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Schottky barrier formation: Al deposition on GaAs(110)

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The Schottky barrier formation for Al on GaAs(110) has been analysed as a function of the metal coverage. For different Al coverages we have calculated the most stable geometries using a consistent free-parameter LCAO method. Our results show that for an Al monolayer, no density of states appears near the semiconductor charge neutrality level. The Fermi level is, however, pinned, and the Schottky barrier completely formed, for a coverage of two metal monolayers. For this limit we recover the intrinsic metal states model and find good agreement with the Schottky barrier height for thick metal layers.

1. Introduction

One of the main experimental facts, recently obtained in the field of Schottky barrier formation, is the evolution of Schottky barrier height as a function of the metal coverage deposited on a semiconductor [1-3]. Typically, for III-V semiconductors, the free surface shows no Fermi level pinning; the metal deposition introduces a quick evolution on the interface Fermi energy that is eventually pinned by a high density of states induced in the semiconductor gap by 1 or 2 metal monolayers. Those results have supplied important information as regards the mechanisms controlling Schottky barrier formation.

These results have also stimulated theoretical work [4-6] 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. Much work [3,6,7] has been recently performed on the deposition of alkali metals on GaAs(110); this is a case that presents some particular advantages, because the metal atoms are very large and do not seem to diffuse into the semiconductor. The Schottky barrier formation appears to be controlled in that case by a competition between the formation of a conventional conduction band that induces a strong density of states in the semiconductor energy gap, and typical electron correlation effects that tend to open a gap inside the metal conduction band (for low metal coverage), reducing the density of states induced by the metal in the semiconductor gap.

The aim of the present communication is to analyze the deposition of Al on GaAs(110) in the submonolayer and the overlayer regimes. Chemisorption properties, Fermi energies and barrier heights are analyzed as a function of the metal coverage. Our analysis tries to elucidate how the Schottky barrier depends on the Al coverage, comparing with the results for the alkali metals case. We will discuss the main differences and similarities between both cases.

Let us mention that the deposition of Al on GaAs is complicated by an exchange reaction whereby Al replaces Ga in the last semiconductor layers. This reaction appears at room temperature, but it is inhibited at very low temperature. Our theoretical work assumes we are in this low temperature limit, and only considers how Al chemisorbes when it is deposited on the semiconductor. Even with this assumption, the problem is far from being a simple task; we will analyse different adsorption sites and look for the geometry having the lowest energy.

The rest of the paper is organized as follows: in section 2 we present a summary of our method

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of calculation, in section 3 we discuss our main results, and in section 4 we present our main conclusions.

2. Model and method of calculation

The electronic structure of GaAs is described using an LCAO model with sp^3s^* hybrids and interactions discussed by Vogl et al. [8]. The interaction between the Al atoms and between Al and the substrate is analyzed by means of an LCAO method [9] 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 [9]: 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

$$T_{ij} = \gamma T_{ij}^{B}, \tag{1}$$

$$T_{ij}^{B} = \frac{h}{2m}\int\left(\psi_i\bar{\nabla}\psi_j - \psi_j\bar{\nabla}\psi_i\right)\bar{n}\ \mathrm{d}s, \tag{2}$$

where γ is typically around 1.3–1.5, a parameter that can be calculated exactly [9].

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:

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

where E_i and E_j are the mean levels of the ith and jth orbitals.

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

$$\hat{H}^{\mathrm{mb}} = \sum_i U_i^{(0)}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \tfrac{1}{2}\sum_{i\neq j,\sigma} J_{ij}^{(0)}\hat{n}_{i\sigma}\hat{n}_{j\bar{\sigma}} + \tfrac{1}{2}\sum_{i\neq j,\sigma} \tilde{J}_{ij}^{(0)}\hat{n}_{i\sigma}\hat{n}_{j\sigma}, \tag{4}$$

where $U_i^{(0)}$ and $J_{ij}^{(0)}$ are the intrasite and intersite bare Coulomb interactions, respectively, and $\tilde{J}_{ij}^{(0)}$ is an effective [9] intersite Coulomb interaction given by:

$$\tilde{J}_{ij}^{(0)} = J_{ij}^{(0)}\left(1 + S_{ij}^2\right) - J_{x,ij}^{(0)}, \tag{5}$$

where $J_{x,ij}^{(0)}$ is the exchange integral between the ith and jth orbitals.

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 suplemented by a Slater-like potential, $V_{x,i\sigma}$. Thus, we replace the Hamiltonian (4) by the following mean-field Hamiltonian:

$$\hat{H}_{\mathrm{eff}}^{\mathrm{mb}} = \sum_i U_i^{(0)}\hat{n}_{i\sigma}\langle\hat{n}_{i\bar{\sigma}}\rangle + \sum_{j\neq i,\sigma} J_{ij}^{(0)}\hat{n}_{i\sigma}\langle\hat{n}_{j\bar{\sigma}}\rangle + \sum_{j\neq i,\sigma} \tilde{J}_{ij}^{(0)}\hat{n}_{i\sigma}\langle\hat{n}_{j\sigma}\rangle + \sum_{i\sigma}\alpha V_{x,i\sigma}\hat{n}_{i\sigma}, \tag{6}$$

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 $g_\sigma(i, j)$ given by

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

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

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

In eq. (6), α is taken to be $\frac{7}{4}$: this is shown [9] to include *interatomic* correlation effects. This implies neglecting *intra-atomic* correlation effects which could be, however, included by using a perturbative approach [10].

In our actual calculation we have solved the LCAO mean-field Hamiltonian using conventional Green-function techniques [11]. 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 atom.

Let us finally comment that, in general, the semiconductor surface is not allowed to relax. Different theoretical calculations have shown [12,13] that Al tends to eliminate very efficiently the surface relaxation appearing at a free semi-

conductor surface. Thus, in all our results, the chemisorption energy of different overlayers is referred to the semiconductor unrelaxed surface.

3. Results

We have analyzed the geometries associated with different Al coverages. We have considered three different cases: half a monolayer, a monolayer, and two monolayers. (Here, one ML is defined as two Al atoms per semiconductor surface cell). For each case, we have looked for the most stable geometry.

3.1. Half a monolayer

Fig. 1 shows the two most energetic geometries. In one case, the Al atoms are bonded to As, while in the second case, Al is bonded simultaneously to As and Ga, occupying the mid-point of the largest bridge distance between the cation and the anion. Although the bridge position seems to be the most energetic geometry, we only find small differences with the As-bonded one.

Fig. 1 also shows the chemisorption energy for each case, as a function of the distance between the Al layer and the last semiconductor layer. The minimum of the interaction potential yields the following chemisorption energies per adsorbed atom:

E_{chem}(As bonded) = −1.8 eV,

E_{chem}(bridge) = −2.1 eV.

We should also mention that for Al bonded to Ga we find the following chemisorption energy:

E_{chem}(Ga bonded) = −1.0 eV.

3.2. The monolayer case

In this case we have two Al atoms per surface unit cell. We have explored different geometries and have found that the most favourable geometries correspond to the following cases: (a) the Al atom bonded to As and Ga (see fig. 2); (b) the Al atom bonded to Ga, and the other atom located on top of As. These cases yield the following chemisorption energies:

(a) $E_{chem} = -5.3$ eV,

(b) $E_{chem} = -4.3$ eV.

It is interesting to mention that the total chemisorption energy we find for the most stable

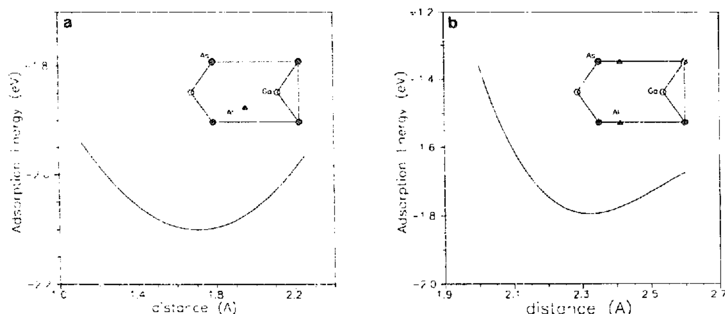

Fig. 1. Chemisorption energy for half a monolayer of Al on GaAs as a function of the metal distance to the last semiconductor layer (in Å): (a) bridge position, (b) As-position. The insets show the corresponding geometries.

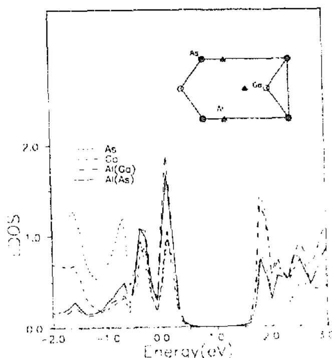

Fig. 2. Local density of states (LDOS) on the metal atoms bonded to Ga and As, and on the cation and the anion of the last semiconductor layer, for the monolayer case shown in the inset. This case corresponds to the most stable Al monolayer geometry. $E = 0$ is the top of the semiconductor valence band.

geometry of the monolayer, is larger than the sum of the chemisorption energies calculated independently for the cases of half a monolayer of Al bonded to either As or Ga. This yields 2.8 eV, showing that the Al atoms atract each other tending to form clusters on the GaAs(110) surface. Even the most stable monolayer case yields a more favourable geometrical configuration than having two Al atoms chemisorbed on the bridge positions.

Fig. 2 shows the geometry of case (a), and the local density of states projected on the two Al atoms and the As and Ga atoms of the last semiconductor layer. Let us comment these results, in the perspective of other theoretical approaches [12] and some experimental evidence [14]. First of all, let us mention that the results that we already have presented for the geometries of half and one monolayers are in good agreement with other results [12] obtained using an LDA method. In particular, the LDA calculation has also obtained the long-bridge position and the Ga and As dangling bonds positions as the most favourable geometries for half a monolayer and one monolayer, respectively. This good agreement between the two different theoretical approaches is very satisfactory, because recently some experimental STM results [14] have suggested that Al adsorbed on GaAs should be located on top of Ga. This conclusion is drawn from the different spots that STM images show for positive and negative biases: basically, these images show that for both biases, brighter spots appear on Ga. In order to see whether these results are compatible with the most stable geometry calculated by the theoretical results, we have shown the different local density of states of an Al monolayer in fig. 2. The important results one can draw from this figure are the following: (a) The unoccupied states located just above the energy gap have mainly a Ga character; in particular the Al bonded to Ga presents also a larger weight in this part of the electronic spectrum. (b) The occupied states located below the energy gap have as much weight on Ga as on As, if not a little more.

This implies that the local states distributed around the energy gap present a strong Ga character; thus, these theoretical data seem to explain the STM results, resolving the apparent contradiction between the most stable Al monolayer as calculated here and in ref. [12], and the STM results of ref. [14]. It is also of interest to mention that the density of states shown in fig. 2 presents an energy gap of around 1.2 eV, in good agreement with the value of 1.0 eV obtained by Suzuki and Fukuda [14] using the scanning tunneling microscope.

3.3. The two-monolayer case

From the point of view of the Schottky barrier formation, one is interested in knowing how the Fermi level is pinned by the electron density of states created in the semiconductor gap. For the monolayer case, we have found that the induced density of states presents an energy gap, around 1.2 eV wide. The crucial point is to know how this gap is closed with further deposition of the metal. This has prompted us to analyze the two-

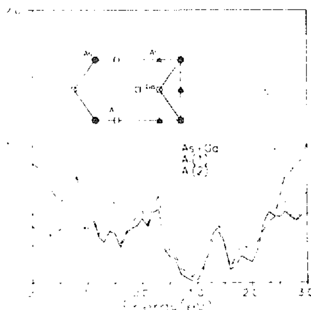

Fig. 3. Local density of states (LDOS) on the two metal layers and the last semiconductor layer for two Al monolayers deposited on GaAs(110). The second Al monolayer is 2.4 Å above the first metal monolayer.

monolayer case. Fig. 3 shows the geometry of the Al overlayer we have considered; distances between the second Al layer and the other atoms have been calculated by maximizing the chemisorption energy. We should comment that this geometry has not been minimized, however, with respect to many other geometrical configurations of the second Al layer. The symmetry of the first layer suggests to use the geometry drawn in fig. 3, since in this case the new Al atoms are directly bonded to a high number of Al atoms located in the first layer. Fig. 3 also shows the local density of states we have calculated for the two-monolayer case, projected onto the different metal layers and the last semiconductor layer. The important point to notice is that the new interaction introduced by the second Al monolayer has closed the gap appearing for the monolayer case. At the same time, we find that the Fermi energy is pinned at 0.6 eV above the semiconductor valence band top. All these results show a good agreement with the behaviour of the GaAs(110)/Al interface for low metal coverage [2]. For a free semiconductor surface initially the Fermi level is not pinned by any electron density of states; at very low metal coverage, we expect to have a few islands with a monolayer height, and then we should find the electron density of states shown in fig. 2. Thus the n- and p-doped semiconductor Fermi levels at the interface would approach each other, but still differing significantly. Then, for a further coverage, Al clusters start to grow and as soon as a second layer of the cluster is formed, the local Fermi energy is going to be pinned by a high density of states. A macroscopic region will present Fermi level pinning if the whole surface is covered by Al; this is related, however, to how the Al atoms grow on the GaAs surface. What is important to realize is that the Fermi energy given by our calculation for two monolayers, should practically coincide with the thick metal overlayer since the barrier height depends only very slightly on the metal coverage [15], once we have created an important density of states in the semiconductor gap. Now, comparing our calculated Fermi level with the experimental one [2], we find quite a good agreement, giving further support to the results presented in this paper.

4. Concluding remarks

The aim of this paper has been to understand the Schottky barrier formation in the case of Al deposition on GaAs(110). It has been established that this barrier formation depends crucially on the interaction between the semiconductor and the first metal layers deposited on the surface [15,16]. These facts have prompted us to analyze the chemisorption energy of the first metal layers deposited on the semiconductor and determining the most favourable geometries. Our results present good agreement with other theoretical results and have been shown to be in agreement with the available experimental evidence. Using the most favourable geometries we have analyzed the Schottky barrier evolution as a function of the coverage. The main conclusion of our analysis is that for an Al monolayer there appears an energy gap around the Fermi energy in the density of states induced by the deposited metal. This explains that for very low Al coverage the Fermi

level cannot be pinned by the intrinsic states that the IDIS model [16,17] would predict to appear around the semiconductor charge neutrality level. Our results also show that for a larger deposition, as soon as a second Al layer is formed (probably, by the formation of Al clusters at the surface), an important density of states is induced by the metal around the semiconductor charge neutrality level. Then, the IDIS model starts to be operative and the interface Fermi level should be located close to that charge neutrality level. This basically implies that the barrier is completely formed, and that no further evolution of the Schottky barrier and the Fermi level would appear for further metal deposition. It should be emphasized that this Schottky barrier evolution is in contrast with what has been found for the alkali atoms [6,7,18]. In this case, the atoms have a large size and for the first monolayer deposition, only one atom is deposited on the semiconductor per unit cell. The monolayer case presents a typical metal density of states around the semiconductor charge neutrality level: it has been argued, however, that metal correlation effects would inhibit the development of that density of states until a further deposition would create the typical metal-induced states [7,18]. For Al, we find a different case: two metal atoms per unit cell are deposited on the semiconductor for the first monolayer. This implies an even number of electrons, and a kind of surface semiconductor electron structure for the first deposited monolayer. The Schottky barrier formation is, then, related to the closing of this gap due to the further deposition of the metal on the semiconductor.

Acknowledgements

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References

[1] K. Stiles, A. Kahn, D.G. Kilday and G. Margaritondo, J. Vac. Sci. Technol. B 5 (1987) 987;
K. Stiles and A. Kahn, Phys. Rev. Lett. 60 (1988) 440.
[2] T. Kendelewicz, P. Soukiassian, M.H. Bahshi, Z. Hurych, I. Lindau and W.E. Spicer, Phys. Rev. B 38 (1988) 7568;
W.E. Spicer, Appl. Surf. Sci. 41/42 (1989) 1.
[3] M. Priestch, M. Danke, C. Laubschat and G. Kaindl, Phys. Rev. Lett. 60 (1988) 436;
M. Priestch, M. Danke, C. Laubschat, T. Mandel, C. Xue and G. Kaindl, Z. Phys. B 74 (1989) 21.
[4] W. Mönch, Europhys. Lett. 63 (1988) 275.
[5] J. Lefebvre, M. Lanoo and G. Allan, Phys. Rev. Lett. 63 (1989) 2500.
[6] J. Ortega and F. Flores, Phys. Rev. Lett. 63 (1989) 2500;
J. Ortega, R. Pérez and F. Flores, Surf. Sci. 251/252 (1991) 442.
[7] T. Maeda Wong, N.J. DiNardo, D. Heskett and E.W. Plummer, Phys. Rev. B 41 (1990) 12372;
N.J. DiNardo, T. Maeda Wong and E.W. Plummer, Phys. Rev. Lett. 65 (1990) 2177.
[8] P. Vogl, P. Hjalmarson and J.D. Dow, J. Phys. Chem. Solids 44 (1983) 365.
[9] E.C. Goldberg, A. Martín-Rodero, R. Monreal and F. Flores, Phys. Rev. B 39 (1989) 5684;
F.J. García-Vidal, A. Martín-Rodero, F. Flores, J. Ortega and R. Pérez, Phys. Rev. B 44 (1991) 11412.
[10] F. Flores and J. Ortega, Europhys. Lett. 17 (1992) 619.
[11] F. Guinea, C. Tejedor, F. Flores and E. Louis, Phys. Rev. B 28 (1983) 4397.
[12] J. Ihm and D. Joannopoulos, Phys. Rev. B 26 (1982) 4429.
[13] S.B. Zhang, M.L. Cohen and S.G. Louie, Phys. Rev. B 34 (1986) 768.
[14] M. Suzuki and T. Fukuda, Phys. Rev. B 44 (1991) 3187.
[15] J. Ortega, J. Sanchez-Dehesa and F. Flores, Phys. Rev. B 37 (1988) 8516.
[16] F. Flores and C. Tejedor, J. Phys. C 20 (1987) 145.
[17] C. Tejedor, F. Flores and E. Louis, J. Phys. C 10 (1977) 2163;
J. Tersoff, Phys. Rev. Lett. 30 (1984) 4874.
[18] J. Ortega, R. Pérez, F.J. García-Vidal and F. Flores, Appl. Surf. Sci. 56–58 (1992) 264.