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Schottky barrier formation between GaAs(110) and alkali metals

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The mechanism responsible of the Schottky barrier formation is analysed by considering a monolayer deposition of Li, Na or K on GaAs(110). These cases are studied by means of a free parameter consistent molecular orbital method. Chemisorption energies, adsorption sites and Schottky barrier heights are calculated and found to be in good agreement with the experimental evidence. Our results tend to give a strong support to the induced density of interface states model.

1. Introduction

A lot of research in the field of Schottky barriers has been directed, in the last two years, to the understanding of the metal–semiconductor barrier formation in the limit of low metal coverages on semiconductors [1–6]. The aim of this research is to clarify the role of the different mechanisms on the pinning of the interface Fermi level.

In general, for the deposition of different metals on GaAs, it is found that the Fermi level evolves as a function of the metal coverage showing a saturation around a monolayer; moreover, the final Fermi level seems to be the same for both n- and p-doped semiconductors [1,2]. For p-type materials, the Fermi level evolution shows an overshoot that seems to be located in the submonolayer regime [1,2].

The link between these results and the different models proposed to explain the Schottky barrier formation is not yet completely clear. Currently Schottky barrier models can be classified into two main groups: (i) In the induced density of interface states (IDIS) model [7–9], the interface Fermi level is controlled by the metal-induced density of states in the semiconductor energy gap. The semiconductor charge neutrality level pins the Fermi level. (ii) In the defect model [10–12], the Schottky barrier is determined by the different kind of defects created by the deposition of the metal on the semiconductor. In order to elucidate which is the appropriate model in the low coverage regime, it is necessary to analyse theoretically the different systems under current experimental investigation [3–5].

The aim of this work is to study, within this perspective, the electronic properties associated with the deposition of a monolayer of Li, Na and K on GaAs(110). In a previous communication [5] we have discussed the case of a monolayer and half a monolayer of K on GaAs(110). In that work we have analysed the evolution of the Schottky barrier with the metal coverage. In the present work, by changing the metal adatom, we analyse how the Schottky barrier depends on the metal deposited on the semiconductor. It has been suggested that the barrier height might depend slightly on the kind of metal deposited on the semiconductor and on its adsorption site at the surface [13]. Our analysis tries to elucidate this point; with this aim, we have also analysed the chemisorption energy of the adsorbed atom and the interface Fermi level as a function of the adsorption site.

In our theoretical analysis we use a consistent molecular orbital theory with no adjustable parameters [14]. All the different parameters of the molecular orbital Hamiltonian are calculated from the basic properties of the atomic con-

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stituents. Our main ingredient is the introduction of a first principles kinetic repulsive energy between the overlapping orbitals of the adsorbate and the substrate allowing us to calculate metal–semiconductor distances and total chemisorption energies.

In section 2 we present our Hamiltonian and our basic approach, while in section 3, we discuss our results and their meaning from the point of view of the Schottky barrier formation.

2. The model and its solution

In our molecular-orbital calculation we start with a given number of orbitals, α, per atom i, $\psi_{i\alpha}$, and introduce the following Hamiltonian:

$$\hat{H} = \sum_{i\alpha\sigma} E_{i\alpha\sigma}\hat{n}_{i\alpha\sigma} + \sum_{i\alpha j\beta\sigma} T_{i\alpha j\beta}\left(\hat{c}^{\dagger}_{i\alpha}\hat{c}_{j\beta} + \hat{c}^{\dagger}_{j\beta}\hat{c}_{i\alpha}\right) + \sum_{i\alpha} U^{(0)}_{i\alpha}\hat{n}_{i\alpha\uparrow}\hat{n}_{i\alpha\downarrow} + \sum_{i\alpha\neq j\beta,\sigma} J^{(0)}_{i\alpha j\beta}\hat{n}_{i\alpha\sigma}\hat{n}_{j\beta\bar{\sigma}} + \sum_{i\alpha\neq j\beta,\sigma}\left(J^{(0)}_{i\alpha j\beta} - J^{(0)}_{x,i\alpha j\beta} + J^{(0)}_{i\alpha j\beta}S^{2}_{i\alpha j\beta}\right)\hat{n}_{i\alpha\sigma}\hat{n}_{j\beta\sigma} + \sum_{j,i\alpha,\sigma} I_{j,i\alpha}\hat{n}_{i\alpha\sigma} + \sum_{i\neq j}\frac{Z_iZ_j}{d_{ij}}, \quad (1)$$

which generalizes the Hamiltonian of ref. [14] to the case of many orbitals. In eq. (1), $T_{i\alpha j\beta}$ is the hopping interaction between orbitals $i\alpha$ and $j\beta$; its value is calculated using the Bardeen tunneling current [15], $T^{\mathrm{B}}_{i\alpha j\beta}$, and introducing the corrections due to the long range of the atomic potentials (details will be published elsewhere). This procedure improves over the previous calculation introduced in ref. [5] and yields much more appropriate hopping interactions.

$U^{(0)}_{i\alpha}$ is the bare intra-atomic Coulomb interaction, $J^{(0)}_{i\alpha j\beta}$ the bare Coulomb interaction between orbitals $\psi_{i\alpha}$ and $\psi_{j\beta}$, $J^{(0)}_{x,i\alpha j\beta}$ the bare exchange interaction between the same orbitals, $I_{j,i\alpha}$ the Coulomb interaction between the jth ion and the $\psi_{i\alpha}$ orbital, and Z_iZ_j/d_{ij} the interaction between ionic charges, Z_i and Z_j. Notice that in Hamiltonian (1), the effective exchange interaction, $J^{(0)}_{x,i\alpha j\beta} - J^{(0)}_{i\alpha j\beta}S^{2}_{i\alpha j\beta}$, appears instead of the bare one $J^{(0)}_{x,i\alpha j\beta}$.

The levels, $E_{i\alpha}$, are given by:

$$E_{i\alpha\sigma} = E^{(0)}_{i\alpha\sigma} + \tfrac{1}{4}\sum_{j\beta} S^{2}_{i\alpha j\beta}\left(\tilde{E}_{i\alpha,\beta} - \tilde{E}_{j\beta,\alpha}\right) - \sum_{j\beta} S_{i\alpha j\beta}T_{i\alpha j\beta}, \quad (2)$$

where

$$\tilde{E}_{i\alpha,\beta} = E^{\mathrm{H}}_{i\alpha} - J^{(0)}_{i\alpha j\beta}\langle n_{j\beta\sigma}\rangle, \quad (3)$$

$E^{\mathrm{H}}_{i\alpha}$ being the Hartree level associated with the $i\alpha$ orbital and $E^{(0)}_{i\alpha}$ the bare atomic orbital energy; the last term of eq. (3) appears because the electron jumping between orbitals $i\alpha$ and $j\beta$ has to find the two orbitals empty. In eq. (2) the term $-\sum_{j\beta}S_{i\alpha j\beta}T_{i\alpha j\beta}$ yields the main contribution to the kinetic repulsive energy between orbitals $\psi_{i\alpha}$ and $\psi_{j\beta}$.

In our calculation we have used the sp^3s^* hybrids of Vogl et al. [16] and the last occupied orbital of the alkali atom. Moreover, the core levels of Ga, As and the alkali metal have also been included in the calculation as we have found that they can introduce non-negligible effects in the total energy of our chemisorbed system.

Hamiltonian (1) has been solved using a Hartree–Fock approximation. For instance, the term $U^{(0)}_{i\alpha}\hat{n}_{i\alpha\uparrow}\hat{n}_{i\alpha\downarrow}$ is replaced by

$$U^{(0)}_{i\alpha}\langle\hat{n}_{i\alpha\uparrow}\rangle\hat{n}_{i\alpha\downarrow} + U^{(0)}_{i\alpha}\langle\hat{n}_{i\alpha\downarrow}\rangle\hat{n}_{i\alpha\uparrow} - U^{(0)}_{i\alpha}\langle\hat{n}_{i\alpha\uparrow}\rangle\langle\hat{n}_{i\alpha\downarrow}\rangle.$$

Correlation effects have also been included in the calculation by replacing the intra-atomic Coulomb interaction in the valence level of the adsorbate, $U^{(0)}_{\mathrm{A}}$, by the reduced interaction $U^{(0)}_{\mathrm{A}} - J^{(0)}_{\mathrm{A}}$, where $J^{(0)}_{\mathrm{A}}$ is the Coulomb interaction between the electrons in the valence states of the alkali atom and the nearest neighbours in the semiconductor; at the same time the alkali atom ionization level is shifted by $J^{(0)}_{\mathrm{A}}\langle\hat{n}_{\mathrm{A}}\rangle$. These modifications, similar to the image effects appearing for the adsorbate levels near metal or semiconductor surfaces, are closely related to the last term of eq. (3), and reflect the correlation associated with the electron jumping between the alkali atom and the semiconductor, due to the hole that the electron leaves behind it.

We should mention that the actual calculation presented here has the following main differences with the one of ref. [5]: (i) First, the hopping interactions, $T_{i\alpha j\beta}$, are calculated with a better accuracy; (ii) the core levels of Ga, As and the alkali atoms have been introduced; (iii) we have chosen to neglect the p-level of the outer shell of the alkali atom since no accurate orbital appears in the conventional tables [17]. Although these changes may introduce differences of around 0.5 eV in the total chemisorbed energy of the adsorbate, the main conclusions of ref. [5] remain unaltered (see below).

In our actual calculation, the total energy of the chemisorbed system is obtained by projecting the Hartree–Fock Hamiltonian into a few layers around the interface. Moreover, consistency has been introduced by means of the electrostatic potential created by the induced charges.

3. Results and discussion

We have analysed the deposition of a monolayer (ML) of Li, Na and K on GaAs(110), moving the ad-atoms along two different chemisorption sites: the adsorbed atoms are located either along the Ga-dangling bonds (site 1) or along the As-dangling bonds (site 2) of the ideal GaAs(110) surface. For the case of Na, we have also analysed positions (3) and (4), which correspond to positions III and IV of fig. 1 in ref. [5]. In our calculation we have assumed the GaAs surface to be unrelaxed and unreconstructed, as seems to be the case even in the submonolayer regime [18].

Fig. 1 shows the chemisorption energy per alkali atom as calculated by moving simultaneously all the alkali atoms in the direction of the ideal GaAs(110) surface dangling bonds. The distances between the alkali layer and the semiconductor surface minimizing the total energy, and their corresponding chemisorption energies, are given in table 1 for the different cases of fig. 1. From table 1 we can obtain the distances between Li, Na or K and the nearest semiconductor atom. At position (1) (the on-Ga site) we obtain 3.0, 3.2 and 3.5 Å, respectively, while at position (2) (the on-As site) the values are slightly smaller: 2.9, 3.1 and 3.4 Å for Li, Na and K, respectively. These values compare well with the sum of covalent radii. The transfer of charge is in all the cases $\sim 0.3e^-$ per

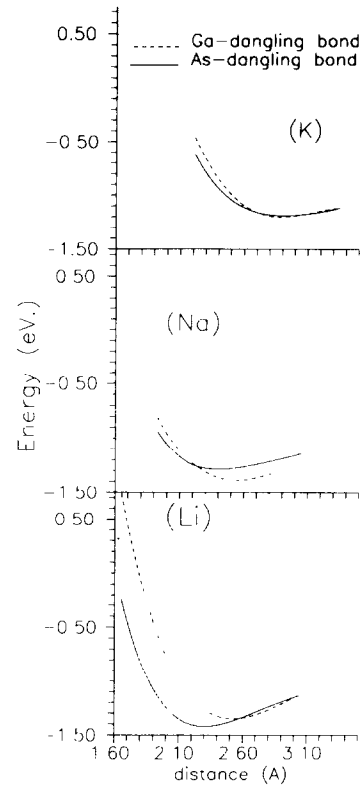

Fig. 1. Chemisorption energy per alkali atom (Li, Na and K) as a function of the distance of the alkali layer to the last GaAs layer. Alkali atoms are moved in the case labelled 1 (2) along the direction of the Ga(As) dangling bond. The zero of energy corresponds to the case of an unrelaxed GaAs(110) surface and isolated alkali atoms.

Table 1
The distances between the alkali layer and the semiconductor surface minimizing the total energy ($d_\perp$), chemisorption energies (E_{Ch}) and interface Fermi levels (E_F) are given for the different alkali atoms and positions considered in the text

Atom	$d_\perp$ (Å)	E_{Ch} (eV)	E_F (eV)
K(1)	2.85	1.19	0.69
K(2)	2.75	1.18	0.69
Na(1)	2.60	1.39	0.65
Na(2)	2.50	1.28	0.80
Li(1)	2.45	1.35	0.63
Li(2)	2.35	1.41	0.89

alkali atom, and goes mainly to the surface Ga atom. We conclude that the bonds at the interface are essentially of covalent character.

As shown in table 1, the chemisorption energies that we find for the alkali atoms on positions (1) and (2) are very similar for a coverage of 1 ML. We have also studied the chemisorption of 1 ML of Na on positions (3) and (4) (see above). In both cases we obtain a chemisorption energy ~ 1.0 eV/atom, which is substantially smaller than those corresponding to positions (1) and (2). We should mention that the case of Na on GaAs(110), as calculated with a self-consistent pseudopotential method [19], shows a different picture to that outlined here: position (3) is found to be the optimum position for the chemisorption of 1 ML of Na, with a chemisorption energy of 2.4 eV and a perpendicular distance of the Na atoms to the semiconductor surface of 1.31 Å (our result is 2.6 Å). The main difference between both theoretical results is the transfer of charge from the alkali layer to the semiconductor surface; while we find a covalent bonding, Fong et al. [19] obtain an ionic one. Experimentally, the chemisorption energy of alkali atoms on semiconductors and metals [20] varies from a value higher than 2 eV for low coverages to around 1 eV for coverages of the order of 1 ML, a value similar to the one found here. Moreover, SEXAFS experiments performed on the K/Si(100)2 × 1 system [21] indicate a K–Si distance equal to the sum of both K and Si covalent radii, showing a covalent bond between the alkali atom and the semiconductor surface as our results suggest.

Fig. 2 shows the local density of states at the GaAs(110) interface layer for the deposition of 1 ML of Na on position (1), compared to the density of states of bulk GaAs. Fig. 2 also shows the local density of states for the Na atoms. The densities of states of the other cases on table 1 are quite similar to that of fig. 2. We find that in all the cases the Fermi level is pinned by an electronic density of states induced in the semiconductor energy gap by the deposition of the alkali atoms. This result would yield a Fermi level almost independent of the semiconductor doping and suggests that the IDIS model is the appropriate one in order to explain the metal–semiconductor barrier formation. We must mention, however, that ultraviolet photoemission spectroscopy (UPS) experiments seem to show no density of states just below the Fermi level on the K/GaAs(110) interface up to coverages of 1 ML [22]; this may be related to the low cross sections of alkali atoms to photoemission. In particular, Nishigaki et al. [23] have shown, by using metastable deexcitation spectroscopy (MDS) for the similar system Cs/Si(111), the existence of occupied valence-band features that are not observed by UPS.

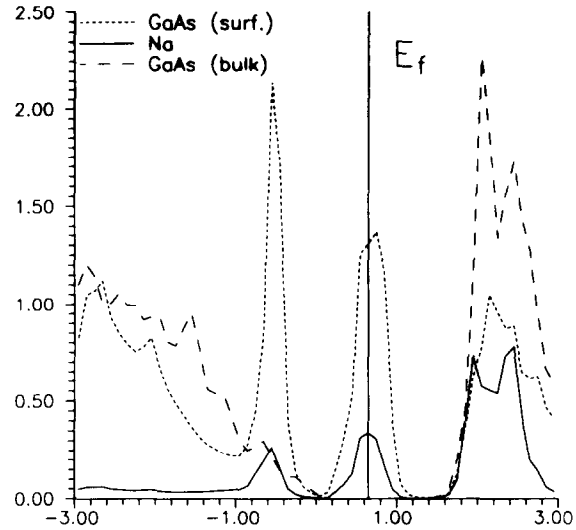

Fig. 2. Local density of states (LDOS) at the GaAs(110) interface layer for the deposition of 1 ML of Na (position 1). The GaAs bulk density of states and the LDOS for Na are also shown. Energies are referenced to the valence band maximum.

The Fermi levels above the valence band maximum (VBM) for the different alkali monolayers are also shown in table 1. For Li and Na a slight dependence of the Fermi level with the geometry of deposition is observed; in the case of Na, the Fermi level above the VBM on position (3) is 0.85 eV, while for position (1) it is 0.65 eV; these changes are in agreement with a suggestion made [13] about the differences between intrinsic and extrinsic charge neutrality levels. However, this dependence is substantially reduced when we go to the case of K. This is mainly due to the bigger size of the K atoms. This almost independence of the Fermi level and chemisorption energy with the

metal site supports the proposal that a physical ML of K, Rb or Cs [6] [2] are not in registry with the substrate, but form incommensurate compact structures which correspond to their bulk metal (110) surfaces.

Different values of the position of the Fermi level above the VBM has been reported experimentally. Prietsch et al. [1] reported 0.53 and 0.55 eV for Na and K, respectively. On the other hand, Kendelewicz et al. [2] give a value of 0.72 eV for K and McLean et al. [24] have given 0.73–0.70 eV for Na. Our results show a fair agreement with these data; notice that taking the most favourable chemisorption site for the adsorbed atoms, we obtain the following interface Fermi levels for Na and K: $E_F(\mathrm{Na}) = 0.65$ eV and $E_F(\mathrm{K}) = 0.69$ eV. These values correspond to the thick layer limit, since the Schottky barrier is practically formed with a metal monolayer [25]. The increasing values that we find for Na and K Fermi energies agree reasonably well with the results of Prietsch et al. [1], suggesting that the interface Fermi level goes to higher energies with increasing metal electropositivity.

In conclusion, our results show a fair agreement with the experimental evidence, and give a strong support to the IDIS model.

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