

Schottky barrier formation in the low metal coverage limit

F. Flores, R. Rincón, J. Ortega, F. J. García-Vidal and R. Pérez

Departamento de Física de la Materia Condensada C-XII.

Facultad de Ciencias. Universidad Autónoma. E-28049 Madrid. Spain.

Abstract

A theoretical discussion of the state of the art in the field of Schottky barrier formation is presented. The thin metal layer limit is analyzed for Al and In on GaAs(110), and the adsorption sites are determined as a function of the metal coverage. Intrinsic and extrinsic charge neutrality levels are also discussed for the In-case.

Contents

- 1 Introduction
 - 2 Model and method of calculation
 - 3 Results
 - 4 Conclusions
- Acknowledgements
References

Abbreviations

CE	Core repulsion energy
CNL	Charge neutrality level
EE	Electrostatic energy
HE	Hybridization energy
IDIS	Induced density of interface states
KE	Kinetic repulsive energy
LCAO	Linear combination of atomic orbitals
LDA	Local density approximation
ML	Monolayer
XC	Exchange and correlation energy
XE	Exchange energy

1 Introduction

During the last 20 years, a lot of work has been addressed to understanding the physics underlying the Schottky barrier formation. The number of experimental techniques has considerably grown, mainly due to the application of modern surface-sensitive experimental tools to study the microscopic interactions at metal-semiconductor interfaces. At the same time, the theoretical approaches to analyze the electronic and structural properties of surfaces and interfaces have advanced in parallel. In spite of all this progress, the physical mechanism controlling the Schottky-barrier formation is still a controversial subject [1, 2, 3].

The overlayer limit (more than 1 or 2 metal monolayers deposited on the semiconductor) has been the case mainly discussed in the past. The Schottky barrier heights for this limit have been analyzed using different models; two of them are receiving the most widespread acceptance: the Defect model [4] and the IDIS [5, 6, 7] (induced density of interface states) model.

From the point of view of the IDIS model, it is important to realize that, when a metal-semiconductor junction is formed, the metal wavefunctions tunneling into the semiconductor energy gap create an important density of interface states that pins the Fermi level. The new density of states associated with the tails of the metal wavefunctions that penetrates into the semiconductor energy gap is locally compensated by a reduction of the density of states in the semiconductor valence and conduction bands. Then, a semiconductor *charge neutrality level* (CNL) can be defined so that the interface density of states below that level in the energy gap and in the valence band compensate each other [6]. In the IDIS model, the CNL strongly pins the interface Fermi energy.

It is important to stress that the semiconductor CNL is independent of the metal if a *jellium model* for the metal is assumed. The CNL may fluctuate around the *intrinsic* value defined by the jellium model, when the different chemical bonds at the interface are considered in detail. This has led to the introduction of the *extrinsic* CNL [8], which fluctuates around the intrinsic one depending on the particular metal of the junction and the interface geometry.

On the other hand, the Defect model assumes that the interface Fermi level is pinned by the density of states associated with the defects created in the semiconductor by the metal deposition. Vacancies and anti-sites have been the defects preferentially analysed. The general approach of the Defect model relies on the analysis of the electronic level associated with the different defects created in the interface; in general, these defects are deduced from the agreement between the

energy levels and the interface Fermi energy.

The main reason why it has not been easy to discriminate between the Defect and the IDIS models is because both models give basically the same predictions. A simple example illustrating this point is the following: the case of a thick metal deposited on Si(111). In the IDIS model the interface Fermi level is pinned by the resonance states associated with the interaction between the semiconductor dangling-bonds and the metal band: the semiconductor dangling-bond surface states are changed into a broad resonance, pinning the Fermi energy around its center of gravity. In the Defect model, the interface Fermi level has been proposed [9] to be pinned by the density of states associated with the vacancies created by the metal deposition. Vacancy levels are also associated with the Si dangling-bond created by the vacancy, which are found to be practically at the same energy as the Si-CN_L: in both cases the Si dangling-bonds are responsible of the density of states pinning the Fermi energy.

There is, however, a point giving an important difference between both models: the amount of states pinning the Fermi level can be very different in both cases. Referring to the example given above, the number of dangling-bonds at the Si(111) surface is very large (one per surface atom), while the number of defects is not expected to be more than 1 % or 10 % of the number of surface atoms.

The main work in the last few years in the field of Schottky barriers has been addressed to understanding the electronic properties and the barrier height evolution in the limit of low metal coverages deposited on semiconductors. There is a growing consensus that the primary physical mechanism determining the barrier heights for metal coverages above one or two monolayers (ML) is the one given by the IDIS model [2, 10]. The problem is now centered on the processes of formation of the first physical monolayer. The experimental work done in the low metal coverage limit on semiconductors has given a deep insight on how the interface Fermi level evolves with the metal deposition [11, 12, 13]. The deposition of different metals on GaAs(110) has shown that, at very low coverages, the Fermi level changes very dramatically with the metal deposition, in some cases present an overshoot for a p-doped semiconductor and, finally, reaches a saturation value for metal coverages of 1 or 2 MLs. These results have stimulated a lot of theoretical work for understanding the chemisorption processes associated with the metal deposition on the semiconductor, and their relation to the mechanism of the metal-semiconductor interface formation [14, 15]. Detailed models such as LDA calculations [16, 17, 18, 19] or LCAO methods [20, 21], have been used to calculate the chemisorption properties of different atoms deposited

on a semiconductor surface, mainly GaAs(110).

In this paper we present a theoretical discussion of the Schottky barrier formation for Al and In on GaAs(110). The results presented here have been calculated using a first principles LCAO method [22]. In section 2 we present briefly our method. Results for the different interfaces are summarized in section 3; our discussion will present the main difference between the chemistry of the Al and In interfaces. We shall show how the In-GaAs(110) barrier is already formed for half a metal monolayer, in contrast with the Al interface; for the In case we will also discuss how the interface geometry is one of the crucial factors determining the Schottky barrier. In particular, the extrinsic and the intrinsic CNLs will be discussed for this interface.

2 Model and method of calculation

In LCAO methods the one-electron wavefunctions are written down in an appropriate basis of atomic orbitals, $\psi_\alpha \equiv \psi_\alpha(\vec{r} - \vec{R}_\alpha)$

$$\varphi_n = \sum_\alpha a_{n\alpha} \psi_\alpha \quad (1)$$

so that the Schrödinger equation is reduced to a set of linear equations

$$\sum_\beta (H_{\alpha\beta}^o - \epsilon_n S_{\alpha\beta}) a_{n\beta} = 0 \quad (2)$$

where $H_{\alpha\beta}^o = \langle \psi_\alpha | \hat{H} | \psi_\beta \rangle$ and $S_{\alpha\beta} = \langle \psi_\alpha | \psi_\beta \rangle$. In general atomic orbitals are not orthogonal, $S_{\alpha\beta} \neq 0$ for $\alpha \neq \beta$; overlap effects are of essential importance for the properties of molecules and crystals [23]. In order to take properly into account these effects, we use as basis functions the Löwdin's *orthonormalized* atomic orbitals [23], ϕ_μ ,

$$\phi_\mu = \sum_\nu (S^{-\frac{1}{2}})_{\mu\nu} \psi_\nu = \psi_\mu - \frac{1}{2} \sum_\nu S_{\mu\nu} \psi_\nu + \frac{3}{8} \sum_{\lambda,\nu} S_{\mu\lambda} S_{\lambda\nu} \psi_\nu - \dots \quad (3)$$

The Hamiltonian of the system is then expressed in terms of the interactions between atomic orbitals, ψ_μ , by neglecting all those terms whose contribution to the total energy is third (or higher) order in the overlap, $S_{\mu\nu}$, between atomic orbitals.

In this approximation, the kinetic repulsive contribution to the total energy due to the orthogonalization of the atomic orbitals, KE , is given by

$$KE = \left(- \sum_{j \neq i, \sigma} S_{ij} T_{ij} + \frac{1}{4} S_{ij}^2 (E_i - E_j) \right) \langle \hat{n}_{i,\sigma} \rangle \quad (4)$$

where E_i and E_j are the mean levels of the i and j orbitals, T_{ij} the hopping integral between both orbitals and $\langle \hat{n}_{i,\sigma} \rangle$ the mean occupancy of the i -orbital.

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

$$\hat{H}^{m.b.} = \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \frac{1}{2} \sum_{i \neq j, \sigma} J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma} + \frac{1}{2} \sum_{i \neq j, \sigma} \tilde{J}_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma} \quad (5)$$

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

$$\tilde{J}_{ij}^{(0)} = J_{ij}^{(0)}(1 + S_{ij}^2) - J_{x,ij}^{(0)} \quad (6)$$

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

Mean-field electrostatic and exchange energies, EE and XE , can be defined as follows

$$EE = \frac{1}{2} \sum_{i,\sigma} U_i^{(0)} \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{i\sigma} \rangle + \frac{1}{2} \sum_{j \neq i, \sigma} J_{ij}^{(0)} \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{j\sigma} \rangle + \frac{1}{2} \sum_{j \neq i, \sigma} \tilde{J}_{ij}^{(0)} \langle \hat{n}_{i\sigma} \rangle \langle \hat{n}_{j\sigma} \rangle \quad (7)$$

$$XE = -\frac{1}{2} \sum_{j \neq i, \sigma} \tilde{J}_{ij}^{(0)} \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \langle c_{j\sigma}^\dagger c_{i\sigma} \rangle \quad (8)$$

where $\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$ is the i - j bond order.

Electron correlation effects are included in our method by means of an approximation that relates the interatomic correlation energy with the exchange energy, XE . Consider a given orbital and its mean occupancy $\langle \hat{n}_{i,\sigma} \rangle$. Correlation effects are due to the fluctuations that appear around this mean value; the correlation energy is the difference between the energy associated with the fluctuating states and the mean energy associated with the mean occupancy. Assuming that the screening charge is spread around like the exchange hole, and taking into account dynamical processes, the following result is obtained for the *exchange-and -correlation* energy, XC

$$XC \simeq \frac{7}{4} EX \quad (9)$$

Let us also mention that the hopping integral, T_{ij} , between the i and j orbitals is related to the Bardeen tunneling current, T_{ij}^B , between both atomic orbitals [24]

$$T_{ij}^B = \frac{\hbar}{2m} \int (\psi_i \bar{\nabla} \psi_j - \psi_j \bar{\nabla} \psi_i) \bar{n} ds; \quad (10)$$

also, it can be shown [25] that the effect of the interaction of a valence orbital with a core orbital is well described by the following displacement of the valence level, E_v ,

$$\delta E_v = S_{vc}^2(E_v - E_c) \quad (11)$$

while the core level, E_c remains unchanged. S_{vc} is the overlap between both orbitals. This last equation defines the repulsive interaction (CE) associated with the core orbitals so that these orbitals do not have to be included explicitly in the calculation.

In order to obtain the total energy, we must add to all these contributions (EE, KE, XC, CE) the hybridization energy (HE). The hybridization term yields the energy associated with all the hopping interactions and with the transfer of charge between different levels.

In this paper, the method described above has been used to calculate the interaction between the adsorbate-atoms and between the adsorbate and the substrate. However, for simplicity, the electronic structure of GaAs is described using a LCAO-model with the sp^3s^* hybrids and the interactions discussed by Vogl et al.[26].

3 Results

In this paper we present some results for the chemisorption of Al and In on GaAs(110), and their relation to the Schottky barrier formation. Although some preliminary results have already been presented elsewhere [27, 28], we discuss here more in detail the chemisorption properties of different metals coverages and their relation to the barrier formation. Fig. 1 shows the main chemisorption sites analyzed in this paper for the deposition of Al and In on GaAs(110): the As (A) and Ga (B) dangling bonds and the long-bridge position (C).

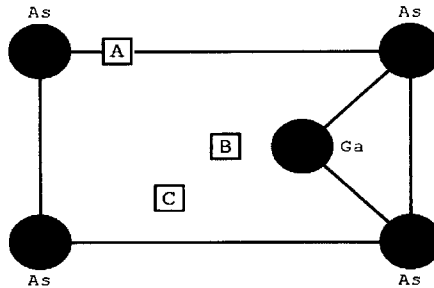


Figure 1: The chemisorption sites discussed in this paper: (A) As dangling bond, (B) Ga dangling bond (C) Long-bridge position

The case of Al has been discussed by analysing the chemisorption energy of different metal coverages on the semiconductor surface (a metal monolayer corresponds to one metal atom per semiconductor surface atom, *i.e.*, 8.9×10^{14} atoms/cm²). Fig. 2 shows this energy as a function of the metal layer distance to the last semiconductor layer, for $\theta = 1/2$. The most favourable chemisorption site corresponds to the long-bridge position, with a maximum chemisorption energy of 2.1 eV (see fig. 2a). In this figure the total chemisorption energy has been split into five different components: (i) the total electrostatic energy (EE), (ii) the exchange and correlation energy (XC); (iii) the hybridization energy (HE); (iv) the repulsive kinetic energy of the valence band (KE); and (v) the repulsive kinetic energy due to the core electrons of the different atoms (CE).

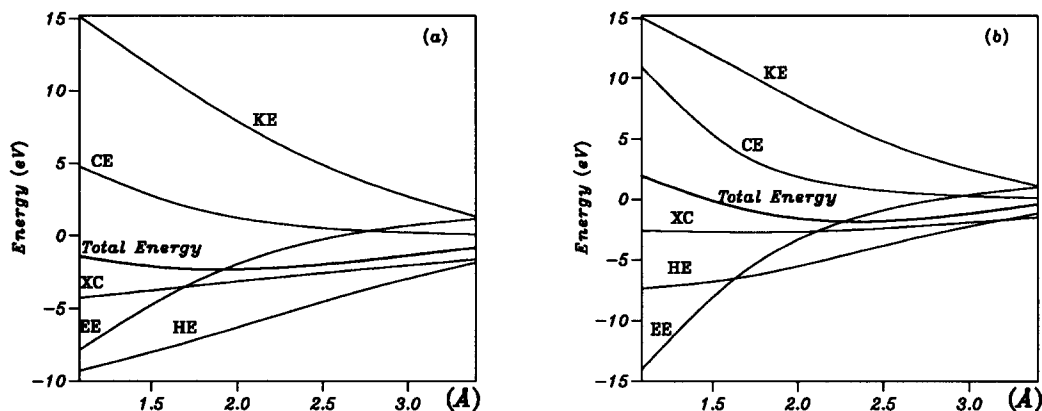


Figure 2: (a) Different contributions to the total energy for the chemisorption of $\theta = 1/2$ Al-atoms on the long-bridge position. Electrostatic energy (EE), exchange and correlation energy (XC), the hybridization energy (HE), the repulsive kinetic energy of the valence band (KE) and the core electrons (CE). (b) The same as (a) for the As-dangling bond position.

The results of this figure show how the chemisorption energy (2.1 eV) is a delicate balance between the attractive interactions (electrostatic, exchange and correlation and hybridization energy) and the repulsive terms (repulsive kinetic energy due to the valence and core electrons).

Fig. 2b shows the same results for Al chemisorbed on As dangling-bond. For this case the chemisorption energy is found 1.8 eV, and the different terms contributing to it resemble

very much the case of fig. 2a. We should mention that the long-bridge position yields a larger chemisorption energy due basically to a larger hybridization. Similar results are found for Al on the Ga dangling bond, a site giving a chemisorption energy of 1.0 eV. More interesting is to analyse the case of an Al-monolayer on GaAs(110). We have found that the geometry that gives the maximum chemisorption energy corresponds to Al-chains bonded to the Ga and As dangling bonds (sites A and B in fig. 1). Fig. 3 shows the different contributions to the total energy (EE, XC, HE, KE and CE) as a function of the distance of the metal-monolayer to the last semiconductor layer. In this figure the two Al atoms chemisorbed on As and Ga are allowed to relax in the direction perpendicular to the surface.

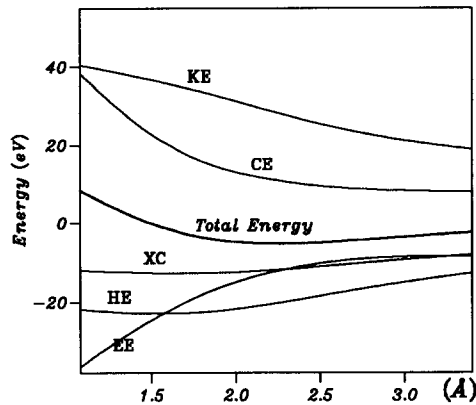


Figure 3: Different contributions to the total energy for the chemisorption of the Al-monolayer.

It is important to realize that the chemisorption energy of the Al monolayer is 5.3 eV, larger than the sum of the energy for the cases of half a monolayer on As and Ga. This result shows that the Al atoms strongly attract each other, tending to form clusters when forming the metal-semiconductor interface. Fig. 3 also show how strongly the Al-Al bond is formed for the monolayer case; even for large Al-semiconductor distances, the different contributions to the total energy are still important, due to the Al-Al interaction; the strong Al-monolayer chemisorption energy is due to the Al-Al attraction. In this regards it is worth realizing that the Al-Al distance (2.45 Å) is close to the sum of the covalent radii of the two atoms.

These results are important from the point of view of the Schottky barrier formation. According with the previous discussion, one can expect that the Al-atoms form clusters on the GaAs(110) surface, when deposited on the semiconductor. However, for very low coverages one can expect to see small islands with the atoms adopting the monolayer-like geometry discussed above. In this low coverage limit, we have found that due to the strong interaction between Al atoms, almost no density of states appear in the semiconductor gap, and no pinning of the interface Fermi level can be induced [27]. This suggests that the Schottky barrier formation can only appear for a larger Al-deposition, when Al-atoms are locally deposited on top of the first layer.

The case of In has also been analyzed using a similar approach. Fig. 4 shows the chemisorption energy for half a monolayer of In on GaAs(110), as a function of the metal-semiconductor distance. Two cases are shown: in fig. 4a, In is deposited on the long-bridge position, while in fig. 4b, Indium is located on the Ga dangling bond. In both figures, the chemisorption energy is split into the five terms given above: EE, XC, HE, KE and CE. The long-bridge position yields the maximum chemisorption energy: 1.9 eV, similar to (although a little smaller than) the Al case. For the Ga dangling-bond site we find a chemisorption energy of 0.8 eV, smaller than the Al case too. The different components of the total energy show a behaviour quite similar to the one found previously for Al.

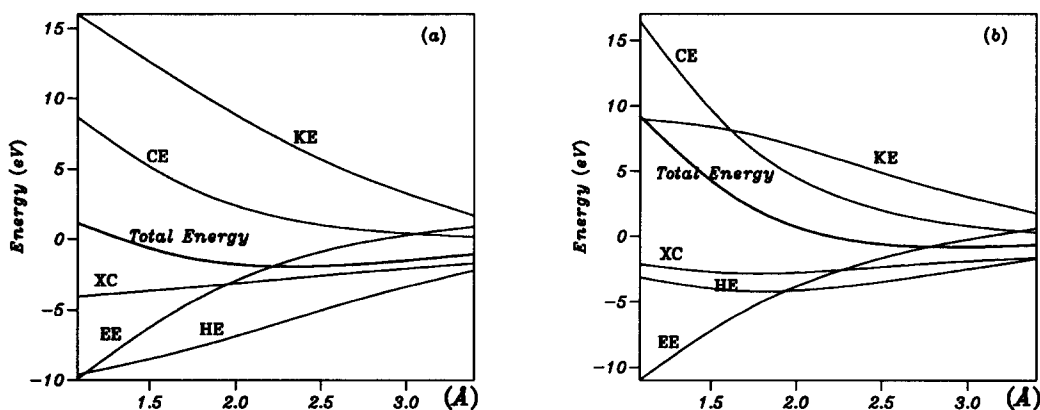


Figure 4: The same as fig. 2a for the deposition of $\theta = 1/2$ In-atoms; (a) on the long-bridge position and (b) on the Ga-dangling bond.

The case of an In-monolayer is, however, very different from the Al-case. The main reason comes from the different atomic size. In-atoms are larger than Al ones, and the geometry found for the Al monolayer is not favourable for the In-case. Fig. 5 shows the chemisorption energy of an In-monolayer as calculated in the following way: half a monolayer of In is kept fixed at the atom sites given by the maximum of the chemisorption energy calculated in fig. 4a (the long-bridge position); then we allow the other atom to relax in the direction perpendicular to the interface at the center position of the first Indium atoms. The maximum energy is obtained with the second half-monolayer of Indium relaxed ~ 2.4 Å away from the first layer. In fig. 5 we see how the second half-monolayer of Indium is repelled by the first one when we try to approach the second half-monolayer to the semiconductor surface.

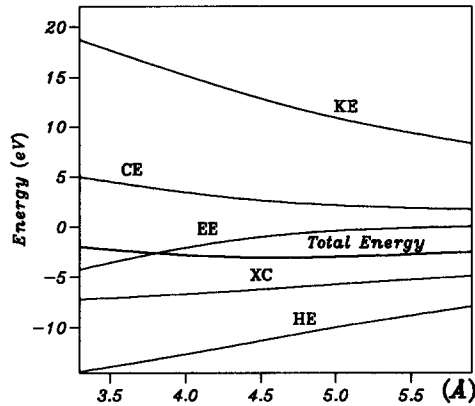


Figure 5: Different contributions to the total energy for the chemisorption of the In-monolayer.

These results have important implications for the Schottky barrier formation. For In, we find that the metal atoms do not attract each other on the GaAs(110) surface, as found for the Al case. This suggests that the interface formation should proceed in a different way. In particular, we can expect that the In atoms tend to form, for very low coverages, small islands and be at the same time isolated. For a coverage close to half a monolayer, we can expect the In atoms to form the geometry found above, i.e., with the atoms in the long-bridge position. The important point is that, for this coverage, the electron density of states induced by the metal shows a surface

band near the semiconductor CNL [28], very much in similarity with the alkali atoms case [20, 21]. The point now is to realize how this density of states is related to the Schottky barrier formation.

In the simplest approximation, we shall neglect the electron correlation effects associated with the metal induced surface band. This point will be discussed later on [29]. For the time being let us neglect these effects, and analyze the Schottky barrier formation as associated with the density of states induced by the metal deposition. Fig. 6 shows the interface Fermi level for $\theta = \frac{1}{2}$ as a function of the distance between the In layer and the semiconductor. In this figure we show different curves corresponding to the In-atom located on the long-bridge position, the As and the Ga sites. We also show the average, $\langle \phi_{bp} \rangle$, of the different Schottky barriers. What is important to notice is the different values of the Schottky barrier we have obtained for the different geometries. This shows that the metal induced interface states are not pinning the Fermi energy at a fixed level. On the contrary, we find important differences for different geometries. These specific Fermi energies are related to the *extrinsic* CNL that appears associated with a specific geometry and a chemical environment. We can define, however, the *intrinsic* CNL as the average of the different *extrinsic* levels found for each geometry [10].

Fig. 6 shows that the intrinsic level, $\langle \phi_{bp} \rangle$ is $\sim 0.65 \text{ eV} \pm 0.05 \text{ eV}$, in good agreement with the results found for the alkali atoms [10, 21]. The specific value we find for half a monolayer of In deposited on GaAs(110) is, however, $\phi_{bp} = 0.49 \text{ eV}$ (for the long-bridge position), a little smaller than the intrinsic CNL.

Finally, we turn our attention to the electron correlation effects that can be expected to appear in the narrow band induced in the semiconductor energy gap. Our discussion is going to be based on previous publications for alkali atoms deposited on GaAs(110) [10, 29]. The important point to realize is the similarity between In and the alkali atoms. In both cases, the atomic size is so large that the deposition of the first metal layer is saturated with only half a ML. We find that this amount of the metal deposited on the semiconductor induces a narrow band in the semiconductor energy gap, close to the CNL. In both cases, we also find that electron correlation effects are very important, the reason being that the effective intrasite Coulomb interaction associated with the induced interface band is much larger than its bandwidth. Correlation effects introduce important modifications in the metal induced density of states. As regards the density of states induced in the semiconductor energy gap what happens is the following: the metal induced band is strongly narrowed to a Kondo-like peak located at the same position as the center of gravity of the initial interface states. Typically, correlation effects are so strong that the one-electron

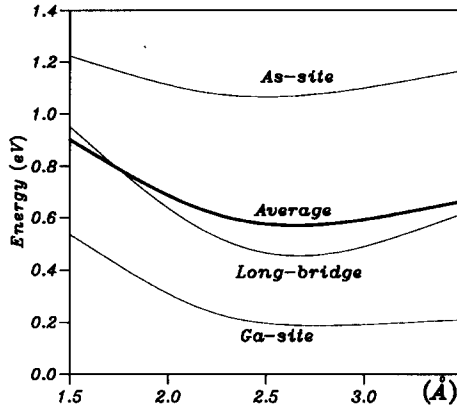


Figure 6: Evolution of the Fermi level as a function of the distance of the In layer to the semiconductor surface, for $\theta = 1/2$. The different curves correspond to the chemisorption sites of fig. 1. We also show a value calculated taking the average of the different curves.

density of states having a width of 0.5 eV is reduced to a Kondo-like peak having a linewidth of 30 meV or even less. Although this peak has not yet been observed, there is strong indirect evidence suggesting that there is an important density of states pinning the Fermi level [12, 11] for half a monolayer, for the cases of In and alkali atoms: in our interpretation, this density of states is associated with the Kondo-like peak appearing at the Fermi level.

It must be also emphasized that some of the one-electron results discussed above for In are independent of the correlation effects we have already discussed. In particular, the interface Fermi level position as shown in fig. 6 for $\theta = 1/2$ is independent of those effects: this is basically related to the 1/2-occupancy of the surface band induced around the CNL.

4 Conclusions

We have presented some chemisorption properties for Al and In on GaAs(110), in order to understand the mechanism associated to the Schottky barrier formation of these interfaces. Our results show a completely different mechanism for both cases. For Al, we find a strong attraction between the Al-atoms, this result suggesting that the Al-atoms have a strong tendency to form

layer of Al-atoms. This geometry creates an interface density of electron states still showing a semiconductor gap. Then, the Schottky barrier can be only formed by a further deposition of Al, when a second layer starts to be deposited on the semiconductor (we should stress that this clusterization can be started for a rather small deposition, less than a monolayer, due to the strong attraction between Al-atoms).

The case of In differs by its large atomic size. We find that the first In-layer is saturated for half a monolayer. This case is similar to the alkali atoms, and the Schottky barrier evolution for In deposited on GaAs should resemble very much the alkali atoms case. This implies that the Schottky barrier will be practically formed for $\theta = 1/2$, with a Kondo-like peak pinning the Fermi level. The interface Fermi level for In is found, however, a little lower, $\sim 0.1-0.2$ eV, than those calculated for the alkali atoms: this reflects the different chemistry and electronegativity of In, that tends to pull down the interface Fermi level. In this regards, it is also worth mentioning that In is found to chemisorb on the long-bridge position while the alkali atoms seem to prefer the Ga dangling bond position.

Acknowledgements

This theoretical work has been partially funded by the Comisión Interministerial de Ciencia y Tecnología (SPAIN) under contracts PB-89-0165 and MAT-88-0544, and the CEE under contract SC1-CT 91-0691.

References

- [1] E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts* (Oxford University Press, 1988 2nd Edition)
- [2] W. Mönch, *Rep. Prog. Phys.*, **53**, 221 (1990)
- [3] F.Flores and C.Tejedor, *J. Phys. C*, **20**, 145 (1987)
- [4] W.E.Spicer, P.W.Chye, P.R.Skeath y I.Lindau, *J. Vac. Sci. Technol.*, **16**, 1422 (1979);
W.E.Spicer, I.Lindau, P.Skeath, C.Y.Su y P.Chye, *Phys. Rev. Lett.*, **44**, 420 (1980)
- [5] V.Heine, *Phys. Rev.* , **138**, 1689 (1965)

- [6] C.Tejedor, F.Flores and E.Louis, *J. Phys. C*, **10**, 2163 (1977)
- [7] J.Tersoff, *Phys. Rev. Lett.*, **30**, 4874 (1984)
- [8] F.Flores, A. Muñoz and J. C. Duran, *Appl.Surf.Sci.*, **41/42**, 144 (1989)
- [9] J. D. Dow and R. E. Allen, *J. Vac. Sci. Technol.*, **20**, 659 (1982)
- [10] F.Flores y J.Ortega, *Appl. Surf. Sci.*, **56-58**, 301 (1992)
- [11] M.Prietsch, M. Domke, C. Laubschat and G. Kaindl, *Phys. Rev. Lett.*, **60**, 436 (1988);
M.Prietsch, M. Domke, C. Laubschat, T. Mandel, C. Xue and G. Kaindl, *Z. Phys. B*, **74**,
21 (1989)
- [12] W.E. Spicer, *Appl. Surface Sci.*, **41/42**, 1 (1989); T.Kendelewicz, P.Soukiassian, M. H.
Bahshi, Z. Hurych, I. Lindau and W.E. Spicer, *Phys. Rev. B*, **38**, 7568 (1988)
- [13] K.Stiles, A.Khan, D.G.Kilday and G.Margaritondo, *J. Vac. Sci. Technol. B*, **5**, 987 (1987);
K.Stiles and A.Kahn, *Phys. Rev. Lett.*, **60**, 440 (1988)
- [14] W.Mönch, *Europhys. Lett.*, **63**, 275 (1988)
- [15] I.Lefebvre, M.Lannoo and G.Allan, *Europhys. Lett.*, **10**, 359 (1989)
- [16] C.Y. Fong, L.H.Yang and I.P.Batra, *Phys. Rev. B*, **40**, 6120 (1989)
- [17] J.Hebenstreit, M.Heineman and M.Scheffler, *Phys. Rev. Lett.* , **67**, 1031 (1991)
- [18] J.Pollmann, P.Krüger and M.Mazur , *App. Surf. Sci.*, **56-58**, 193 (1992)
- [19] Jae-Yel Yi and J.Bernholc, *Phys. Rev. Lett.*, **69**, 486 (1992)
- [20] J.Ortega and F.Flores, *Phys. Rev. Lett.*, **63**, 2500 (1989)
- [21] J. Ortega, R. Pérez, F.J.García-Vidal and F.Flores, *Appl. Surf. Sci.*, **56-58**, 264 (1992)
- [22] F.J.García-Vidal, A. Martín-Rodero, F. Flores , J. Ortega, and R. Pérez , *Phys. Rev. B*, **44**
11412 (1991)
- [23] P.O.Löwdin, *J. Chem. Phys.*, **18**, 365 (1950)

- [24] F.Flores, A.Martín-Rodero, E.C. Goldberg y J.C. Durán, *Il Nuovo Cimento*, **10**, 303 (1988)
- [25] E.C.Goldberg, A.Martín-Rodero, R.Monreal y F.Flores, *Phys. Rev. B*, **39**, 5684 (1989)
- [26] P. Vogl, P. Hjalmanson and J. D. Dow, *J. Phys. Chem. Solids*, **44**, 365 (1983)
- [27] J.Ortega, R.Rincón, F.J.García-Vidal, R.Pérez and F.Flores, *Appl. Surf. Sci.*, **60/61**, 736 (1992); J.Ortega, F.J.García-Vidal, R.Pérez, R.Rincón, F.Flores, C.Coluzza, F.Gozzo, G.Margaritondo, Y. Hwu, L. Lozzi and S. La Rosa, *Phys. Rev. B*, **46**, 10277 (1992)
- [28] J.Ortega, R.Rincón, F.J.García-Vidal and F.Flores, *Appl. Surf. Sci.*, to be published
- [29] F.Flores and J.Ortega, *Europhys. Lett.* **17**, 619 (1992)