

## A THEORETICAL ANALYSIS OF THE HETEROJUNCTION BAND OFFSETS AS CONTROLLED BY INTRALAYER DEPOSITION

A. MUÑOZ

*Loomis Laboratory of Physics, Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, IL 61801, USA*

*and*

*Departamento de Física Fundamental y Experimental, Universidad de La Laguna, 38204 La Laguna, Tenerife, Spain*

R. PÉREZ, J.C. DURÁN and F. FLORES

*Departamento de Física de la Materia Condensada, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain*

Received 21 June 1988; accepted for publication 4 October 1988

Different heterojunction interfaces have been analysed by means of a self-consistent tight-binding approach. The deposition of different intralayers is found to introduce changes in the band offsets of the heterojunction depending on the intralayer electronegativity. Specific results for GaP–H–Si, GaP–Cs–Si, GaP–Al–Si and ZnSe–Al–Ge are presented. In this last case, we have analysed the effect of having more than one monolayer at the interface: we find that the band-offset modifications are totally induced by a single monolayer.

### 1. Introduction

Recent experimental [1–3] and theoretical [4–6] work seems to confirm that the formation of semiconductor interfaces can be appropriately described by means of the induced density of interface states (IDIS) model [7,8]. The crucial concept introduced in this approach is the semiconductor charge neutrality level, the average of the mid-gaps appearing along the three-dimensional Brillouin zone. The charge neutrality level for each semiconductor defines how the electric charge is transferred across an interface: in particular, in a semiconductor–semiconductor junction electronic charge is transferred from the semiconductor having the higher charge neutrality level to the other one. This transfer of charge induces an important dipole that tends to equalize the charge neutrality levels of both semiconductors. In a zeroth-order approximation the band offset between two semiconductors is determined, within the IDIS model, by aligning their charge neutrality levels.

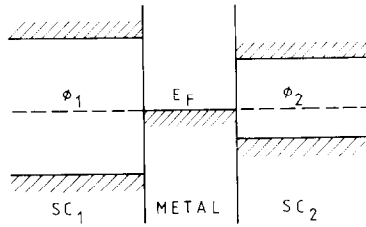


Fig. 1. Semiconductor–metal–semiconductor interface, with the metal Fermi energy and the semiconductor charge neutrality levels aligned to each other.

In a metal–semiconductor interface similar arguments suggest that the Schottky barrier can be obtained by aligning the metal Fermi energy to the semiconductor charge neutrality level.

We should remark that the IDIS model imposes strong restrictions to the possibility of changing or controlling the barrier heights of different interfaces [9]. Fig. 1 shows a hypothetical semiconductor–metal–semiconductor junction: in this particular case, a metal is assumed to be deposited between two semiconductors with the purpose of trying to change the semiconductor–semiconductor band offset. According to the previous discussion, the metal Fermi energy has to be aligned with the two semiconductors charge neutrality levels, and the semiconductor–semiconductor band offset remains unchanged irrespective of the metal deposited at the interface.

We should comment that this result can only be taken as zeroth-order approximation. The purpose of this work is to show that using more accurate calculations one can find small changes (say a few tenths of an electronvolt) in the band offset of two semiconductors, by depositing an adequate intralayer at the interface.

This means that the IDIS model should be taken as a zeroth-order approach which explains in a simple way the physics operating at different interfaces; accurate results can be only obtained, however, by means of more complex calculations. Let us mention that the changes found in this paper with respect to the results of the IDIS model, a few tenths of an electronvolt are small when compared with most of the semiconductor optical gaps: in this respect notice that the charge neutrality level is an average over different optical gaps, typically several electronvolts.

## 2. Theoretical approach

In this work different interfaces have been analyzed using a self-consistent tight-binding approach. In fig. 2 we present the geometry of the GaP–H–Si interface, with a monolayer of H between the two semiconductors.

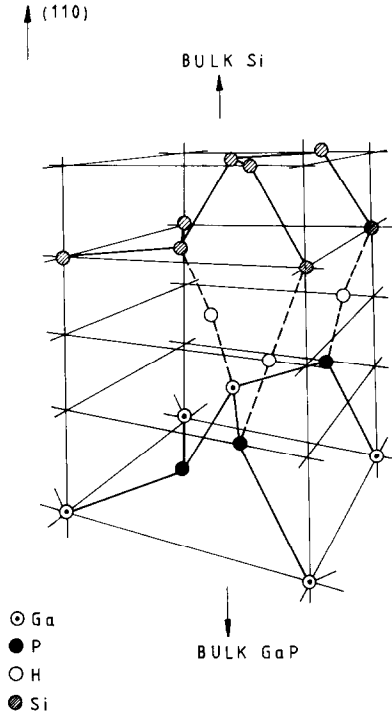


Fig. 2. Geometry of the GaP-H-Si(110) interface.

In our approach [10], we describe the electronic properties of any junction by means of a linear combination (LCAO) of the atomic orbitals,  $\psi_{in}$ , of each atom. We assume  $\psi_{in}$  and its eigenvalue,  $E_{in}$ , in the corresponding atom to be known. Starting with this basis, one can use a LCAO approach and show [10] that the effective tight-binding Hamiltonian associated with the crystal built up from the single atoms is defined by the following parameters:

$$(H_{\text{eff}})_{\alpha\alpha} = E_{\alpha} + \frac{1}{4} \sum_{\beta} (S_{\alpha\beta})^2 (E_{\alpha} - E_{\beta}) - S_{\alpha\beta} T_{\alpha\beta}, \tag{1a}$$

$$(H_{\text{eff}})_{\alpha\beta} = T_{\alpha\beta}, \tag{1b}$$

where  $\alpha = (i, n)$ ,  $S_{\alpha\beta} = \langle \psi_{\alpha} | \psi_{\beta} \rangle$  and

$$T_{\alpha\beta} = -\frac{1}{2} \gamma \int_{\sigma_{\alpha\beta}} (\psi_{\alpha} \nabla \psi_{\beta}^* - \psi_{\beta} \nabla \psi_{\alpha}^*) dS, \tag{2}$$

where  $\sigma_{\alpha\beta}$  is a surface splitting the whole volume,  $\Omega$ , into two subspaces  $\Omega_i$  and  $\Omega_{i'}$ , such that the following condition is satisfied:

$$\int_{\Omega_i} \psi_{in} \psi_{i'n'}^* d\mathbf{r} = \int_{\Omega_{i'}} \psi_{in} \psi_{i'n'}^* d\mathbf{r} = \frac{1}{2} \int_{\Omega} \psi_{in} \psi_{i'n'}^* d\mathbf{r} = \frac{1}{2} S_{in, i'n'}. \tag{3}$$

In eq. (2)  $\gamma$  is a factor associated with the long-range behaviour of the atomic potentials, that can be chosen in most cases around 1.4 [10].

Eqs. (1) and (2) yield the parameters of the tight-binding Hamiltonian as a function of the atomic constituents. In our approach, instead of calculating all the different parameters from those equations, we use them to obtain the interactions between the atoms at the interface [11]. As regards each semiconductor, we use in the bulk the Vogl et al. parameters [12] which are known to give rather accurate electronic band structures.

The interface electronic structure is calculated, using previous parameters, and introducing a Hartree self-consistency between the transfer of charge at the interface and the induced electrostatic potential on each atom [13]. Notice that this consistency introduces in the calculation charge neutrality conditions related to the charge neutrality level of the IDIS approach: this explains why this tight-binding calculation goes beyond the IDIS model.

### 3. Results and discussion

The self-consistent tight-binding method has been applied to the analysis of two different cases: (i) the first one corresponds to a GaP–Si heterojunction, where we have assumed that different intralayers of Cs, Al and H have been deposited; (ii) in the second case we have considered a ZnSe–Ge interface, with an Al intralayer of variable thickness.

Intralayers in a GaP–Si(110) heterojunction have been analysed experimentally by Perfetti [14], who found that different intralayers might induce different changes in the valence band offset.

Fig. 2 shows the geometry of the interface we have considered for a GaP–H–Si heterojunction. Hydrogen has been assumed to be bonded to the different atoms of the interface, with a distance to each one given by the sum of the covalent radii of the atoms forming the bond. Figs. 3a and 3b show the interface density of states for GaP–Si and GaP–H–Si respectively; notice the important effect induced by the intralayer of hydrogen on the interface density of states. The density of states of the hydrogen layer is practically zero around the semiconductor energy gap; at the same time, due to the H layer, localized interface states appear in both semiconductors. These results can be understood by pointing that H has been bonded to Ga, P and Si. In a very simplified picture, the 1s level of H can be assumed to be bonded to the dangling bonds of GaP and Si. In this picture the wave function of the interface states appears as the antisymmetric combination of the dangling bonds of both crystals, with a zero amplitude at the H layer. This is, indeed, what fig. 3b shows, since we find an identical density of states in the first layers of GaP and Si for the interface bands. Notice that these results are not in contradiction with the well-known result that a H layer on a semiconductor

surface removes the surface states: in this case, the 1s level of H is bonded to the semiconductor dangling bond, forming bonding and antibonding states far away from the semiconductor gap. On the other hand, we have found that for this case the valence band offset changes from 0.64 eV for the ideal GaP-Si(110) case to 0.45 eV for GaP-H-Si of fig. 2. Small changes about 0.45 eV, of around  $\pm 0.03$  eV, can be induced in the band offset by introducing appropriate changes in the interface parameters: these small changes show that the band-offset modification found in our calculation is significative.

In order to analyse the dependence of the GaP-Si valence band offset on the intralayer electronegativity, we have also considered the GaP-Al-Si and the GaP-Cs-Si interfaces. For GaP-Al-Si, we have assumed that the Al layer

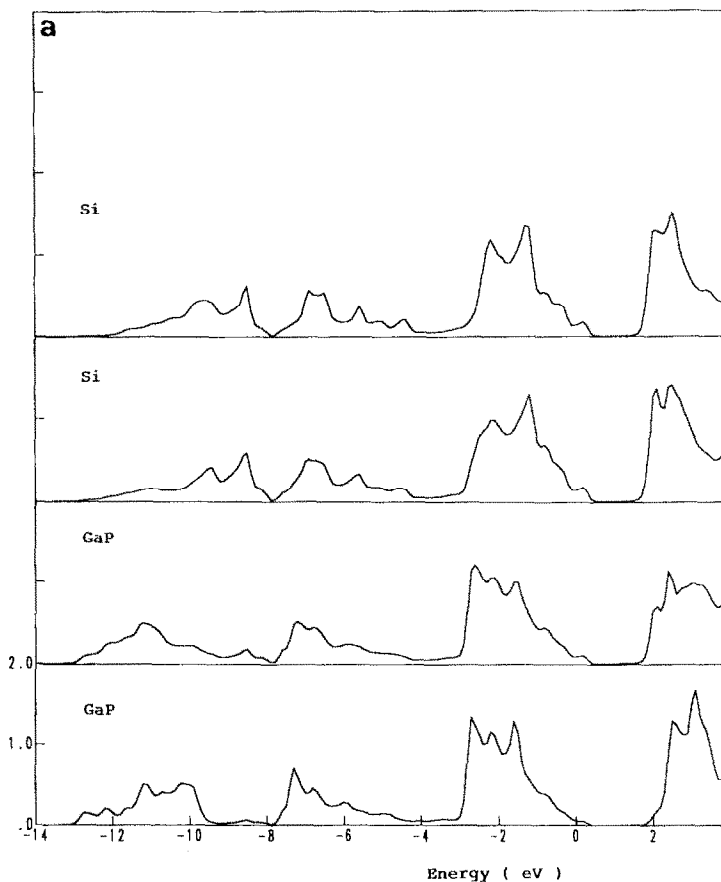


Fig. 3. Local density of states (arbitrary units) at different layers: (a) a GaP-Si and (b) a GaP-H-Si interface.  $E = 0$  is the top of the GaP valence band.

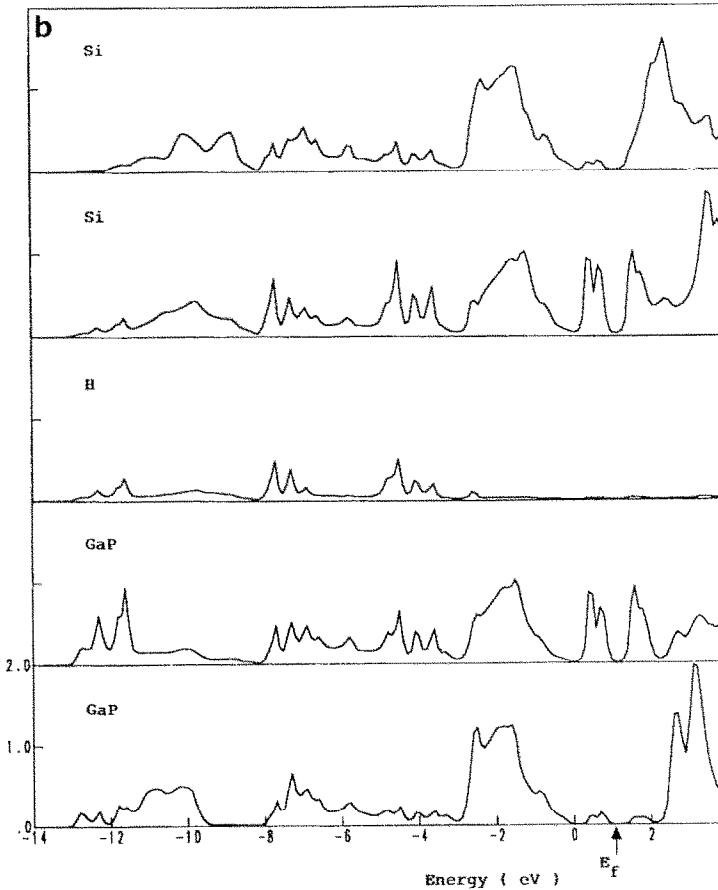


Fig. 3. Continued.

is bonded to the P atoms and, then, we have completed the layer until an ideal Al(110) face is obtained (this is similar to the geometry assumed in ref. [15] for a monolayer of Al between ZnSe and Ge). For GaP–Cs–Si, the Cs atoms have been assumed to be bonded either to P or Ga; in both cases we have calculated the heterojunction band offset.

Table 1 shows our results for the change in the band offset of GaP–Si as a function of the intralayer electronegativity. The error bars introduced in the band-offset changes are related either to the different geometries assumed in the calculation (in the case of Cs) or to the different parameters of the interface interaction (in the case of Al and H). We should comment that in a more complete approach the position of the intralayer atoms ought to be calculated by a full minimization of the total interface energy. The final

Table 1

Changes in the band offset (in eV) of the GaP–Si(110) heterojunction as a function of the deposited intralayer

Cs	Al	H
$0.4 \pm 0.15$	$0.15 \pm 0.06$	$-0.19 \pm 0.03$

atomic states might differ from the ones assumed in this paper, introducing some changes in the band offset calculated here. The analysis presented for Cs, as the ad atom is located at different sites of the interface, suggests that those changes can modify the band offset by  $\pm 0.15$  eV; this uncertainty leaves the main conclusion of this paper unchanged.

The important conclusion coming out of the results of table 1 is that the heterojunction band offset can be controlled with the electronegativity of the atomic species deposited at the interface. We should also comment that these conclusions are in qualitative agreement with Perfetti's results [14]: in particular, let us mention that Perfetti found changes of 0.1, 0.15 and  $-0.4$  eV for the Cs, Al and H intralayers, respectively. In particular, the change between the extreme cases of Cs and H intralayers shows the same tendency in the experimental and theoretical results.

A different point related to the previous experimental evidence [14] is the following: How much do the band-offset changes depend on the number of monolayers of a given atomic species deposited at the interface? We have investigated this problem with our self-consistent tight-binding approach, by considering the ZnSe–Al–Ge interface. In ref. [15] we found that a monolayer of Al introduces an important change in the valence band offset, 0.35 eV [16]. We have now calculated the same interface by increasing the number of Al monolayers, and found that up to an accuracy of  $\pm 0.05$  eV the band offset is independent of the increasing thickness of the intralayer (details will be published elsewhere). The conclusion is that a monolayer is enough to create the band-offset changes between two semiconductors.

Finally we should comment that the results of this paper show that the transitivity rule for semiconductors can be altered by the introduction of appropriate intralayers between the semiconductors. This result is connected with the modification of the semiconductor charge neutrality level due to the geometry and ionicity of the metal deposited on the semiconductor surface.

In conclusion, our theoretical analysis confirms previous experimental data [14] and show that an appropriate use of adequate intralayers opens the possibility of controlling the barrier heights of semiconductor interfaces.

### Acknowledgments

This work has been partially supported by the Scientific Cooperation Contract N5.ST2J-0254-7-E (EDB) between the European Communities and

the Universidad Autónoma de Madrid (Spain). One of us (A.M.) is indebted to the Consejería de Educación del Gobierno Autónomo Canario for partial financial support.

## References

- [1] F. Flores and C. Tejedor, *J. Phys. C* 20 (1987) 145.
- [2] M. Priestsch, M. Domke, C. Laubschat and G. Kaindl, *Phys. Rev. Letters* 60 (1988) 436.
- [3] K. Stiles and A. Khan, *Phys. Rev. Letters* 60 (1988) 440.
- [4] C. Van de Walle and R.M. Martin, *J. Vacuum Sci. Technol. B* 4 (1986) 1055.
- [5] M. Cardona and N.E. Christensen, *Phys. Rev. B* 35 (1987) 6182.
- [6] A. Muñoz, J.C. Durán and F. Flores, *Surface Sci.* 181 (1987) L200.
- [7] C. Tejedor, F. Flores and E. Louis, *J. Phys. C* 10 (1977) 2136;  
C. Tejedor and F. Flores, *J. Phys. C* 11 (1978) L19.
- [8] J. Tersoff, *Phys. Rev. Letters* 52 (1984) 465.
- [9] F. Flores, in: *Proc. NATO Workshop on Band Structure Engineering in Semiconductor Microstructures*, Il Giocco, Italy, April 1988, Ed. R.A. Abram;  
R.M. Martin, in: *Proc. NATO Workshop on Band Structure Engineering in Semiconductor Microstructures*, Il Giocco, Italy, April 1988, Ed. R.A. Abram.
- [10] F. Flores, A. Martín-Rodero, E.C. Goldberg and J.C. Durán, *Nuovo Cimento D* 10 (1988) 303.
- [11] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* 14 (1974) 177.
- [12] P. Vogl, H.P. Hjalmarson and J.D. Down, *J. Phys. Chem. Solids* 44 (1983) 365.
- [13] F. Guinea, J. Sánchez-Dehesa and F. Flores, *J. Phys. C* 16 (1983) 6499.
- [14] P. Perfetti, *Surface Sci.* 189/190 (1987) 362.
- [15] J.C. Durán, A. Muñoz and F. Flores, *Phys. Rev. B* 35 (1987) 7721.
- [16] D.W. Niles, G. Margaritondo, P. Perfetti, C. Quaresima and M. Capozzi, *Appl. Phys. Letters* 47 (1985) 1092.