ELSEVIER

Surface Science 307–309 (1994) 309–314

surface science

Schottky-barrier formation for non-ideal interfaces: As-rich GaAs(110) metal junctions

R. Saiz-Pardo *, R. Rincón, R. Pérez, F. Flores

Departamento de Física de la Materia Condensada C-XII, Facultad de Ciencias, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

(Received 20 August 1993)

Abstract

Schottky barriers have been analyzed theoretically for clean and passivated GaAs(110)-surfaces. Passivation is obtained by the deposition of an As-monolayer on the semiconductor surface. The Schottky-barrier formation is studied for a K-monolayer on the clean and passivated semiconductor surfaces. Our results show that passivation changes dramatically the mechanism of Schottky-barrier formation. These differences are explained by the different states found for the ideal and passivated surfaces. In particular we find that the As-passivation decreases the n-type Schottky barrier for K by 0.6 eV.

1. Introduction

Schottky barriers for ideal abrupt metal–semiconductor interfaces are well understood [1]. The standard metal–semiconductor junction behaviour is controlled basically by the semiconductor dangling-bonds associated with its free surface. Consider a GaAs(110)-surface with a cation and an anion-like dangling bond: the metal–semiconductor interaction is determined by the reactivity between the metal orbitals and the semiconductor surface states; the semiconductor charge neutrality level controlling the Schottky-barrier is the result of the metal interacting more strongly with one of those two dangling bonds [2]. In particular, different metal atoms and different geometries can change the *extrinsic* charge neutrality level and the Schottky barrier [3].

Non-ideal metal–semiconductor interfaces can present a different behaviour if the semiconductor dangling-bond states are dramatically modified by an external agent. In this paper, we have analyzed the effect of having the semiconductor dangling-bond states passivated by an external monolayer deposited between the metal and the semiconductor. The effect of this passivation is to saturate the cation and the anion-like states, leaving behind a surface with a very low tendency to chemical reactivity [4]; this process can be expected to change dramatically the Schottky barrier due to the very different chemical environment the metal atoms will see. We have chosen to analyze the case of an As-monolayer deposited on GaAs(110): other cases like P and Sb present

---

* Corresponding author.

SSDI 0039-6028(93)E0787-U

similar effects, but As represents a very interesting case because it has been suggested [5] that As-clusters between a metal and GaAs might modify the Schottky-barrier formation mechanism found for ideal interfaces.

The rest of the paper is organized as follows: in Section 2 we present a brief summary of the theoretical method used to analyze interface problems. In Section 3, we present our results for the different systems we have considered. In Section 4, we analyze the previous results from the point of view of the Schottky-barrier formation. Conclusions are presented at the end of this section.

2. Method of calculation

We follow a free-parameter LCAO-method [6] supplemented with a density functional approach [7] to analyze the many-body terms appearing in the fundamental Hamiltonian. Our starting point is the LCAO-Hamiltonian:

$$\begin{aligned}\hat{H} = {} & \sum_{i,\sigma} E_i^{\sigma} \hat{n}_{i\sigma} + \sum_{\sigma,(i,j)} T_{ij}^{\sigma} \left(\hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^{\dagger} \hat{c}_{i\sigma} \right) \\ & + \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + \tfrac{1}{2} \sum_{i,j\neq i,\sigma} \left[J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma} \right] \\ & + \sum_i \frac{Z_i Z_j}{d}, \end{aligned} \tag{1}$$

where $U_i^{(0)}$ and $J_{ij}^{(0)}$ are the intra- and inter-orbital Coulomb interactions associated with the atomic orbitals, ψ_i and ψ_j; $\tilde{J}_{ij}^{(0)} = J_{ij}^{(0)} - J_{x,ij}^{(0)} + J_{ij}^{(0)} S_{ij}^2$; $J_{x,ij}^{(0)}$ is the corresponding exchange interaction and $S_{ij} = \langle \psi_i | \psi_j \rangle$. As shown in Ref. [6], the one-electron terms, E_i and T_{ij}, can be obtained from the atomic properties of the ingredients forming the solid. Still, Eq. (1) defines a many-body Hamiltonian that has to be analyzed by using a specific approximation. We have recently [7] introduced a density functional approach to LCAO-Hamiltonians to calculate their electron properties. Basically, we follow a Kohn–Sham approach and define the total energy, E_0, of the system as a functional of the different orbital occupancies, $n_{i\sigma}$. Many-body contributions are given by:

$$\begin{aligned} E^{\text{m.b.}} = {} & \langle \phi_0 | \sum_i U_i^{(0)} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + \tfrac{1}{2} \sum_{i,j\neq i,\sigma} \left[J_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} \hat{n}_{i\sigma} \hat{n}_{j\sigma} \right] | \phi_0 \rangle, \end{aligned} \tag{2}$$

where ϕ_0 is the ground state of the system.

Following Kohn and Sham, we introduce the following local potential:

$$V_{i\sigma}^{\text{m.b.}} = \frac{\partial E^{\text{m.b.}} n_{i\sigma}}{\partial n_{i\sigma}}, \tag{3}$$

that describes the many-body terms in a local approach.

Then, our local Hamiltonian is defined by the following equation:

$$\hat{H}_{\text{eff}} = \hat{H}^{\text{o.e.}} + \sum_i V_i^{\text{m.b.}} \hat{n}_i, \tag{4}$$

the equivalent of the Hamiltonian used in LDA, $\hat{H}^{\text{o.e.}}$ being the one electron terms.

Still, we have to obtain $E^{\text{m.b.}}$ as a function of the different occupation numbers, $n_{i\sigma}$. Details will be published elsewhere [7]. Here, we only mention that $E^{\text{m.b.}}$ can be split into its hartree, E^{H}, and its exchange and correlation, E^{XC}, terms. It can be proved that:

$$\begin{aligned} E^{\text{H}} = {} & \sum_i U_i^{(0)} n_{i\uparrow} n_{i\downarrow} \\ & + \tfrac{1}{2} \sum_{i,j\neq i,\sigma} \left[J_{ij}^{(0)} n_{i\sigma} n_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} n_{i\sigma} n_{j\sigma} \right], \end{aligned} \tag{5}$$

while

$$E^{\text{XC}} = -\tfrac{1}{2} \sum_{i,\sigma} \tilde{J}_i n_{i\sigma} (1 - n_{i\sigma}), \tag{6}$$

where $\tilde{J}_i$ is an average interaction between the $n_{i\sigma}$-charge and its exchange-correlation hole, $(1 - n_{i\sigma})$, spread mainly around the nearest neighbours. Eqs. (3), (5) and (6) define the following local potential:

$$\begin{aligned} V_{i,\sigma}^{\text{m.b.}} = {} & U_i n_{i\bar{\sigma}} + \sum_{j(\neq i)} \left[J_{ij}^{(0)} n_{j\bar{\sigma}} + \tilde{J}_{ij}^{(0)} n_{j\sigma} \right] \\ & + \tilde{J}_i \left(-\tfrac{1}{2} + n_{i\sigma} \right), \end{aligned} \tag{7}$$

where the last term yields the exchange-correlation contribution.

In our approach, we calculate n_i solving Hamiltonian (4), with $V_i^{m.b.}$ given by Eq. (7). Once we determine n_i, the total energy is obtained adding to the one-electron term the many-body contributions given by Eqs. (5) and (6).

In the calculations presented here, instead of attempting a full self-consistent calculation we have parametrized the semiconductor LCAO Hamiltonian using Vogl et al.'s parameters [8], and have applied our method to the calculation of the adsorbate–semiconductor interaction. This yields the different chemisorption energies for As and the metal–As layers, and also the electronic properties of the interface.

We should also mention that the total Hamiltonian has been solved by projecting the whole semiconductor crystal into the last four layers. Then, we solve self-consistently the system formed by those four layers [6] and the different adsorbed species.

3. Results

The method described above has been applied to the calculation of the interaction of different adsorbates and GaAs(110). First of all we discuss the case of an As-monolayer passivating the semiconductor surface. In a second step, we discuss the Schottky-barrier formation for an alkali metal layer deposited on the semiconductor with (and without) the As-monolayer. In our calculations, we look for the most stable geometry obtaining the chemisorption energies for different adsorption sites. For the sake of simplicity, we have neglected the semiconductor surface relaxation and have calculated the chemisorption energy between the adlayer and the unrelaxed GaAs(110)-surface. Relaxation can lower a little the energies calculated for low coverages, but it is not expected to change our results for the coverages discussed in this paper.

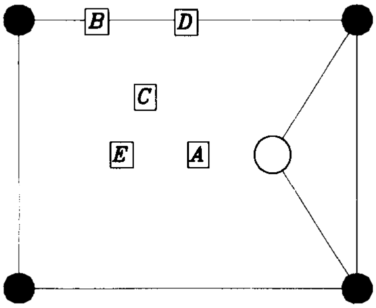

Fig. 1. GaAs(110)-surface geometry showing the different sites for the adsorbate chemisorption we have considered.

3.1. As on GaAs(110)

Fig. 1 shows the GaAs(110)-surface and the different sites we have considered for the adsorption of As. For the case of half a monolayer ($\theta = 1$ means two atoms per unit cell) we have found that the most favourable site for the As-adsorption is the three-fold coordinated position (D in Fig. 1): the chemisorption energy is found to be 3.4 eV.

The monolayer case ($\theta = 1$) has the most favourable energy with the two ad-atoms adsorbed on the two semiconductor dangling-bonds (A and B in Fig. 1). The chemisorption energies per adsorbed atom for this monolayer case are 3.7 eV. Similar energies have been calculated for Sb using LDA approach [10,11]. Notice that this energy roughly corresponds to 1.8 eV per bond, in good agreement with the cohesive energy of semiconductors. Our results show how the As-atoms tend to attract each other forming the rows shown in the inset of Fig. 2. This figure also shows the local density of states on the As-monolayer. The important point to notice about these results is the semiconductor-like structure that appears due to having all the electrons saturating either the bonds between the As-atoms and the semiconductor or filling the As-lone pairs (this implies that the As-monolayer coverage creates a passivated surface).

3.2. K on GaAs(110): clean and passivated surfaces

K-deposition on clean GaAs(110)-surfaces have been analyzed by many authors. Here, we present

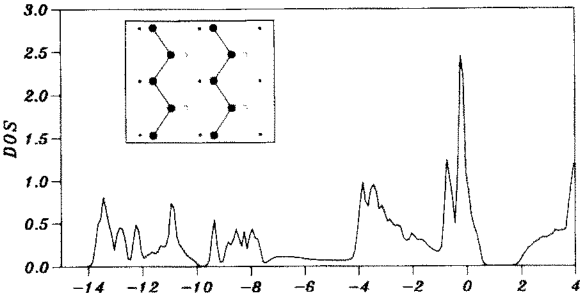

Fig. 2. Local density of states on the As-adatoms. $E = 0$ corresponds to the GaAs valence band top. In the inset, we show the minimum energy configuration for this coverage ($\theta = 1$). Large dark circles represent the As-adatoms. Small circles represent the Ga (open) and As (dark) atoms on the last semiconductor layer.

the results calculated with the full many-body potential discussed above; they will be used for comparison with the passivated surface.

In our calculations, we have found that the most favourable position for the K-adsorption is the three-fold site (D in Fig. 1). This result has been obtained for $\theta = 1/2$, as a full monolayer cannot be accommodated on the semiconductor surface. The adsorption energy is found to be 2.3 eV.

Fig. 3 shows the local density of states on the last semiconductor layer; the Fermi energy is located at 0.53 eV above the valence band top. The important results about this solution are the following: (i) K-atom transfers 0.32 electrons to the semiconductor; (ii) the surface band in the semiconductor energy gap has only 15% K-character, and its main weight comes from the Ga-atoms; (iii) the Fermi level is pinned by the half-occupied surface band created by the interaction between the K-orbitals and the semiconductor Ga-like dangling bonds. We should comment that at this very low coverage, the intrinsic surface band induced by the metal deposition presents important electron correlation effects; a full understanding of the Schottky-barrier formation can only be obtained by analysing in detail those many-body effects associated with the half-occupied surface band. Details have been discussed elsewhere [9]: let us mention that from this theoretical analysis one finds that the Fermi level calculated above in the one-electron calculation represents a good description of the final level defining the Schottky-barrier height.

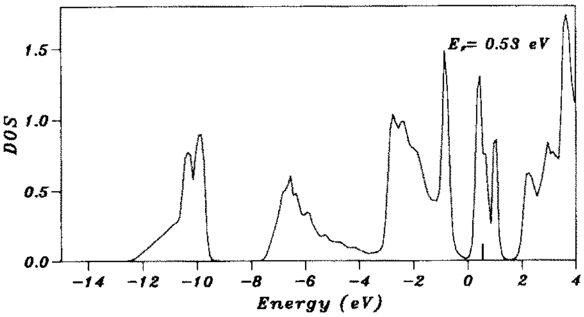

Fig. 3. Local density of states on the last semiconductor layer for a K-adatom per unit cell. The K-site corresponds to the most favourable position: three-fold position, with two Ga-atoms and one As-atom as semiconductor nearest neighbours.

Let us turn our attention to the GaAs–As passivated surface and consider the effect of depositing on it a K-half-monolayer. Our interest is concentrated on understanding how the As-monolayer can change the Schottky-barrier formation.

In our calculations, we have looked for the most favourable adsorption site for K. For the case of $\theta = 1/2$, we have analyzed the four positions shown in the inset of Fig. 4: two sites corresponds to the As-lone pairs of the last layer,

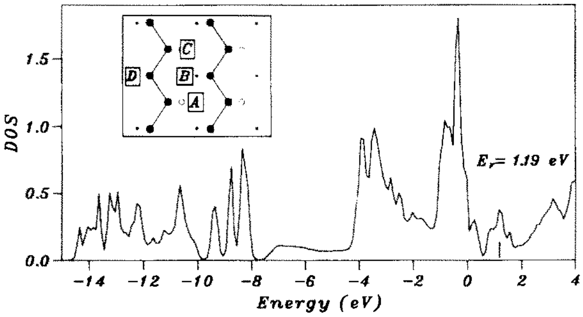

Fig. 4. Local density of states on the As-monolayer for a K-atom per unit cell. In the inset, we represent: (a) the last GaAs(110) layer (small circles represent the Ga (open) and As (dark) atoms on the last semiconductor layer); (b) the As-monolayer (dark large circles); (c) the K-sites we have considered (A,B,C and D).

and the two other sites correspond to different three-fold positions with K-coordinated to three As-atoms. Our calculations yield very similar adsorption energies for the four sites. Our results are the following:

$E_K(A) = 0.72$ eV; $E_K(B) = 0.76$ eV;

$E_K(C) = 0.71$ eV; $E_K(D) = 0.69$ eV;

showing slightly larger energies for the three-fold sites. These results can be understood considering the passivated character of the semiconductor surface. This shows the low tendency to chemical reactivity of the semiconductor surface, and explains that the adsorbed atom has almost the same chemisorbed energy for each surface site. Compare also the adsorption energies for the passivated surface, ~ 0.7 eV, with the value found for the clean semiconductor surface, ~ 2.3 eV. It is also worth remarking that the solution for the passivated surface presents a charge transfer between the metal atom and the surface, completely different to the one found for the clean semiconductor: our results show that this charge transfer is now very small (we find less than 0.06 electrons transferred *from* the semiconductor to the metal atom). Again these results show the low reactivity between the ad-atom and the passivated semiconductor.

Fig. 4 shows the local-density of states in the As-monolayer for K-adsorbed on the B-site (the most energetic configuration). The most important result about this figure is the Fermi level position that is located at 1.19 eV WRT the valence band top. For the other adsorption sites we find the following Fermi energies:

$E_F(A) = 1.27$ eV; $E_F(C) = 1.14$ eV;

$E_F(D) = 1.08$ eV.

All the results show a very similar Fermi level, fluctuating around 1.15 eV, the density of states shown in Fig. 4 being also very similar to the ones found for the other cases.

Compared with the results of the clean surface, we find an important change associated with the Fermi level position and the Schottky-barrier height. Our results show for the passivated semiconductor surface a Fermi level that is located around 0.6 eV higher in energy than the one found for the clean surface. We shall discuss in the next section how we can understand these results using simple physical ideas. Let us mention here that the density of states associated with the surface band shown in Fig. 4 has mainly a K-character.

4. Discussion and conclusions

The main result found above, regarding the Schottky-barrier formation, is that the passivated surface yields a Fermi level pinning upon K-deposition that is much higher in energy (~ 0.6 eV) than the one found for the clean surface. The most simple way to understand these results is by considering the electronic structure for the clean and passivated surfaces and the interaction of these surfaces with the K-layer.

Regarding the clean surface, GaAs(110) shows two surface states: the As-like dangling-bond is occupied and located around the top of the semiconductor valence band top, while the Ga-like dangling-bond is empty and located around the conduction band bottom.

The passivated surface only presents As-lone pairs that are located around the semiconductor valence band top, with an electronic structure similar to the As-like dangling bonds of the clean semiconductor surface.

The deposition of K on GaAs(110) introduces the following effects: (i) For the clean surface, we find the K4s-state above the Ga-like state; the main interaction appears between these two states with the result of having the Ga-like states shifted to lower energies and the K-charge transferred to this intrinsic surface state. This explains why the Fermi energy is found around the semiconductor midgap, and the intrinsic surface band has mainly a Ga-character and is half-occupied. (ii) For the passivated surface, we only find the K4s-state interacting weakly with the As-lone pairs located around the semiconductor valence band top. The result of this weak interaction is that the induced band of Fig. 4 has mainly a K-character and that the surface band is higher in energy than the one found for the clean surface.

In conclusion, the different Schottky-barrier formation and the different Fermi energy levels found for clean and passivated GaAs(110) surfaces are explained by the different surface states one finds for the two initial surfaces. For the clean surface, the two dangling-bond states are controlling the Schottky-barrier formation, the K-deposition inducing a Ga-like intrinsic state in the middle of the semiconductor energy gap. For the passivated surface, the As-lone pairs are responsible of the final Schottky barrier. In this last case, the As-lone pairs are weakly interacting with the K 4s-level, yielding an intrinsic state (having a metal-like character) that is much higher in energy (~ 0.6 eV) than the one found for clean surfaces. One can expect that these arguments have a general validity, with passivated surfaces yielding lower n-type Schottky barriers than clean surfaces.

5. Acknowledgements

Support by the Spanish CICYT (no. PB 92-0168-C) and the CEE (SCI-CT-91-0691) is acknowledged. F.F. also acknowledges financial support by Iberdrola S.A.

6. References

[1] Formation of Semiconductor Interfaces, Eds. P. Perfetti, S.U. Campisano, G. Margaritondo and O. Bissi (North-Holland, Amsterdam, 1992);
F. Flores and J. Ortega, Appl. Surf. Sci. 56–58 (1992) 301.
[2] M. Lanoo et al., in: Metallization and Metal–Semiconductor Interfaces, NATO ASI Series B, Vol. 195 (Plenum, New York, 1989).
[3] F. Flores, A. Muñoz and J.C. Durán, Appl. Surf. Sci. 41/42 (1989) 144.
[4] P. Krüger and J. Pollmann, Phys. Rev. Lett. 64 (1990) 1808.
[5] J.M. Woodall and J.L. Freeouf, J. Vac. Sci. Technol. 21 (1982) 574.
[6] F.J. García-Vidal, A. Martín-Rodero, F. Flores, J. Ortega and R. Pérez, Phys. Rev. B 44 (1991) 11412.
[7] F.J. García-Vidal, R. Pérez, J. Ortega and F. Flores, to be published.
[8] P. Vogl, P. Hjalmarson and J.D. Dow, J. Phys. Chem. Solids 44 (1983) 365.
[9] W.G. Schmidt, B. Wenzien and F. Bechstedt, Proceedings of the 4th International Conference on the Formation of Semiconductor Interfaces, Eds. B. Lengeler and B. Krahl-Urban (1993).
[10] G.P. Srivastava, Phys. Rev. B 46 (1992) 7300.
[11] F. Flores and J. Ortega, Europhys. Lett. 17 (1992) 619.