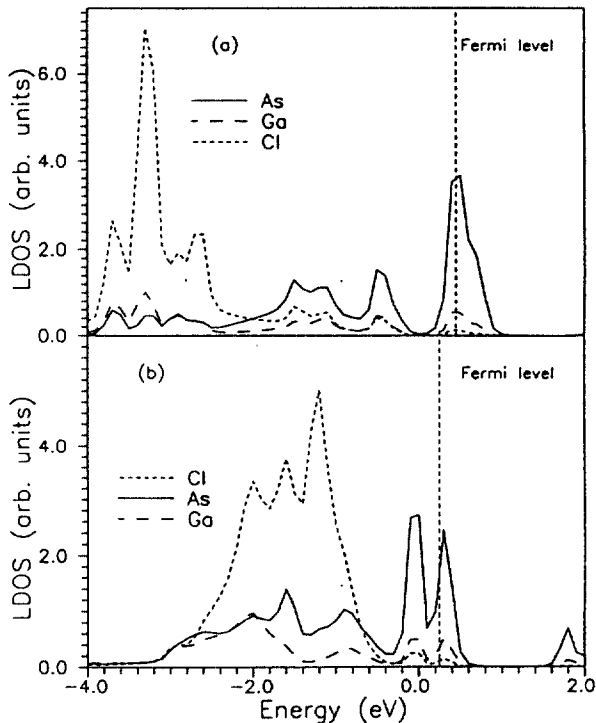


Fig. 6. LDOS for chlorine chemisorption on GaAs (110). (a) the Cl-atoms ($\theta = \frac{1}{2}$) are bonded to the Ga-dangling bonds on the ideal surface. (b) the Cl-atoms ($\theta = \frac{1}{2}$) are chemisorbed on the unrelaxed surface

interface are: $\delta q(\text{Cl}) \sim 0.45 e^-$, $\delta q(\text{As}) \sim -0.42 e^-$ and $\delta q(\text{Ga}) \sim -0.08 e^-$. These results suggest core-level shifts in agreement with the experiments.

The initial oxidation of the GaAs (110) surface has been widely studied. Core-level [33–35] as well as valence band [36, 37] photoemission spectroscopy, scanning tunneling spectroscopy [38], Auger-electron spectroscopy and low-energy electron energy loss spectroscopy [39] have been used trying to elucidate which are the first steps of oxidation of a semiconductor surface. It has been observed that upon exposition to O_2 the As-3d and the Ga-3d core-levels are shifted $\sim 3\text{eV}$ and $\sim 1\text{eV}$, respectively, to higher binding energies. Also, a peak around 4.5 eV below the valence band maximum has been measured in the photoemission spectra. On the theoretical side, both tight-binding calculations [40] and generalized-valence-bond cluster calculations [41] suggest that O chemisorbs mainly on the surface As-atom.

We have analyzed different geometries of O chemisorption on GaAs (110) ($\theta = \frac{1}{2}$) and we have found that the most stable configurations correspond to the cases: (i) O bonded on the As-dangling bonds, and (ii) O bonded simultaneously to As and Ga, occupying the mid-point of the shortest bridge distance between the cation and the anion. The chemisorption energy for this case is around $E_q \sim 3.8\text{eV}$, which is considerably larger than the energy of chemisorption on the Ga-dangling bond, $E_q \sim 2.3\text{eV}$. In the first two cases we obtain a peak in the density of states $\sim 4\text{eV}$ below the VBM associated with the As-O bond.

For a ML coverage, we have studied two different cases: (i) one O-atom bonded to the As-dangling bond while the other is placed on the short bridge position and (ii) the O-atoms are chemisorbed on both As and Ga dangling bonds. In the first case we obtain a chemisorption energy $E_q \sim 2.0\text{eV}$ which is considerably lower than the energy obtained for $\theta = \frac{1}{2}$, when only one of both sites is occupied.

However, when both dangling bonds are saturated the chemisorption energy per O-atom increases, $E_q \sim 3.9\text{eV}$, in similarity with the case of Al on GaAs (110).

It has been suggested that the main oxygen-uptake on GaAs (110) occurs in two subsequent chemisorption states [37, 39]. The first one (T_1) has been associated with the chemisorption of molecular oxygen, while the second one (T_2) consists on chemisorbed atomic oxygen. Our theoretical results indicate that when oxygen is dissociatively chemisorbed (state T_2), the geometry in which two O-atoms are chemisorbed on the As-dangling bond and in the short-bridge position surrounding the same As-atom is not energetically favourable. Our results also suggest that on the 1 ML coverage the O-atoms would tend to saturate both dangling bonds.

6. Conclusions

The aim of this paper has been to correlate and compare the chemisorption properties of different atoms adsorbed on GaAs (110). We have studied specifically Li, Na, K, Al, H, Cl and O, having their electronegativities increasing from the very electropositive atoms (alkali metals) to Cl and O.

The results presented in this paper show very general trends that can be summarized in the following points:

(i) Very electropositive atoms bond weakly to the semiconductor. Their main effect is to transfer some electronic charge to the crystal and to fill partially the cation-like surface states. Then, these half-filled states are displaced in energy towards the semiconductor CNL.

(ii) Aluminum is a little more reactive than the alkali atoms. A single atom would tend to be located between Ga and As, interacting with both dangling bonds: an Al atom has enough electrons to form bonds with both the cation and the anion-like surface states. At a larger coverage, the Al atoms attract each other and they tend, however, to be bonded to either Ga or As forming a full monolayer. For this monolayer, the interaction between the Al-orbitals and the dangling bond states yields a density of states that presents an energy gap of 1.2 eV, and some bonding and antibonding structure inside the conduction and valence bands of the semiconductor, respectively.

(iii) Hydrogen, with one electron per atom, tends to be bonded to either Ga or As. For an ideal GaAs surface, both chemisorption energies are very similar, E_q (on As) $\sim 2.7\text{eV}$ and E_q (on Ga) $\sim 2.5\text{eV}$. In any case, hydrogen forms strong bonding and antibonding states with the cation or the anion-like surface states. Thus, for H adsorbed on As, one electron is transferred to the Ga-dangling bond, while for H adsorbed on Ga, one electron is taken from the As-dangling bond. In either case, we find a half-occupied dangling bond located around one of the semiconductor edges (in the upper part, for H on As; in the lower part, for H on Ga).

(iv) Cl, having a single bond with the adsorbate, is very similar to H, and tends to form strong bonds with either As or Ga. For Cl, the Ga-like dangling bond reacts more strongly and we surmise that Cl should be bonded preferentially to Ga. As one electron is transferred from As to the bonding state formed between Ga and Cl, the Fermi energy is pinned by the half-occupied As-like dangling-bond surface state, in good agreement with the experimental evidence [31].

(v) Finally, O is very strongly bonded to GaAs and, in similarity with Al, can form two bonds per atom with the substrate. This explains why a single O-atom tends to be bonded simultaneously to As and Ga, occupying the midpoint of the shortest bridge distance between the cation and the anion. At higher coverages we find, however, that the O-atoms would tend to be bonded to either As or Ga; this is also similar to the results found for Al, an atom having also the possibility of forming more than one bond.

Acknowledgements

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