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GaP–Si band-offset modifications due to alkali metal intralayer deposition

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A *consistent parameter free* LCAO method is used to calculate the electronic properties of different monolayers of Li, Na and K deposited on GaP(110) and Si(110) surfaces, as well as deposited as an intralayer at the GaP–Si(110) interface. Total energies and the most favourable interface geometries are calculated for the different cases. Our results show that the alkali metal intralayer increases the heterojunction band-offset by 0.4 eV. A slight increase in the band-offset is found for more electropositive metal atoms.

1. Introduction

Recent theoretical [1–4] and experimental work [5–9] suggest that heterojunctions band-offsets can be modified by the deposition of a metal (or a semiconductor) intralayer at the interface. The aim of this paper is to present theoretical results for the deposition of a monolayer of Li, Na, K at the GaP–Si(110) heterojunction. This work is part of a general project trying to understand how different metals modify the heterojunction band-offsets in lattice-matched nonpolar surfaces. In particular, we are looking for the dependence of these modifications on the metal electronegativity, atomic sizes, interface geometry, etc.

In our approach we follow a *consistent parameter free* method [10] devised to calculate interface properties without having to resort to phenomenological parameters that only describe the interface very crudely. In section 2, we present a summary of the method used in this work, while in section 3 we discuss our theoretical results. First, we have analysed the two independent semiconductor surfaces with a metal monolayer deposited on them. Next, we have considered the metal intralayer deposited at the heterojunction. Our approach allows us to calculate not only heterojunction barriers but total energies, too, and so the most favourable interface adsorption site for the deposited metal. Finally, in section 4 we present our conclusions from the point of view of the semiconductor interface barrier formation.

2. The method of calculation

The method we follow to analyse the problem is discussed in full detail elsewhere [10]. Let us only mention here the main points used to calculate the interface electronic properties.

In our approach we use a LCAO method with a prescription to calculate the hopping elements between different orbitals and the one-body and many-body contributions to the total energy.

The hopping integrals, T_{ij}, are basically related to the Bardeen tunneling currents [11], T_{ij}^{B} between the corresponding orbitals, ψ_i and ψ_j. Thus:

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

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

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γ is greater than 1 (typically around 1.3–1.5) and can be calculated exactly.

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:

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

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:

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

where $U_i^{(0)}$ and $J_{ij}^{(0)}$ are the intrasite and intersite bare Coulomb interactions, respectively, and $\bar{J}_{ij}^{(0)}$ an effective [10] intersite Coulomb interaction given by:

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

where $J_{x,ij}^{(0)}$ is the exchange integral between the i and j 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 [10]. This means using a mean field approximation supplemented by a Slater-like potential, $V_{x,i\sigma}$. Thus, we replace Hamiltonian (4) by the following mean-field Hamiltonian:

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

$V_{x,i\sigma}$ is related to the exchange pair distribution function $g_\sigma(i,j)$ given by:

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

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

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

In eq. (6), α is taken to be 3/2: this is shown to include interatomic correlation effects [10]. It should be commented that in order to obtain eq. (6) the intra-atomic correlation interaction associated with the term $U_i^{(0)}n_{i\uparrow}n_{i\downarrow}$ has been neglected.

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

We should also comment that the semiconductor surfaces are not allowed to relax. The adsorption energies for different metal monolayers are calculated for different interface geometries by changing the distance between the adatoms and the semiconductor surfaces. Let us comment that this energy is obtained by subtracting from the total energy the energies of the two semiconductor surfaces and the energy of the isolated alkali atoms.

3. Results and discussion

In a first step we have analysed the case of an alkali metal monolayer deposited on either the GaP(110) or the Si(110) surfaces. In our calculations we have assumed the metal atoms to be adsorbed on four different sites, two of them on either the Ga or the P dangling bonds, and the equivalent sites for Si (see refs. [12,13] for the details of the different geometries). The calculated chemisorption energies show that the on-Ga site and the equivalent site for Si, yield the most favourable adsorption positions. Fig. 1 shows, for the most favourable position, the chemisorption energies per alkali atom for a monolayer of K, Na and Li deposited on GaP(110) and Si(110) as a function of the distance between the metal and the semiconductor last layer. It should be commented that the K layer gives less chemisorption

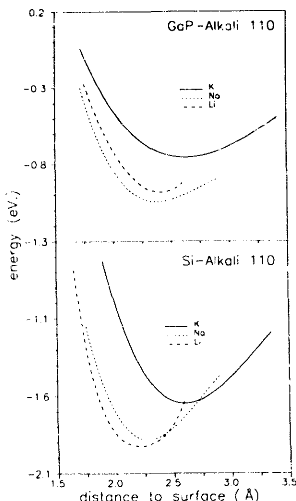

Fig. 1. Chemisorption energy per alkali atom (in eV) as a function of the distance (in Å) of the alkali layer to the last semiconductor layer for both systems Si/alkali and GaP/alkali (110), in the geometry which gives the total energy minimum. In both cases the alkali atoms are placed on dangling bonds (on Ga in GaP/alkali, and on one of the two equivalent Si atoms in Si/alkali), and they are moved along them.

energy than the other metal layers: this is due to the strong overlap between the K s-orbitals of the valence level. When we consider a half-monolayer case, the K layer yields the maximum chemisorption energy [13] as corresponds to a metal having the largest electropositivity. It is also interesting to notice that the chemisorption energies are larger for Si than for GaP (typically 0.8 eV): this is due to the the strong interaction with the half occupied Si surface bonds that are located around the middle of the semiconductor energy gap. Another important difference between the two semiconductors is the density of interface states induced in the semiconductor energy gap. As fig. 2 shows for K on GaP and Si, this density of states is much narrower for GaP, this fact suggesting that electron correlation effects can be important in this particular case. It has been argued elsewhere [14] that these effects are important when the induced interface bandwidth is small compared with the effective intrasite Coulomb interaction associated with the metal adatom. This is the case for GaP, but for Si these correlation effects are negligible. For GaP, we have calculated that these effects increase the chemisorption energy by ~ 0.3 eV. This shows that the chemisorption energies for Si are typi-

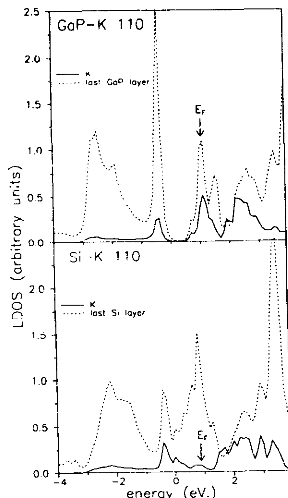

Fig. 2. Local density of states (LDOS) at the K–Si(110) and K–GaP(110) interfaces. The solid lines represent the LDOS at the K atoms, while dashed lines show the LDOS at the last semiconductor layer. E_F indicates the interface Fermi level position. $E = 0$ corresponds, in both cases, to the semiconductor valence band top.

cally only ~ 0.5 eV larger than the ones calculated for GaP.

Fig. 2 also shows the interface Fermi energy for the K case that is found to be: E_F(K – GaP) = 1.0 eV, E_F(K – Si) = 0.8 eV, referred to the corresponding semiconductor valence band top. The high density of states found at E_F for the monolayer case shows that the metal–semiconductor barrier is completely formed for this coverage. Correlation effects tend to reduce the induced density of states associated with the alkali metal–GaP system [14], but the final density of states at the Fermi energy is high enough to pin the Fermi level at the position calculated above.

Next, we analyse the heterojunction case with an alkali metal monolayer deposited at the interface. The metal atoms are bonded to Ga and Si, in the position that we have calculated previously to yield the maximum chemisorption energy. Moreover, we have minimized the interface energy by allowing both adatom–semiconductor distances to change along the direction of the dangling bonds.

Fig. 3 shows the local density of states at the last semiconductor layers and the K layer as calculated for the GaP–K–Si interface at the energy minimum, that has been calculated to yield a chemisorption energy of 1.60 eV, not far from that calculated for the K–Si case. For this minimum, the K–semiconductors distances have been calculated to be: d(K–GaP) = 4.00 Å, d(K–Si) = 3.90 Å, this result showing that the K monolayer has increased its distance to the GaP and Si semiconductors by 0.75 and 0.86 Å, respectively. This is associated with having a K atom sharing its bond with Ga and Si simultaneously.

Comparing the density of states of fig. 3 with the results given in fig. 2 we find an important difference: the reduction in the heterojunction case of the induced density of states at the GaP–semiconductor energy gap. This reflects the effect of Si on the interface density of states: The Si–K bond is stronger than the Si–Ga one, and the metal induced density of states in the GaP layer tends to be reduced. This also explains that the chemisorption energy appears to be very similar to the K–Si(110) case. Let us also mention that the same features appear in the GaP–Na–Si and

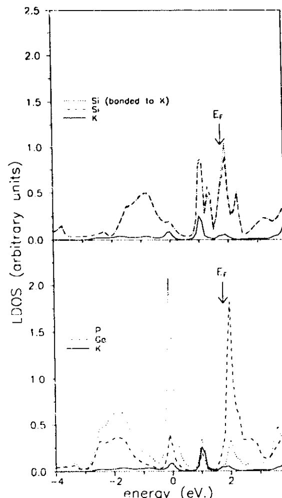

Fig. 3. Local density of states (LDOS) at different atoms in the last semiconductor layers and the K layer in the GaP–K–Si(110) heterojunction. Notice that K (solid line) is shown with both semiconductors. E_F indicates the interface Fermi level position. E = 0 corresponds to the GaP valence band top. The scale is the same as fig. 2 for comparison.

GaP–Li–Si interfaces (details will be published elsewhere).

Next, we discuss the GaP–Si band-offset changes introduced by the metal intralayers. Our results yield the following figures:

$$\Delta E_V(\mathrm{GaP-K-Si}) = 1.14\ \mathrm{eV}$$

$$\Delta E_V(\mathrm{GaP-Na-Si}) = 1.11\ \mathrm{eV},$$

$$\Delta E_V(\mathrm{GaP-Li-Si}) = 1.10\ \mathrm{eV},$$

while for the ideal interface:

$$\Delta E_V(\mathrm{GaP-Si}) = 0.71\ \mathrm{eV}.$$

The conclusion that one can draw from these results is that the band-offset is changed almost

by the same amount by the three metal monolayers, although there appears a slight increase in these changes as we move in the direction Li → Na → K.

4. Concluding remarks

The main conclusion coming out of our calculation is that an alkali metal intralayer introduces significant changes in the GaP–Si(110) interface, increasing ΔE_V by 0.4 eV. The changes found are similar to the ones calculated (with a consistent parameterized tight-binding approach) for the GaP–Cs–Si(110) interface [2], and the physical reason behind it, to be discussed in more detail below, is associated with the behaviour of the extrinsic charge neutrality levels of both semiconductors [1–3]. We should also mention that experimental band-offset changes have been reported for the Cs-intralayer case [7] in GaP–Si(110), although these changes were found a little smaller than the ones calculated here or in ref. [2].

It is also very satisfactory, from the point of view of band-offset engineering, to find slight changes in the calculated band-offsets as a function of the metal electropositivity: More electropositive metal atoms introduce a larger change in the band-offset. Similar results have been found for the Schottky barriers of the alkali atoms on GaAs(110) [15]: The interface Fermi energy has been determined to change by a few thousandths of an eV when going from Na to K, as we find in the actual case for the GaP–Si heterojunction.

The final point we want to address in this paper is related to the saturation values of the band-offset changes when the intralayer thickness is increased, and its relation to the Schottky barriers of each metal–semiconductor interface, namely, the GaP and Si–alkali metal junctions. We have discussed elsewhere [13,14] that alkali atoms yield Schottky interfaces with the Fermi level practically determined by the *intrinsic* charge neutrality level of the semiconductor. Then, one may wonder how the GaP–Si band-offset can be changed with an alkali metal intralayer if each metal–semiconductor interface is completely formed. If this were the case, the GaP–alkali–Si band-offset would be given by aligning the *intrinsic* charge neutrality levels of both semiconductors, and this would yield the band-offset for the ideal GaP–Si junction [16,17]. The point to notice here, in order to understand the results of this paper, is that the induced density of states in the energy gap of GaP for the GaP–alkali metal–Si heterojunction is rather low, substantially lower than the one found for the GaP–alkali metal interface. Comparing figs. 2 and 3 we see this reduction. Due to this fact and to the transfer of charge from the alkali metal layer to the semiconductors (around 0.25 e^- per alkali atom goes to each semiconductor), in GaP the Fermi level is much higher in energy than the charge neutrality level. This means that for our actual case, the band-offset with a metal monolayer is not given by aligning the two semiconductor charge neutrality levels, that are found at almost the same position as in the metal–semiconductor interface. This discussion shows that for an alkali metal monolayer the GaP–metal–Si heterojunction is not yet completely formed. In other words, our results suggest that the band-offset, ΔE_V, for the GaP–Si heterojunction should decrease to values close to 0.7 eV if the alkali metal intralayer is thicker than a monolayer. We are currently investigating the results in ΔE_V of increasing the alkali metal thickness from one to several monolayers.

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