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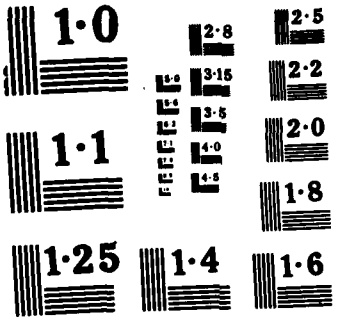

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THEORETICAL CALCULATIONS SUPPORTING INVESTIGATION OF METAL CONTACTS TO ULTRA-SMALL SEMICONDUCTOR STRUCTURES

by

F.Flores, G.Platero, J.Sánchez-Dehesa, C.Tejedor,
J.A.Vergés, J.Durán and A.Muñoz

October 1985

EUROPEAN RESEARCH OFFICE
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CONTENTS

page

ABSTRACT 1

A. GENERAL INTRODUCTION 2

1. Introduction
2. Paper No.1: "Anion induced surface states for the ideal (100)-faces of GaAs, AlAs and GaSb"
3. Paper No.2: "Electronic structure of (100)-semiconductor heterojunctions"
   Paper No.3: "Band-offset calculations of (100)-semiconductor heterojunctions: A simple consistent method"
4. Paper No.4: "Initial stages of the Schottky-barrier formation for abrupt covalent interfaces"
   Paper No.5: "Initial stages of the Schottky-barrier formation for an abrupt Al-GaAs(100) interface"
5. Conclusions
6. References

B. PAPERS 9

Paper No.1: "Anion induced surface states for the ideal (100)-faces of GaAs, AlAs and GaSb", by G.Platero, J.Sánchez-Dehesa, C.Tejedor, F.Flores and A.Muñoz 9

Paper No.2: "Electronic structure of (100)-semiconductor heterojunctions", by G.Platero, J.Sánchez-Dehesa, C.Tejedor and F. Flores 28

Paper No.3: "Band-offset calculations of (100)-semiconductor heterojunctions: A simple consistent method", by G.Platero, J.Sánchez-Dehesa, C.Tejedor and F. Flores 33

Paper No.4: "Initial stages of the Schottky barrier formation for abrupt covalent interfaces", by G.Platero, J.A.Vergés and F.Flores 55

Paper No. 5: "Initial stages of the Schottky barrier formation for an abrupt Al-GaAs(100) interface", by G.Platero, J.Durán and F.Flores 61

ABSTRACT

Metal-ultrasmall superlattice junctions have been analysed by using a consistent tight-binding method. Hetero-junctions and metal-semiconductor interfaces have been discussed independently by assuming that each semiconductor superlayer has more than six layers.

We present results for the electronic structure of (100)-semiconductor heterojunctions; in particular, we consider the (100)-GaAs-AlAs, GaSb-InAs and InAs-GaSb interfaces. For GaAs-AlAs we have found that the valence band offset is 0.41 eV, and that there is an interface dipole of 0.13 eV (for no inter-face dipole, the valence band offset would be of 0.28 eV). Our results also show that the two GaSb-InAs and InAs-GaSb interfaces present different band-offset discontinuities.

We have also analysed the initial stages of the Schottky-barrier formation for Al on an As-terminated GaAs-(100) face. Two cases have been analysed: (i) firstly, we have considered a half monolayer of Al, with these atoms located in the ideal position corresponding to a Ga-atom of the ideal continued GaAs crystal; (ii) in the second case, we have considered a full monolayer with the Al atoms forming a (100)-face of an Al crystal. Our results show that the Schottky barrier is formed for a monolayer, and that the barrier height is 0.55 eV, similar to the value found for a metal-GaAs(110) junction.

The consistency found for the GaAs-AlAs(100) and the Al-GaAs(100) interfaces defines completely the barrier heights associated with the Al-GaAs-AlAs(100) junction.

A. GENERAL INTRODUCTION

1. INTRODUCTION

The mechanism of the Schottky barrier formation is a matter of current controversy. Different models have been proposed, and it is clear that none has a universal acceptance since no single model can explain all the experimental evidence. This is related to the different kind of interfaces appearing in a metal-semiconductor junction; according with the experimental evidence there are: (i) abrupt interfaces [1,2] with a well defined separation between the metal and the semiconductor, and (ii) reactive interfaces [3,6] with the metal and the semiconductor interdiffusing and/or forming a new chemical compound at the interface.

Two different models, related to the two kind of interfaces commented on above, appear to attract fairly wide support in the scientific community: (i) The intrinsic interface states model [7-11], which attributes the Schottky barrier height to the Fermi level pinning by the metal induced density of states near the semiconductor mid-gap. (ii) The defect model [12-16], which assumes that the Schottky barrier formation results from the creation of a significant number of defects at or near the interface. Obviously, the defect model is assumed to be valid for reactive interfaces, while the intrinsic interface states model seems to be related to abrupt interfaces.

In this work, we have started an investigation of the Schottky barrier formation in metal-ultrasmall superlattices, for cases for which there is an abrupt interface between the metal and the superlattice.

Different theoretical approaches have been used to analyse those ideal abrupt interfaces. It is worth mentioning three different approaches: (i) in the simplest case, the mechanism of the Schottky barrier formation [8,11] is based on the concept of the charge neutrality level. Here, when a semiconductor and a metal are intimately coupled, the semiconductor density of surface states broadens but keeps its centre of gravity almost constant. Hence, the interface's Fermi level almost coincides with the Fermi level for the free surface. Then, the barrier height is determined by equalising both the metal

Fermi level and the semiconductor charge neutrality level. (ii) In the most elaborate kind of calculation [17], the barrier height is determined by means of a self-consistent calculation using pseudopotential theory and the local density formalism. (iii) In an intermediate approach [9,10], we have used recently a consistent calculation for a tight-binding model. The idea behind this approach is to extend the charge neutrality level concept [8] to a more sophisticated calculation, which takes into account the small variations that interface dipoles introduce in the "rule of thumb" associated with the charge neutrality approach.

In the work presented in this project we have followed this last method: the "consistent tight-binding approach", a method that has been applied successfully to metal-semiconductor junctions [9,10]. On the other hand, we have analysed the metal-ultrasmall superlattice junctions in several steps: (i) in a first step, we have discussed the properties of free-surface semiconductors. The purpose of this work is to analyse the consistency of the tight-binding method in a simple case, and to find out how the surface perturbation penetrates into the crystal. (ii) In a second step, we have considered the semiconductor-semiconductor interface, assuming it to be decoupled from the metal-semiconductor junction. The idea behind this approach is that the metal-superlattice junction properties are determined by the independent semiconductor-semiconductor and metal-semiconductor interfaces (we only consider in this work a configuration with the metal-semiconductor interface parallel to the semiconductor-semiconductor interface of the superlattice). As our results show, this is a valid assumption if each semiconductor superlayer has more than six semiconductor layers. (iii) In a final step, we consider the metal-semiconductor junction and analyse the Schottky barrier height for the initial stages of the barrier formation.

In the following paragraphs we present a brief discussion of the results obtained in the different papers collected in the last part of this report. In §2, paper No.1: "Anion-induced surface states for the ideal (100)-faces of GaAs, AlAs and GaSb", by G.Platero, J.Sánchez-Dehesa, C.Tejedor, F.Flores and

A.Muñoz, is presented. In §3, we discuss papers No.2 and 3:

"Electronic structure of (100)-semiconductor heterojunctions", by G.Platero, J.Sánchez-Dehesa, C.Tejedor and F. Flores, and

"Band-offset calculations of (100)-semiconductor heterojunctions: A simple consistent method", by G.Platero, J.Sánchez-Dehesa, C.Tejedor and F.Flores.

Finally, in §4, we discuss papers No.4 and 5:

"Initial stages of the Schottky barrier formation for abrupt covalent interfaces", by G.Platero, J.A.Vergés and F. Flores, and

"Initial stages of the Schottky barrier formation for Al on GaAs(100)", by G.Platero, J.Durán and F.Flores.

In §5, we present our final comments.

2. PAPER No.1: "Anion-induced surface states for the ideal (100)-faces of GaAs, AlAs and GaSb".

In this paper we apply our consistent tight-binding method to analyse the anion-induced surface states of the ideal (100)-faces of GaAs, AlAs and GaSb.

Our results show that consistency is crucial in order to obtain the surface state levels and the Fermi energy. For example, for GaAs we have found that the Fermi level is located at 0.33 eV above the valence band top; had we not applied our consistent procedure, we would have obtained the Fermi level at 0.77 eV above the valence band top.

On the other hand, the results of paper No.1 show that the surface perturbation penetrates three layers in the semiconductor, in such a way that the fourth layer is practically unaltered by the surface. This is an important result that will be used later on, in order to analyse semiconductor interfaces.

3. PAPERS No.2 AND 3: "Electronic structure of (100)-semiconductor heterojunctions" and "Band-offset calculations: A simple consistent method".

In these papers we apply the consistent tight-binding method to the calculation of the band-offsets for the (100)-GaAs-AlAs, GaSb-InAs and InAs-GaSb heterojunctions. In our method we have included spin-orbit coupling in the parameters

of the different semiconductor's Hamiltonians and used sp^3s^* hybrids in each atom.

Each heterojunction is analysed by projecting the whole structure of both semiconductors onto the six layers located around the interface, three layers corresponding to one semiconductor. This means that the whole Hamiltonian for both crystals is reduced to an effective matrix-Hamiltonian having 60x60 elements.

Consistency is introduced by means of diagonal perturbaions at the interface layers. Using the effective matrix-Hamiltonian we calculate the electronic charge at each layer, and define consistency relating the diagonal perturbations with the induced charge through a kind of electrostatic (or Hartree) equation.

For GaAs-AlAs, we have found that the valence band offset is 0.41 eV, and that there is an interface dipole of 0.13 eV (for no interface dipole, the valence band offset would be of 0.28 eV).

Recent experimental information [18] yields a value of 0.65 eV for the valence band offset. It must be noticed that this value has been accepted long since to be 0.25. We think that our results (including an uncertainty of 0.1 eV associated with the approximations of our theoretical model) are quite satisfactory.

4. PAPERS No.4 AND 5: "Initial stages of the Schottky barrier formation for abrupt covalent interfaces" and "Initial stages of the Schottky barrier formation for Al on GaAs(100)".

In these papers we have analysed the initial stages of the Schottky barrier formation for Al on Si(111) and GaAs(100).

Si(111) has been chosen, in a first step, as a well-known case for analysing the initial stages of the Schottky barrier formation. Again, we have applied the consistent tight-binding method and analysed the evolution of the electronic density of surface states in the semiconductor gap as a function of the deposition of Al on Si. Two cases have been considered: (i) a third of monolayer, and (ii) a full monolayer. It is

well-known that for a third of monolayer[19] there is an energy gap in the density of states, in such a way that the barrier height does not appear as completely formed. Our analysis for a full monolayer have shown that: (i) the barrier is completely formed in this case, with the electronic density of states filling the semiconductor energy gap, and (ii) the charge neutrality level (and the barrier height) depends on the geometrical position of the metal atoms on the silicon surface. Our analysis, and the comparison with the experimental evidence, shows that the metal atoms, for a monolayer, are located in the top position.

Finally, we have considered the initial stages of the Schottky barrier formation for the case of Al deposited on an anion-terminated GaAs(100)-surface. Here, we have analysed a half and a complete monolayer of Al; for a half monolayer, an Al atom is located in the ideal configuration corresponding to a Ga atom of the ideal crystal growing towards the metal. The main result of our analysis is that, for a half monolayer, we find a cation-like surface state band similar to the one appearing in the ideal (100)-cation surface. For a full monolayer, we find that the barrier height is completely formed, and that the Fermi level is shifted with respect to the half monolayer case by 0.31 eV towards the conduction band. We conclude that the barrier height for an Al-GaAs(100) face is 0.55±0.05 eV, similar to the value found for a metal-GaAs(110) face (0.65±0.05 eV).

5. CONCLUSIONS

Metal-ultrasmall superlattice junctions have been analysed using a consistent tight-binding method. Energy levels in the junction and the superlattice are determined by analysing each interface which appears to be decoupled of each other if the size of each superlayer is greater than six layers of the corresponding semiconductor. Accordingly, heterojunctions and metal-semiconductor interfaces have been discussed independently. For the case of Al on GaAs-AlAs(100), we have found the following main results: (i) For a GaAs-AlAs(100) heterojunction, the valence band offset is 0.41 eV; (ii) for an Al-GaAs(100) junction, with Al growing on an As-terminated crystal, the barrier height

appears to be 0.55 eV.

These two values define completely the Al-GaAs-AlAs(100) junction and allows us to obtain ϕ_{bn} *for any given GaAs-AlAs superlattice. This can be easily achieved by referring the electronic levels of the superlattice to the valence band structure of the two ideal infinite semiconductors.*

REFERENCES

1. A.McKinley, R.H.Williams and A.W.Park, J.Phys.C, 12, 2447 (1979)
2. R.Ludeke, T.C.Chiang and T.Miller, J.Vac.Sci.Technol., B1, 581 (1983)
3. J.M.Andrews and J.C.Phillips, Phys.Rev.Lett., 35, 56 (1975)
4. G.Ottaviani, K.N.Tu and J.W.Mayer, Phys.Rev.Lett., 44, 284 (1980)
5. R.H.Williams, V.Montgomery and R.R.Varma, J.Phys.C, 11, 1989 (1978)
6. L.J.Brillson, C.F.Brucker, N.G.Staffel, A.D.Katnani and G. Margaritondo, Phys.Rev.Lett., 46, 838 (1981)
7. V.Heine, Phys.Rev., A138, 1689 (1965)
8. C.Tejedor, F.Flores and E.Louis, J.Phys.C, 10, 2163 (1977)
9. F.Guinea, J.Sánchez-Dehesa and F.Flores, J.Phys.C, 16, 6499 (1983); 17, 2039 (1984)
10. J.Sánchez-Dehesa and F.Flores, Solid State Commun., 50, 29 (1984)
11. J.Tersoff, Phys.Rev.Lett., 52, 465 (1984)
12. M.S.Daw and D.L.Smith, Phys.Rev.B, 20, 5150 (1979)
13. W.E.Spicer, I.Lindau, P.R.Skeath and C.Y.Su, J.Vac.Sci. Technol., 17, 1019 (1980)
14. R.E.Allen and J.D.Dow, Phys.Rev.B, 25, 1423 (1982)
15. O.F.Saukey, R.E.Allen and J.D.Dow, Solid State Commun., 49, 1 (1984)
16. R.H.Williams, J.Vac.Sci.Technol., 18, 929 (1981)
17. S.G.Louie, J.R.Chelikowski and M.L.Cohen, Phys.Rev.B, 15, 2154 (1977)
18. R.C.Miller, A.C.Gossard, D.A.Kleinman and O.Munteanu, Phys. Rev.B, 29, 3740 (1984); R.C.Miller, D.A.Kleinman and A.C. Gossard, Phys.Rev.B, 29, 7085 (1984)
19. J.G.Northrup, Phys.Rev.Lett., 53, 683 (1984)

B. PAPERS

ANION-INDUCED SURFACE STATES FOR THE IDEAL (100)-FACES OF GaAs, AlAs and GaSb

G.Platero, J.Sánchez-Dehesa, C.Tejedor, F.Flores and A.Muñoz

Departamento de Física del Estado Sólido,

Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

We present a simple consistent tight-binding method to calculate the electronic properties of ionic semiconductor surfaces. The method is applied to calculate the anion-induced surface states of the ideal (100)-faces of GaAs, AlAs and GaSb. It is shown that consistency is crucial to obtain the surface state levels and the Fermi energy, and that the surface perturbation penetrates three layers in the crystal.

I. INTRODUCTION

Many different theoretical and experimental work have been addressed to the understanding of the surface states of clean semiconductors [1,2]. Most of the work have been done in covalent surfaces and GaAs [3]. Specific work on the (100)-surfaces of ionic crystals have been stimulated by Molecular Beam Epitaxy and the growing of superlattices.

The main experimental data for the (100)-surface has been collected in GaAs [4,5], but interesting information for other semiconductors, GaSb and InAs, is also available [6,7].

From the theoretical point of view, let us mention the early work of Appelbaum et al.[8], where a self-consistent solution for the cation-like (100)-surface of GaAs is presented. Ivanov et al.[3] have calculated the cation-like and the anion-like surface states of the GaAs (100)-face by means of a tight-binding approach, but no kind of consistency is provided in this calculation.

In this paper we have addressed the problem of calculating the anion-like surface states of GaAs, AlAs and GaSb. It is well known that the (100)-faces of those crystals present different reconstructions depending on the kind of preparation [4-7]. It has been suggested [7] that the different GaAs surface reconstructions are associated with a kind of metal-insulator transition: this means that dangling-bonds are paired to produce bonds having no density of states at the Fermi level. For GaSb(100) surfaces, however, reconstructions seem to be related with a three-fold or a five-fold periodicity [7]: unless the presence of vacancies is involved, this means that

the electronic properties of these surfaces must differ markedly of the GaAs(100)-faces.

In spite of these comments, we have only considered in this paper the ideals anion-like (100)-surfaces of GaAs, AlAs and GaSb [9]; we consider these surfaces to be of interest by themselves, mainly considering that ideal crystals (with no reconstruction) appear in a superlattice built up with these semiconductors. The purpose of this paper is to present, for these surfaces, a simple method which includes the basic consistent properties associated with charge neutrality conditions. By means of the self-consistent conditions imposed at the surface we also analyse how deep in the crystal the surface perturbation penetrates, and the Fermi level position, a quantity very sensitive to the charge neutrality conditions and intimately related to the charge neutrality level of the semiconductor [10].

The calculation presented in this paper for the anion-like surfaces has been done by using a simple tight-binding approach (similar to Ivanov et al.'s calculation [3]), *but* supplemented by a kind of self-consistency appropriate for this model. This consistency, and the charge neutrality conditions, has been proved to be crucial for the understanding of other interfaces [11,12]. The main idea is to introduce diagonal perturbations at several layers (the layers affected are determined specifically at each case) at the interface. These perturbations are determined by introducing self-consistency between the potentials and the surface charges.

In §2 we discuss our model, our method of calculation and how self-consistency is introduced in the problem. In §3 we

present our results and our conclusions.

II. THE MODEL, METHOD OF CALCULATION AND CONSISTENCY

We describe the semiconductors by means of a tight-binding model, using sp^3s^* hybrids [13] in each atom and include interaction parameters extending up to the first neighbours. Table 1 gives the parameters used in our calculation for GaAs, AlAs and GaSb. We assume that, except for the diagonal perturbations commented on above, at the interface we have the same parameters as in the bulk. In our calculation we have also included the spin-orbit interaction [14] that appears to be important for Sb. The parameters given in Table I are similar to the ones proposed by Vogl et al.[13] except by small corrections introduced to allow for the spin-orbit interaction (the parameters given in Table 1 have been chosen to give the right levels at the symmetric points Γ and X).

The Hamiltonian defining our surface model is, therefore, well known except for the diagonal perturbations applied at some layers of the interface (see below).

As regards our method of calculation, we follow the procedure explained in ref.[15]. In summary, our method consists in looking for the surface components of the Green function of the system. By means of a decimation technique, we can project the bulk components of the Green function onto a few layers of the interface. In our actual case, we have projected all the electronic bulk structure onto the last three semiconductor surface layers. This means that the whole Hamiltonian is reduced to an effective matrix Hamiltonian having 30x30 elements

(including spin and five orbitals per layer). This matrix defines the effective interactions for the surface atoms, in such a way that now we analyse the surface by introducing in this effective Hamiltonian the diagonal perturbations to be discussed just below.

Turning our attention to self-consistency, let us start our discussion by considering the electrostatic potential associated with the ideal charges existing in the bulk when assumed to be extended until the same surface. Figure 1 shows this situation after averaging in the plane parallel to the surface. Notice that for a cation we assume to have $(3+\alpha)$ units of charge per atom, and $(5-\alpha)$ units of charge per atom for an anion *except* for the last layer. It is well known [16] that for a (100)-ionic face, the charge of the last anion must be $(5-\frac{\alpha}{2})$, this value being determined by the condition of having a finite potential inside and outside the crystal. Let us also comment that this surface charge is also associated with the surface state occupancy; for the (100)-anion surface we find two surface states (see below) with a total occupancy of 5/4 (one is fully occupied and the other one only in 1/4).

However, the ideal charges shown in Figure 1 are not consistent with the potentials of an ideal semiconductor extending unperturbed up to the surface. Instead, charges are transferred, in our case, among the last three layers, say, 1, 2 and 3. Now, we introduce two diagonal perturbations, V_1 and V_2, at layers 1 and 2, looking for a kind of Hartree self-consistency between these potentials and the charges transferred among layers. Thus, calling δn_1, δn_2 and δn_3 ($\delta n_1+\delta n_2+\delta n_3 = 0$), the

changes in the layers charges measured with respect to the ideal values shown in Figure 1 , we write down the following equations of consistency:

$$V_1 = \frac{4\pi}{A} d(\delta n_1 + \delta n_2) \qquad (1)$$

$$V_2 = \frac{4\pi}{A} d\ \delta n_1 \quad . \qquad (2)$$

where A is the surface area per atom.
(Notice that the charge neutrality condition $\delta n_1 + \delta n_2 + \delta n_3 = 0$ is automatically satisfied, up to a given accuracy, by imposing the appropriate surface states occupancies).

Eqs.(1) and (2) yield the consistent equations to be used in order to determine V_1 and V_2. Notice that, on the other hand, V_1 and V_2 are the diagonal perturbations to be introduced in the effective Hamiltonian (a 30x30 matrix) discussed above.

It is of interest to note that a good approximation to the self-consistent equations (1) and (2) can be obtained by looking for values of V_1 and V_2, say, $V_1^{(0)}$ and $V_2^{(0)}$, such that $\delta n_1 \approx \delta n_2 = 0$. The idea behind this approximation is that a very small change in δn_1 and δn_2 introduces very strong variations in V_1 and V_2 through the induced potentials given by eqs.(1) and (2).

III. RESULTS AND COMMENTS

Figure 2a shows the local density of states for the last As-layer of GaAs, as calculated by using no consistency ($V_1 = V_2 = 0$). Figures 2b and 2c show the local density of states projected onto the p_x+p_y (bridge bond) and the $s+p_z$ (dangling bond)

orbitals of As. From these figures we see that the 1/4-occupied surface state band is a bridge-like state, while the occupied surface state band is a dangling-bond state, in agreement with Ivanov et al's results [3]. Notice that the Fermi level is inside the 1/4-occupied band and is located, for this non-consistent case, at 0.77 eV above the valence band top. It is of interest to comment that the 1/4-occupied surface band affords a check to the accuracy of our calculations, and to the number of layers to be used in order to obtain a good consistent result. In our actual case, layers 1, 2 and 3 yield 0.74 electrons (instead of 0.75) for the empty number of states in the partially occupied surface band; had we used only two layers, instead of three, we would have obtained 0.67 electrons. This shows that using three layers give an accuracy better than 0.01 electrons for the total number of electrons in the surface band. On the other hand, this discussion shows that the surface perturbation penetrates three layers in the crystal.

Figure 3a shows the local density of states for the As-layer of GaAs, as calculated in the consistent procedure. For this case, we have obtained the following values for the diagonal perturbations, V_1 and V_2:

$V_1(GaAs) = -0.52$ eV

$V_2(GaAs) = 0.17$ eV.

Figures 3b and 3c show this density projected onto the bridge/bond and the dangling-bond orbitals, respectively. Note that in this consistent case, $E_F = 0.33$ eV, differing from the

previous case in (-0.44 eV), a value close to V_1, the perturbation acting on the last layer (V_2 is positive and its effect is to shift upwards the surface bands).

For AlAs we show in Figure 4a the local density of states for the last As-layer as calculated in the consistent case. Our results yield

$V_1(AlAs) = -0.17$ eV

$V_2(AlAs) = 0.21$ eV .

The local density of states for the last As-layer projected onto the bridge-bond and the dangling-bond orbitals are shown in Figures 4b and 4c. The Fermi level for this case is located at 0.66 eV above the valence band top.

For GaSb we show in Figure 5a the local density of states for the last Sb-layer, as calculated in the selfconsistent case. Here:

$V_1(GaSb) = -0.23$ eV

$V_2(GaSb) = 0.25$ eV.

Figures 5b and 5c show the local density of states for the last Sb-layer projected onto the bridge-bond and the dangling-bond orbitals. The Fermi level for this case is located at 0.35 eV above the valence band top. On the other hand, effects associated with the spin-orbit coupling are small, as can be seen by comparing results for GaAs and AlAs (small spin-orbit coupling) and GaSb (large spin-orbit coupling).

Let us finally comment that the partially occupied bands for the three semiconductors, GaAs, AlAs and GaSb, are located around the mid-gap, and that their band widths are similar, $\sim$ 0.5 eV. These states correspond to bridge orbitals; in this case, other people have found broader bands [3,8]. This is related to the kind of approximation used in our initial Hamiltonian; we have taken a sp^3s^* basis with interaction up to first nearest neighbours only. When these interactions are extended up to second neighbours, the bridge-like surface band broadens [3]. However, we can expect, from the results for other interfaces [10,11,12], the surface Fermi energy and the charge neutrality level to be practically independent of the Hamiltonian parameters, depending mainly on the semiconductor electronic structure for the bulk. This seems to be the case even for reconstructed surfaces; indeed, the experimental evidence shows that the surface Fermi level for GaAs is practically independent of the actual reconstruction: E_F = 0.4 ± 0.1 eV [4], or 0.55 ± 0.1 eV [5] above the valence band top. These values are, strikingly, in very good agreement with the value obtained above, E_F = 0.33 eV.

In conclusion, we have presented a simple consistent tight-binding calculation for the (100)-faces of ionic semiconductors. The method has been applied to the anion faces of GaAs, AlAs and GaSb, our results showing that the surface perturbation generates three layers in the crystal. Self-consistency is shown to be crucial in order to obtain appropriate values for the Fermi energy (and the charge neutrality level), our results showing differences of 0.4 eV between the results for the Fermi energy of consistent and nonconsistent calculations.

Acknowledgements

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References

1. J.E.Inglesfield and B.W.Holland, in *The chemical physics of solid surfaces and heterogeneous catalysis*. Vol.I: *Clean solid surfaces*, D.A.King and D.P.Woodruff, Eds. (Elsevier, Amsterdam, 1981)
2. F.Flores, "Surfaces and interfaces", Trieste Spring College on Crystalline Semiconducting Materials and Devices (1985), in press
3. I.Ivanov, A.Mazur and J.Pollmann, Surface sci., 92, 365 (1980)
4. P.K.Larsen, J.H.Neave, J.F.van der Veen, P.J.Dobson and B.A.Joyce, Phys.Rev.B, 27, 4966 (1983)
5. T.C.Chiang, R.Ludeke, M.Aono, G.Landgren, F.J.Himpsel and D.E.Eastman, Phys.Rev.B, 27, 4770 (1983)
6. R.Ludeke, IBM J.Res.Develop., 22, 304 (1978)
7. RLudeke, Phys.Rev.Lett., 39, 1042 (1977)
8. J.A.Appelbaum, G.A.Baraff and D.R.Hamann, Phys.Rev.B, 14, 1623 (1976)
9. D.J.Chadi, C.Tanner and J.Ihm, Surface Sci., 120, L425 (1982)
10. C.Tejedor, F.Flores and E.Louis, J.Phys.C, 10, 2163 (1977); E.Luis and F.Flores, J.Physique(Paris), 42, 1313 (1981); J.Tersoff, Phys.Rev.Lett., 52, 465 (1984)
11. F.Guinea, J.Sánchez-Dehesa and F.Flores, J.Phys.C, 17, 2039 (1984)
12. B.Djafari-Rouhani, L.Dobrzynski, F.Flores, M.Lannoo and C. Tejedor, Solid State Commun., 27, 29 (1978)
13. P.Vogl, H.P.Hjalmaron and J.D.Dow, J.Phys.Chem.Solids, 44, 365 (1983)
14. D.J.Chadi, Phys.Rev.B, 16, 790 (1977)

15. F.Guinea, C.Tejedor, F.Flores and E.Louis, Phys.Rev.B, 28, 4397 (1983)

16. F.García-Moliner and F.Flores, *Introduction to the theory of solid surfaces* (Cambridge Univ.Press, 1979)

TABLE 1: Tight-binding and spin-orbit parameters (in eV). Notation is $E_\alpha = \langle\alpha|H|\alpha\rangle$, $V_{\alpha\beta} = \langle\alpha|H|\alpha\rangle$ and $\lambda^{so} = \langle x\uparrow|H_{so}|z\downarrow\rangle$.

	GaAs	AlAs	GaSb
E_{sa}	-8.345	-7.525	-7.305
E_{pa}	0.985	0.940	0.720
E_{sc}	-2.655	-1.165	-3.885
E_{pc}	3.615	3.540	2.780
E_{s^*a}	8.591	7.483	6.635
E_{s^*c}	6.739	6.727	5.985
V_{ss}	-1.613	-1.666	-1.543
V_{xx}	0.505	0.483	0.434
V_{xy}	1.255	1.061	0.997
V_{s_aP}	1.117	1.276	1.238
V_{s_cP}	2.240	1.369	1.159
$V_{s^*_aP}$	1.210	1.130	1.247
$V_{s^*_cP}$	1.202	1.249	1.054
λ^{so}_a	0.140	0.140	0.324
λ^{so}_c	0.058	0.008	0.058

Figure Cpations

Fig.1.- Schematic representation of charges and electrostatic potentials at the surface.

Fig.2.- Local density of states (in a.u.) for the last As-layer of the anion-terminated (100) surface of GaAs with no shift of the surface atomic potentials with respect to those of the bulk. a) Local density projected on the five atomic orbitals of As. b) Local density projected on the bridge-bond p_x+p_y. c) Local density projected on the dangling-bond $s+p_z$.

Fig.3.- Local density of states (in a.u.) for the last As-layer of the anion-terminated (100) surface of GaAs with consistent potentials V_1=-0.52 eV and V_2=0.17 eV. a) Local density projected on the five atomic orbitals of As. b) Local density projected on the bridge-bond p_x+p_y. c) Local density projected on the dangling-bond $s+p_z$.

Fig.4.- Local density of states (in a.u.) for the last As-layer of the anion-terminated (100) surface of AlAs with consistent potentials V_1=-0.17 eV and V_2=0.21 eV. a) Local density projected on the five atomic orbitals of As. b) Local density projected on the bridge-bond p_x+p_y. c) Local density projected on the dangling-bond $s+p_z$.

Fig.5.- Local density of states (in a.u.) for the last Sb-layer of the anion-terminated (100) surface of GaSb with consistent potentials V_1=-0.23 eV and V_2=0.25 eV. a) Local density projected on the five atomic orbitals of As. b) Local density projected on the bridge-bond p_x+p_y. c) Local density projected on the dangling-bond $s+p_z$.

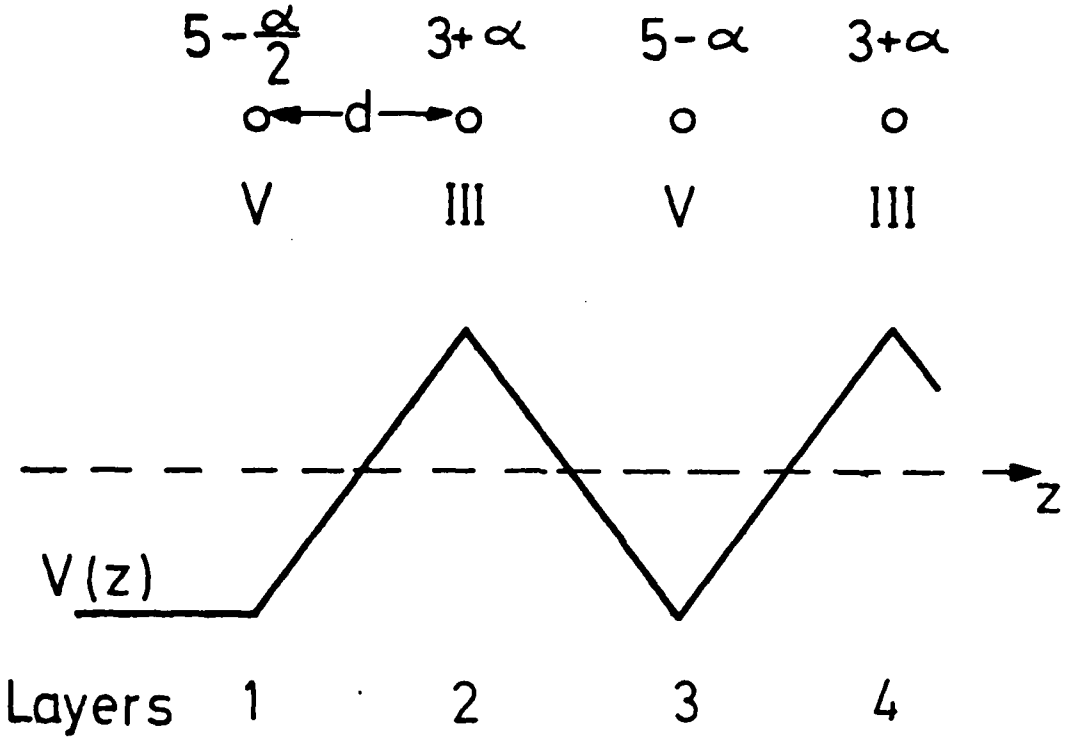


Fig. 1

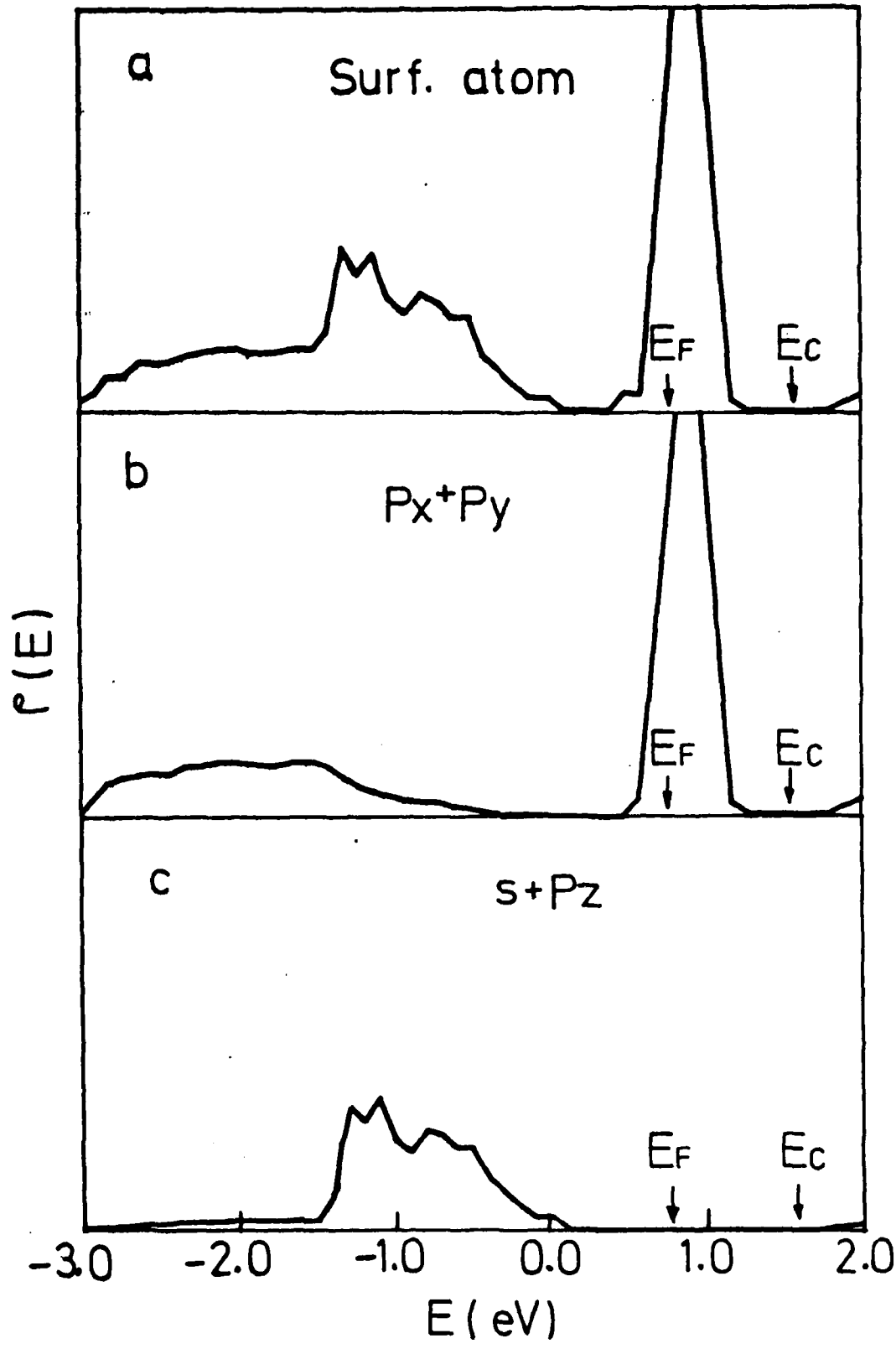


Fig. 2

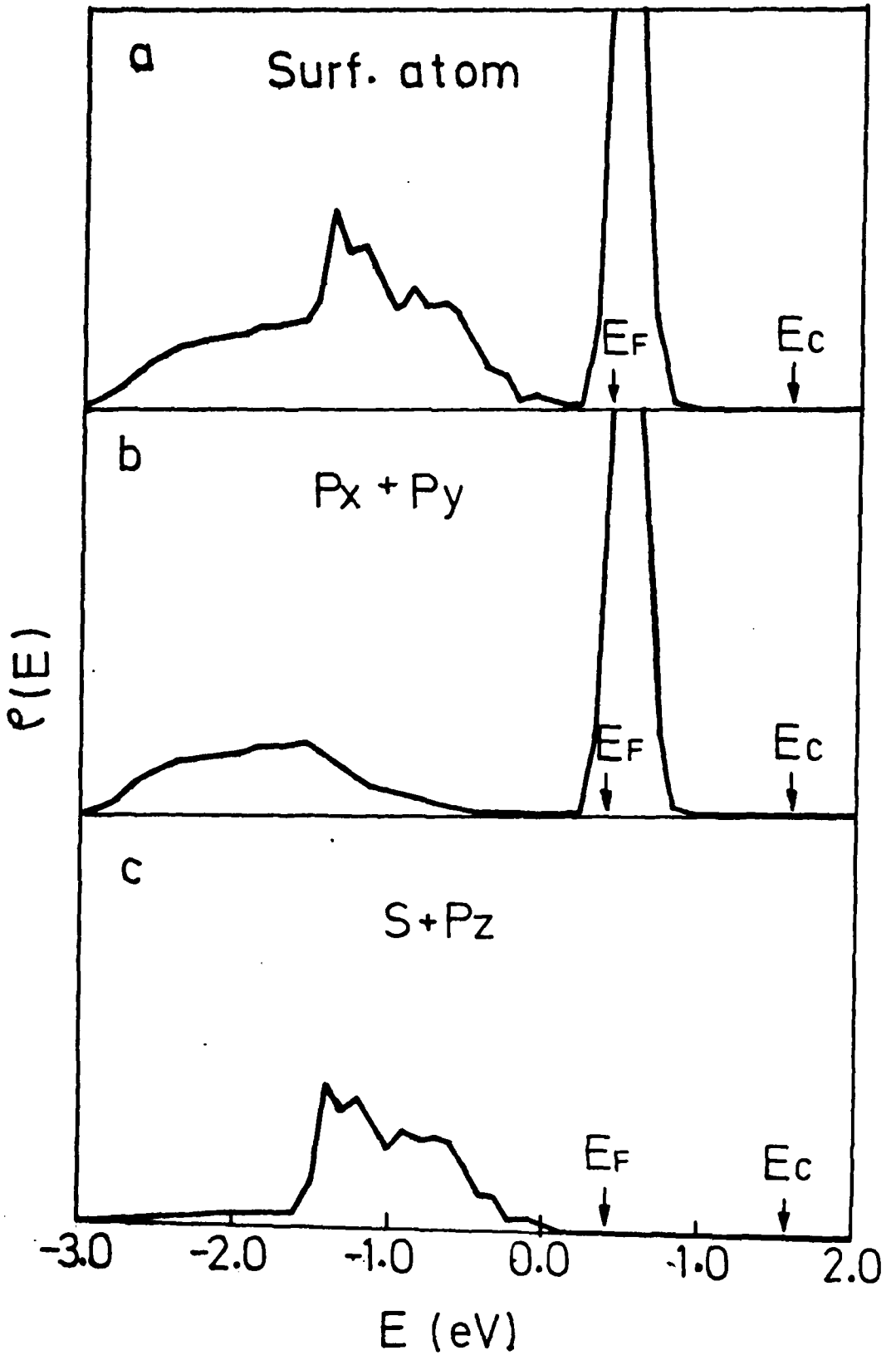


Fig 3

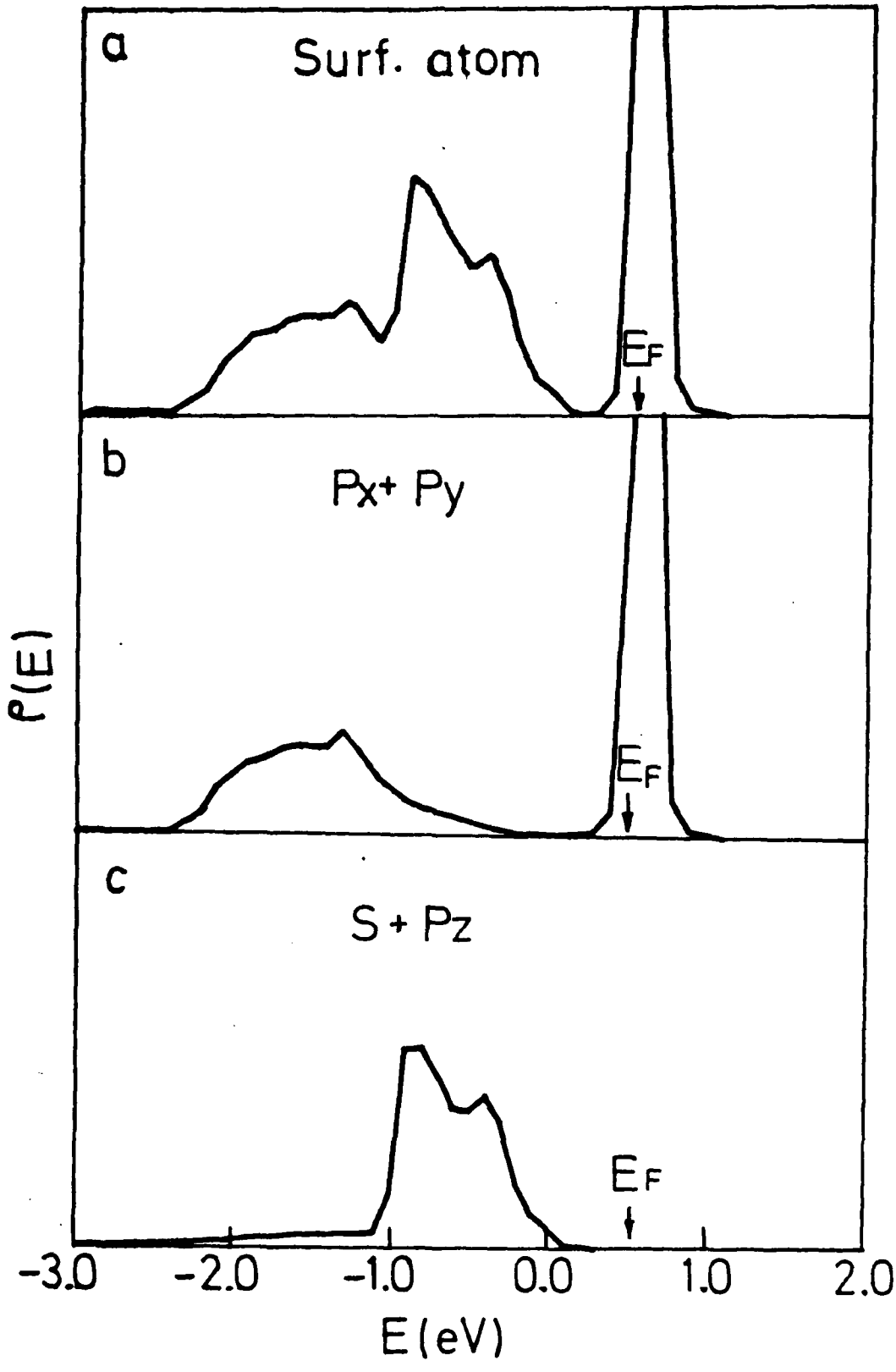
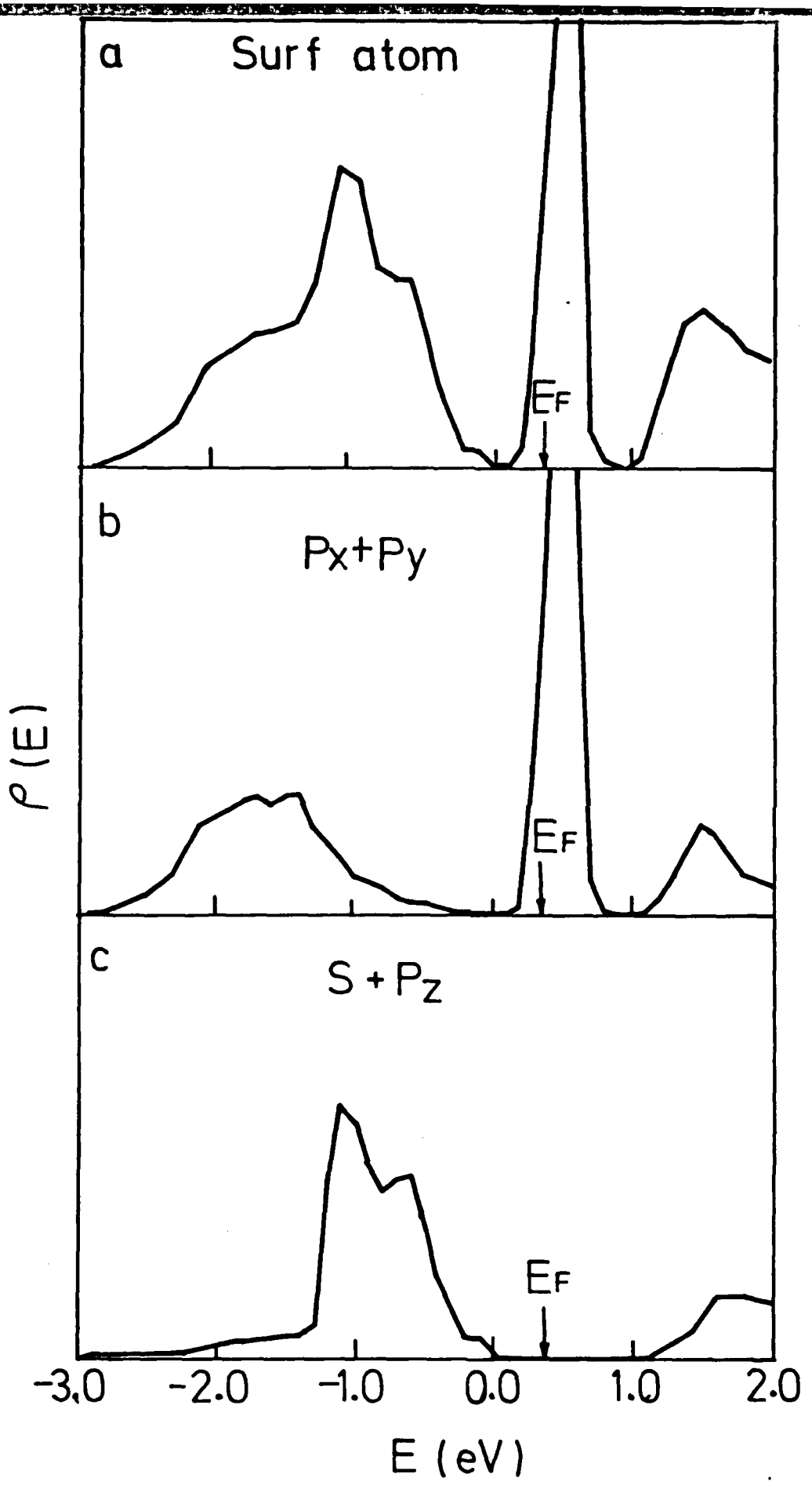


Fig. 4


a
Surf atom
E_F
b
Px+Py
E_F
c
S + Pz
E_F
ρ(E)
-3.0
-2.0
-1.0
0.0
1.0
2.0
E (eV)

ELECTRONIC STRUCTURE OF (100) SEMICONDUCTOR HETEROJUNCTIONS

G. PLATERO, J. SÁNCHEZ-DEHESA, C. TEJEDOR and F. FLORES

Departamento de Física del Estado Sólido, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

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The electronic structure of (100) abrupt semiconductor heterojunctions has been analysed by means of a self-consistent tight-binding method. Band offsets for the junctions GaAs–AlAs, InAs–GaSb and GaSb–InAs have been calculated and compared with the experimental evidence.

1. Introduction

The extensive use of synchrotron-radiation photoemission has produced an enormous amount of experimental information on semiconductor heterojunction band discontinuities [1, 2]. In spite of the existence of a few self-consistent calculations to determine these magnitudes for some particular cases [3–5], the theoretical effort is more concentrated on simpler models [6–8] suitable for a large set of heterojunctions. In general these models try to obtain band discontinuities from bulk properties including in some cases [7] corrections due to the charge redistribution at the interface (IF). The physical ideas introduced long ago for metal–semiconductor junctions [9] and semiconductor heterojunctions [8] are properly developed in this paper by performing detailed calculations for heterojunctions within the same scheme recently used for metal–semiconductor junctions [10]. The main contribution to band offsets comes from the alignment of the charge neutrality points of both semiconductors, i.e. the energies up to which the density of states must be occupied to obtain local charge neutrality in the bulk of each semiconductor. Afterwards, a non-negligible correction must be introduced due to the charge redistribution in a few layers around the IF. We apply the method to GaAs–AlAs and InAs–GaSb (100) heterojunctions where some controversy exists on the electronic band structure [11, 12].

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2. Method

We describe both semiconductors by means of a tight-binding method, including only first-nearest-neighbour interaction. Self-consistency is introduced in the calculation by means of different diagonal perturbations, V_i, at five layers around the interface; these parameters are determined by imposing electrostatic consistency among the perturbations, V_i, and the charges, n_j, induced at each layer [10].

A crucial point coming out of this analysis is that small transfers of charge between the two crystals induce large electrostatic potentials [10]. Based on this fact, we can use a first-order approximation and assume that the charges of both crystals are unaltered except for two layers at the IF (see fig. 1), in such a way that the electrostatic potentials of both crystals are lined up.

Fig. 1 describes this first approximation. In the bulk of an ionic semiconductor there is a non-zero charge, Q, on each anion and $-Q$ on each cation creating an electrostatic potential. The alignment of the mean electrostatic potentials of semiconductors α and β is obtained when the charges on the two IF layers are $-(3Q_\alpha + Q_\beta)/4$ and $(Q_\alpha + 3Q_\beta)/4$ as fig. 1 shows (distance between layers are assumed to be the same in all cases). This is for two semiconductors with no common anion or cation as is the case of InAs–GaSb. For GaAs–AlAs, where there is a common ion, the sequence of charges is

$$\ldots, Q_\alpha, (-Q_\alpha)\ \tfrac{1}{2}(Q_\alpha + Q_\beta)\ (-Q_\beta)\ Q_\beta, \ldots .$$

In a first approximation we determine $V_1 \ldots V_5$ in order to have the sequence of charges just discussed (the IF is assumed not to perturb deeper layers).

The computation of local charge densities requires the calculation of the local densities of states on each layer parallel to the IF. For this purpose we compute the Green function of the system projected on each layer by means of a tight-binding approach where the spin–orbit interaction is included in a

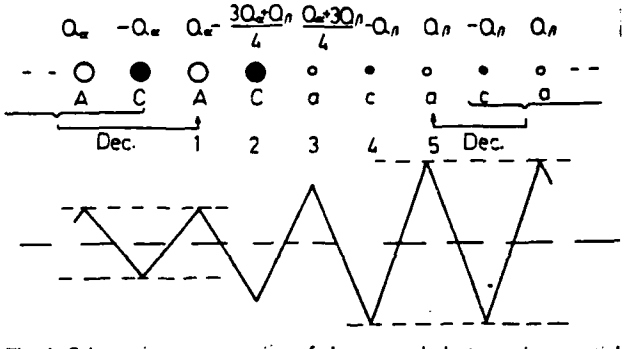

Fig. 1. Schematic representation of charges and electrostatic potentials at the IF in the case of a heterojunction with no common anion or cation.

sp^3s^* basis (details of this calculation will be published elsewhere).

The relative position of the two semiconductor is given usually interms of the offset $\Delta E_v^{(0)}$ between the tops of the valence bands. If the potential, $V_5^{(0)} - V_1^{(0)}$, we have calculated in the first approximation coincides with the difference between the mean potentials of the two semiconductors, having excluded the Hartree potentials, no net flux of charge would take place and the solution calculated in the first approximation appears to be already consistent. However, this is not usually the case and a full self-consistent calculation is necessary; changes in $V_5 - V_1$ would give the change in $\Delta E_v^{(0)}$ due to the self-consistent calculation.

3. Results

We have applied the method described in section 2 to the heterojunction GaAs–AlAs, InAs–GaSb and GaSb–InAs along the (100) direction. Technical points have been treated as in ref. [10] except for the integration in $k_\parallel$ that we have performed by means of 16 special points in the irreducible part of the two-dimensional Brillouin zone. Fig. 2 shows the local density of states on several atomic layers both around the IF and at the bulk for the GaSb–inAs heterojunctions as an example of the type of results we get. Numerical results for the potentials at the IF and the band offset are given in table 1 both for the first step of our procedure and for the final consistent results. It is of interest to note that the final consistent calculation is rather close to the

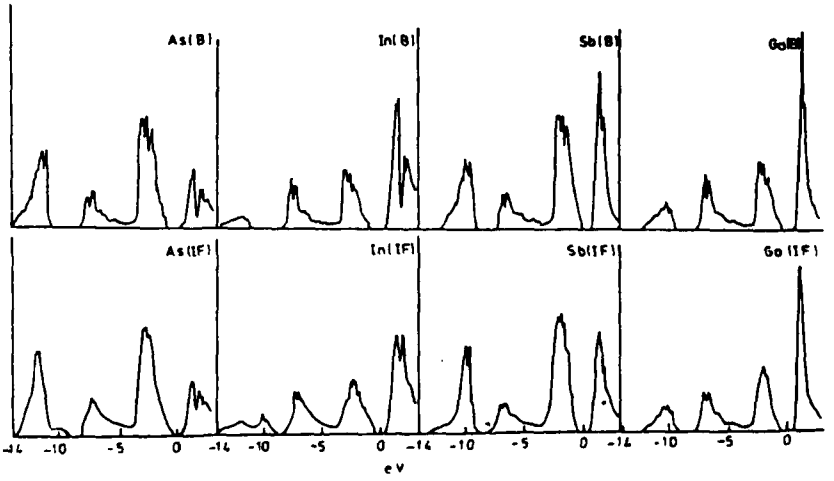

Fig. 2. Local density of states for bulk (B) and interface (IF) layers as a function of the energy (in eV) in the GaSb–InAs heterojunction.

Table 1
Atomic levels around the IF V_i and valence band offset ΔE_v (in eV) for three different heterojunctions; the magnitudes with superscript have been obtained in the first step of the calculation (see text); the magnitudes without superscript are the final consistent values; $V_1^{(0)}$ and V_1 are taken zero

	As Ga As Al As	As In Sb Ga Sb	Sb Ga As In As
$V_2^{(0)}$	−0.011	−0.086	−0.343
V_2	0.025	0.024	−0.480
$V_3^{(0)}$	−0.185	−0.261	−0.449
V_3	−0.219	−0.299	−0.383
$V_4^{(0)}$	−0.308	−0.187	−0.450
V_4	−0.286	−0.201	−0.431
$V_5^{(0)}$	−0.251	−0.170	−0.335
V_5	−0.248	−0.044	−0.341
$\Delta E_v^{(0)}$	−0.505	0.610	−1.115
ΔE_v	−0.502	0.736	−1.121

results given by the first step: similar conclusions have been reached in the metal/semiconductor junction [10]. As stated above, this is due to the small transfer of charge appearing between both crystals.

Comparing now our results with the experimental information we find:
(i) GaAs–AlAs. In this case ΔE_V has been accepted long since to be 0.25 eV, a result obtained by extrapolating [14] for $x \to 1$ the experimental data for GaAs–$Ga_{1-x}Al_xAs$. However, recent experimental information [11] yields $\Delta E_V = 0.65$ eV and a heavy hole effective mass $m_h^* = 0.34$. Since the tight-binding parameters we use in our calculation must give good energy levels at high symmetry points, we cannot get any desired value of m_h^*. The best value we get is $m_h^* = 0.41$; then, we obtain the result $\Delta E_V = 0.50$ eV given in table 1. The comparison with experimental results requires an estimation of the error involved in our approximations. We think that this uncertainty must be of the order of 0.1 eV which would imply satisfactory agreement between our result and the most recent experimental value.
(ii) InAs–GaSb. In this case the most interesting result is that we find a difference of 0.4 eV between the band offset of InAs–GaSb and GaSb–InAs. The difference is high enough to allow for the experimental determination of either the particular IF appearing in actual samples, or the electric field associated with two different IFs appearing at a superlattice.

Acknowledgements

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References

[1] A.D. Katnaui and G. Margaritondo, Phys. Rev. B28 (1983) 1944.
[2] G. Margaritondo, Phys. Rev. B31 (1985) 2526, and references therein.
[3] G.A. Baraff, J.A. Appelbaum and D.R. Hamann, Phys. Rev. Letters 38 (1977) 237;
W.E. Pickett, S.G. Louie and M.L. Cohen, Phys. Rev. B17 (1978) 815;
K. Kunc and R.M. Martin, Phys. Rev. B24 (1981) 3445.
[4] J. Ihm, P.K. Lam and M.L. Cohen, Phys. Rev. B20 (1979) 4120.
[5] J. Sánchez-Dehesa and C. Tejedor, Phys. Rev. B26 (1982) 5824.
[6] W.A. Harrison, J. Vacuum Sci. Technol. 14 (1977) 1016;
W.R. Frensley and H. Kroemer, Phys. Rev. B16 (1977) 2642.
[7] F. Flores and C. Tejedor, J. Phys. C12 (1979) 731.
[8] J. Tersoff, Phys. Rev. B30 (1984) 4874.
[9] C. Tejedor, F. Flores and E. Louis, J. Phys. C10 (1977) 2163.
[10] F. Guinea, J. Sànchez-Dehesa and F. Flores, J. Phys. C16 (1983) 6499;
J. Sánchez-Dehesa, F. Flores and F. Guinea, J. Phys. C17 (1984) 2039;
J. Sánchez-Dehesa and F. Flores, Solid State Commun. 50 (1984) 29.
[11] R.C. Miller, A.C. Gossard, D.A. Kleinman and O. Munteanu, Phys. Rev. B29 (1984) 3740;
R.C. Miller, D.A. Kleinman and A.C. Gossard, Phys. Rev. B29 (1984) 7085.
[12] M. Altarelli, Phys. Rev. B28 (1983) 842.
[13] F. Guinea, C. Tejedor, F. Flores and E. Louis, Phys. Rev. B28 (1983) 4397.
[14] R. Dingle, in: Advances in Solid State Physics, Vol. 15. Festkörperprobleme, Ed. M.J. Queisser (Pergamon/Vieweg, London/Braunschweig, 1975) p. 21.

BAND-OFFSET CALCULATIONS OF (100)-SEMICONDUCTOR HETEROJUNCTIONS: A SIMPLE CONSISTENT METHOD

G.Platero, J.Sánchez-Dehesa, C.Tejedor y F.Flores

Departamento de Física del Estado Sólido,
Universidad Autónoma, Cantoblanco, 28049 Madrid,
Spain

A simple consistent tight-binding method is presented to analyse the electronic structure and the band-offset of ionic semiconductor interfaces. Our model is an extension of the model based on the charge neutrality level concept, and our procedure allows us to calculate the induced interface dipole between both semiconductors. We present results for GaAs-AlAs, GaSb-InAs and InAs-GaSb (100) heterojunctions. Our results yield a reasonable agreement with the experimental evidence, and show different band-offsets for the GaSb-InAs and InAs-GaSb heterojunctions.

1. INTRODUCTION

Many electronic properties of superlattices depend crucially on the band offsets between the different semiconductors forming the junction. Much experimental and theoretical work has been addressed to measuring and calculating the band discontinuities at the heterojunctions [1,2].

The theoretical work can be classified into two main groups. In one class of papers, people have tried to give simple prescriptions to calculate the band discontinuities [3-6], using bulk properties of each semiconductor. One of the most promising ideas in this kind of approach was introduced some time ago in Ref.5, and recently reformulated and discussed by Tersoff [6] and Margaritondo [2]. The main concept behind this model is the charge neutrality level, the energy up to which electronic levels are filled in a free surface. Band alignments between semiconductors are obtained by aligning the two charge neutrality levels of both semiconductors: the idea supporting this "rule of thumb" is that, otherwise, a strong electrostatic dipole would be induced at the interface trying to restore the equilibrium position defined by the charge neutrality levels alignment. The recent results presented by Margaritondo [2] give a strong support to this kind of approach, although the agreement between theory and experiment is by no means perfect.

In a second class of papers, some people have tried to analyse heterojunctions by means of a full self-consistent calculation using a pseudopotential approach [7-9]. No doubt this is the more exact approach, and were the calculations simpler to perform and less computer time-consuming, we would have in

this method the more appropriate theoretical recipee to analyse heterojunctions.

The aim of this paper is to present a method to calculate heterojunctions filling the gap between the two kind of work referred to above. Here we present a theoretical model to calculate the heterojunction, based on a tight-binding method supplemented with an appropriate consistency; this method offers a step forward compared with the simpler models discussed above. Moreover, and this is the crucial idea behind our approach, our model is an extension of the model based on the charge neutrality level concept. In other words, the consistency of our calculation tries to take into account the charge neutrality conditions and the induced interface dipole that gives the basis to the simple model referred to above. Let us mention that similar ideas have been put forward for the metal-semiconductor junctions [10-12]. In this case, a tight-binding model supplemented with a Hartree consistency has been recently used to calculate the Schottky barrier heights. Results have been encouraging, showing a good agreement with the experimental evidence and other more elaborate approaches.

In §2 we discuss our model, our method of calculation and the consistency. In §3 we present and discuss our results as applied to GaAs-AlAs, GaSb-InAs and InAs-GaSb (100) heterojunctions.

2. MODEL, METHOD OF CALCULATION AND CONSISTENCY

The electronic band structures of the different semiconductors are described by means of a tight-binding model, using

sp^3s^* hybrids [13] in each atom and including interaction parameters that extend up to first neighbours. Table 1 gives the parameters used in our calculation for GaAs, AlAs, GaSb and InAs. In our model, we assume that the two crystals match perfectly and that the bulk parameters extend up to the interface, except for some diagonal perturbations introduced at some interface layers to impose consistency (see below). In our calculation we have also included the spin-orbit interaction that appears to be important for heavy atoms like Sb. The parameters given in Table 1 are similar to the ones proposed by Vogl et al.[3], except by small corrections introduced to allow for the spin-orbit interaction (the parameters given in Table 1 have been chosen to give the right levels at specific symmetric points). The parameters defining the semiconductor-semiconductor interactions are associated with the last layer of the crystals: they are defined by taking the interaction parameters for the crystal formed by the corresponding anion and cation.

Having defined our interactions (except for the diagonal perturbations near the interface), we have a well-known Hamiltonian. Our next task is to discuss how we calculate the interface properties: charge, density of states, etc.

In our method of calculation we follow the procedure explained in Ref.14. In few words, our method consists in looking for the surface components of the Green function of the system. By means of a decimation technique, we can project the bulk components of the Green function onto a few layers of the interface. In our actual case, we have projected all the electronic bulk structure of each semiconductor onto the last three layers

of the same semiconductor, the reason being that calculations in free surfaces [15] show that only the last three layers of the semiconductor are perturbed by the surface. Thus, for GaSb-InAs, this means that the whole system is projected onto six layers, three for GaSb and three for InAs. For GaAs-AlAs, the same procedure yields only five layers, since there is a central As-atom belonging to the two semiconductors at the same time. This means that the whole Hamiltonian is reduced to an effective matrix-Hamiltonian having 60x60 elements in GaSb-InAs and 50x50 elements in GaAs-AlAs (including spin and five orbitals per layer). From this matrix, we can analyse the different properties of the interface, once we have introduced at each layer the diagonal perturbations to be related to the interface consistency.

Let us consider now how to get consistency in our problem. We present our discussion in two steps, starting with the InAs-GaSb heterojunction (GaAs-AlAs will be discussed later on).

In Figure 1 we show an ideal InAs-GaSb heterojunction after averaging the charges in the sense parallel to the surface. For InAs we assume that the charges per atom inside the crystal are $3-\beta(In)$ and $5+\beta(As)$, while for GaSb the charges are assumed to be $3-\alpha(Ga)$ and $5+\alpha(Sb)$. The ideal case shown in Figure 1 is defined by assuming that the electrostatic potential inside each crystal is the same as in the bulk, and that both mean electrostatic potentials are equal. Notice that for these conditions, the charges in each layer coincide with the bulk charges except for the last layers of each semiconductor (in Figure 1, As for InAs and Ga for GaSb). Charges in those layers must be modified in order to have both mean electrostatic crystal potentials at

the same level. This condition yields (see Figure 1):

$$\alpha' = \frac{3\alpha+\beta}{4} \tag{1a}$$

$$\beta' = -\frac{3\beta+\alpha}{4} \quad . \tag{1b}$$

The ideal situation shown in Figure 1 allows us to define a starting point for which the different parameters appearing in the Hamiltonian are given by the bulk parameters of each crystal if the two mean levels of both crystals are corrected in order to take into account the condition of equality for the mean electrostatic potentials. That means that for the charges shown in Figure 1, we can expect to have at each layer the ideal parameters defined for a bulk Hamiltonian: thus, assume we take the parameters of Table 1 for InAs; then, for GaSb we must take for the atomic levels of each atom the values of Table 1 but corrected by a constant, Δ, putting the mean electrostatic potential of both crystals at the same level. This value, Δ, can be taken from an independent information about the surfaces of each crystal [16,17]. On the other hand, the hopping interaction between the orbitals of Ga and As, at the interface, are taken from the values corresponding to GaAs.

Once we have defined this initial situation, we now allow for changes in the charges and potentials of the layers around the interface. Notice that for the initial potentials defined above, we can obtain the charges at each layer by solving the total Hamiltonian: in general, the charges at each layer do not coincide with the initial charges shown in Figure

1. In our consistent procedure, we allow for changes in the potentials of layers 2, 3, 4, 5 and 6 (taking layer 1 as a reference layer), and assume that the mean level of GaSb is shifted by the same value of layer 6. Then, the changes in the potentials, δV_2, δV_3, ..., δV_6 are related to the charges of each layer through a kind of consistent equation. This means that δV_i are defined as the electrostatic potential created by the charges δn_i, as measured with respect to the ideal case shown in Figure 1. Thus,

$$\begin{aligned}
\delta V_2 &= \alpha d \delta n_1 \\
\delta V_3 &= \alpha d \delta n_1 + \alpha d (\delta n_1 + \delta n_2) \\
&\quad \vdots \\
\delta V_6 &= \alpha d \delta n_1 + \alpha d (\delta n_1 + \delta n_2) + \ldots + \alpha d (\delta n_1 + \delta n_2 + \delta n_3 + \delta n_4 + \delta n_5),
\end{aligned} \tag{2}$$

where d is the interlayer distance (assumed to be a constant) and $\alpha = 4\pi/A$, A being the area per surface atom.

Notice that in our actual case we have found that equation

$$\delta n_1 + \delta n_2 + \ldots + \delta n_5 + \delta n_6 = 0 \tag{3}$$

is verified with a very good approximation (this means that the interface perturbation only penetrates three layers into each semiconductor).

Eqs.(2) define our consistent conditions, and allow us

to obtain the final perturbations, δV_i, and the final charges at the interface.

The GaAs-AlAs interface can be analysed in similar terms. Figure 2 defines the starting point for this heterojunction. Here, we assume that the electrostatic crystal potential for each crystal is not modified up to the central layer of As. In this initial situation, we assume both crystals to have the same mean electrostatic potential (as in the previous case, that means that the atomic levels of one crystal, say GaAs, have to be shifted by a constant, Δ, with respect to the atomic levels of AlAs). The greater difference with the previous case appears for the central atom: as Figure 2 shows, the ideal potential associated with each ideal crystal yields a different potential for the central As-atom. We define the starting case by taking for this central atom the averaging of the two potentials associated with each crystal. Then, the starting potential looks like the one shown by the continuous line of Figure 2; for this potential we have to introduce some transfer of charge among layers 2, 3 and 4. It is easy to see that the initial charges defined by the initial electrostatic potential are given by (see Figure 2):

$$\delta' = \frac{7\delta+\gamma}{8} \tag{4a}$$

$$\gamma' = \frac{7\gamma+\delta}{8} \tag{4b}$$

$$\omega = \frac{\gamma+\delta}{2} \quad . \tag{4c}$$

Once we have defined the initial case, we look for consistency allowing for changes in the potentials at layers 2, 3, 4 and 5. Then, V_2... and V_5 are determined consistently by writing the following Hartree equations:

$$\begin{aligned}
\delta V_2 &= \alpha d \delta n_1 \\
\delta V_3 &= \alpha d \delta n_1 + \alpha d(\delta n_1 + \delta n_2) \\
&\quad \cdot \\
&\quad \cdot \\
&\quad \cdot \\
\delta V_5 &= \alpha d \delta n_1 + \alpha d(\delta n_1 + \delta n_2) + \ldots + \alpha d(\delta n_1 + \ldots + \delta n_4) \quad ,
\end{aligned} \tag{5}$$

where d is the interlayer distance, and $\alpha = 4\pi/A$, A being again the area per surface atom.

Eqs.(5) define the consistent equations for the GaAs-AlAs interface. Notice that δn_i must be consistent with the values calculated by introducing δV_i in the total Hamiltonian.

3. RESULTS AND DISCUSSION

We have analysed the ideal interfaces associated with the following heterojunctions: GaAs-AlAs, InAs-GaSb and GaSb-InAs. (for InAs-GaSb the interface corresponds to atoms of As and Ga, while for GaSb-InAs, it corresponds to Sb and In). Technical points have been treated as in Ref.10, except for the integration in the momentum parallel to the interface, which we have performed by means of 16 special points in the irreducible part of the two-dimensional Brillouin zone.

In our calculations, we have used the following values of Δ [16,17]:

Δ (GaAs-AlAs) = 0.26 eV

Δ (GaSb-InAs) = 0.78 eV.

The different diagonal perturbations calculated consistently for the different interfaces are given in Table 2. For GaAs-AlAs we have obtained an interface dipole of -0.13 eV (the value of V_5 in Table 2), and the following discontinuity between the top of the valence bands:

$$\Delta E_V = \Delta + V_5 = 0.41 \text{ eV (GaAs-AlAs)} \quad . \tag{6}$$

(Δ is the valence band-offset for no interface dipole).

Figure 3 shows the local density of states on several atomic layers around the interface of a consistent GaAs-AlAs junction. For GaSb-InAs, we have calculated an interface dipole of -0.26 eV (the value of V_6 in Table 2), and the following discontinuity in the top of the valence bands [21]:

$$\Delta E_V = \Delta + V_6 = 0.52 \text{ eV (GaSb-InAs)} \quad , \tag{7}$$

while for InAs-GaSb, our calculations yield for the interface dipole 0.53 eV, and

$$E_V = \Delta + V_6 = 1.31 \text{ eV (InAs-GaSb)} \quad . \tag{8}$$

Figures 4 and 5 show the local density of states on several layers around the interfaces of GaSb-InAs and InAs-GaSb, respectively.

The important difference between the GaSb-InAs and InAs-GaSb interfaces comes from the different interface dipoles appearing in both cases (-0.26 eV and 0.53 eV, respectively). Note that we can go from one to the other interface by substituting an In for a Ga atom. The different dipoles appearing for both interfaces are associated with the sequences ...-Sb-Ga-As-... and ...-Sb-In-As-... of both junctions. Thus, the different atoms of Ga and In are controlling the way in which the electronic charge is transferred from Sb to As and, finally, from one to other crystal. The crucial point is that the InAs bond is associated with an important transfer of electronic charge towards As; when In is substituted for Ga, part of this charge is transferred from As to Sb creating an interface dipole decreasing the valence band discontinuities.

Comparing now our results with other experimental and theoretical information we find:

(i) GaAs-AlAs. For this case, ΔE_V has been accepted long since to be 0.25 eV [18], a result obtained by extrapolating for $x \to 1$, the experimental data for GaAs-$Ga_{1-x}Al_xAs$. However, recent experimental information [19] yields ΔE_V = 0.65 eV. Our result of 0.41 eV is in a reasonable agreement with that information; note in that respect that the accuracy of our calculation is around ±0.05 eV, and that the error involved in the approximations of our method is estimated to be around ±0.1 eV.

(ii) InAs-GaSb and GaSb-InAs. In this case we find the

following band-offset discontinuities: 1.31 eV (InAs-GaSb) and 0.52 eV (GaSb-InAs). These values have to be compared with the experimental data of 0.57 eV [20]. According with the errors involved in our method (see above), we conclude that only the value found for the GaSb-InAs interface seems to be in good agreement with the experimental evidence. This seems to suggest that the actual interface of GaSb and InAs correspond to the GaSb-InAs case. However, a word of caution must be put here, since the calculations presented in this paper have been performed neglecting the mismatch between both crystals; the effect of this mismatch ought to be analysed before definitive conclusions are drawn.

Let us finally comment that the different band-offset discontinuities found for the GaSb-InAs and InAs-GaSb interfaces seem to be at variance with results reported by Picket et al.[8]. In this sense, it is of interest to comment that in this last calculation the number of layers used in each superlayer of each semiconductor is small enough (only 5) to allow for an important interaction between different interfaces; note in this respect that the interface perturbation penetrates at least three layers in each semiconductor.

Acknowledgments

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REFERENCES

1. A.D.Katnami and G.Margaritondo, Phys.Rev.B, 28, 1944 (1983)
2. G.Margaritondo, Phys.Rev.B, 31, 2526 (1985)
3. W.A.Harrison, J.Vac.Sci.Technol., 14, 1016 (1977)
4. W.R.Freusley and H.Kroemer, Phys.Rev.B, 16, 2642 (1977)
5. C.Tejedor and F.Flores, J.Phys.C, 11, L19 (1978); F.Flores and C.Tejedor, J.Phys.C, 12, 731 (1979)
6. J.Tersoff, Phys.Rev.B, 30, 4874 (1984)
7. G.A.Baraff, J.A.Appelbaum and D.R.Hamann, Phys.Rev.Lett., 38, 237 (1977)
8. W.E.Pickett, S.G.Louie and M.L.Cohen, Phys.Rev.B, 17, 815 (1978)
9. K.Kunc and R.M.Martin, Phys.Rev.B, 24, 3445 (1981)
10. F.Guinea, J.Sánchez-Dehesa and F.Flores, J.Phys.C, 16, 6499 (1983)
11. J.Sánchez-Dehesa, F.Flores and F.Guinea, J.Phys.C, 17, 2039 (1984)
12. J.Sánchez-Dehesa and F.Flores, Solid State Commun., 50, 29 (1984)
13. P.Vogl, H.P.Hjalmarson and J.D.Dow, J.Phys.Chem.Solids, 44, 365 (1983)
14. F.Guinea, C.Tejedor, F.Flores and E.Louis, Phys.Rev.B, 28, 4397 (1983)
15. G.Platero, J.Sánchez-Dehesa, C.Tejedor, F.Flores and A. Muñoz, to be published
16. J.Sánchez-Dehesa and C.Tejedor, Phys.Rev.B, 26, 5824 (1982)
17. J.Ihm, P.K.Lam and M.L.Cohen, Phys.Rev.B, 20, 4120 (1979)

18. R.Dingle, Festkörperprobleme, 15, 21 (1975)

19. R.C.Miller, A.C.Gossard, D.A.Kleinman and O.Munteanu, Phys. Rev.B, 29, 3740 (1984); R.C.Miller, D.A.Kleinman and A.C. Gossard, Phys.Rev.B, 29, 7085 (1984)

20. G.A.Sai-Halasz, L.L.Chang, J.M.Welter, C.-A.Chang and L.Esaki, Solid State Commun., 27, 935 (1978)

21. G.Platero, J.Sánchez-Dehesa, C.Tejedor and F.Flores, Surface Sci.(1985), Proc.1st Int.Conf.on the Formation of Semiconductor Interfaces. This is a preliminary report about the work presented in this paper: there are some changes in the final results due to a better accuracy in the numerical calculation.

TABLE 1.- Tight-binding and spin-orbit parameters (in eV). Notation is $E_\alpha = \langle\alpha|H|\alpha\rangle$, $V_{\alpha\beta} = \langle\alpha|H|\alpha\rangle$ and $\lambda^{so} = \langle x\uparrow|H_{so}|z\downarrow\rangle$.

	GaAs	AlAs	GaSb	InAs
E_{sa}	-8.345	-7.525	-7.305	-9.545
E_{pa}	0.985	0.940	0.720	0.835
E_{sc}	-2.655	-1.165	-3.885	-2.725
E_{pc}	3.615	3.540	2.780	3.645
E_{s^*a}	8.591	7.483	6.635	7.410
E_{s^*c}	6.739	6.727	5.985	6.740
V_{ss}	-1.613	-1.666	-1.543	-1.400
V_{xx}	0.505	0.483	0.434	0.483
V_{xy}	1.255	1.061	0.997	1.098
V_{s_ap}	1.117	1.276	1.238	0.753
V_{s_cp}	2.240	1.369	1.159	1.352
$V_{s^*_ap}$	1.210	1.130	1.247	0.844
$V_{s^*_cp}$	1.202	1.249	1.054	0.977
λ^{so}_a	0.140	0.140	0.324	0.140
λ^{so}_c	0.058	0.008	0.058	0.131

TABLE 2.- Diagonal perturbations (in eV) on the different layers around the interface.

	δV_1	δV_2	δV_3	δV_4	δV_5	δV_6
As-Ga-As-Al-As	0	0.01	-0.18	-0.30	-0.13	-
In-As-In-Sb-Ga-Sb	0	-0.01	-0.08	-0.25	-0.22	-0.25
Ga-Sb-Ga-As-In-As	0	-0.01	-0.29	-0.48	-0.56	-0.55

Figure Captions

Figure 1. Electrostatic potential of an ideal InAs-GaSb heterojunction after averaging the charges in the sense parallel to the interface.

Figure 2. As Fig.1 for a GaAs-AlAs heterojunction.

Figure 3. Local density of states on different atomic layers around the interface of a GaAs-AlAs junction.

Figure 4. As Fig.3 for GaSb-InAs.

Figure 5. As Fig.3 for InAs-GaSb.

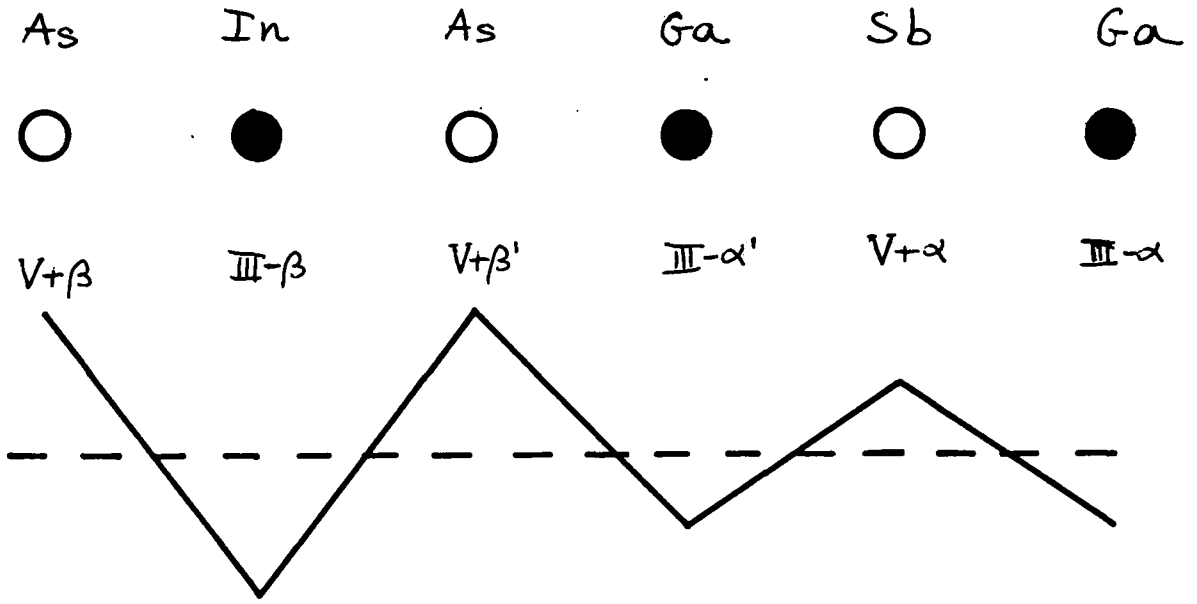

Fig. 1

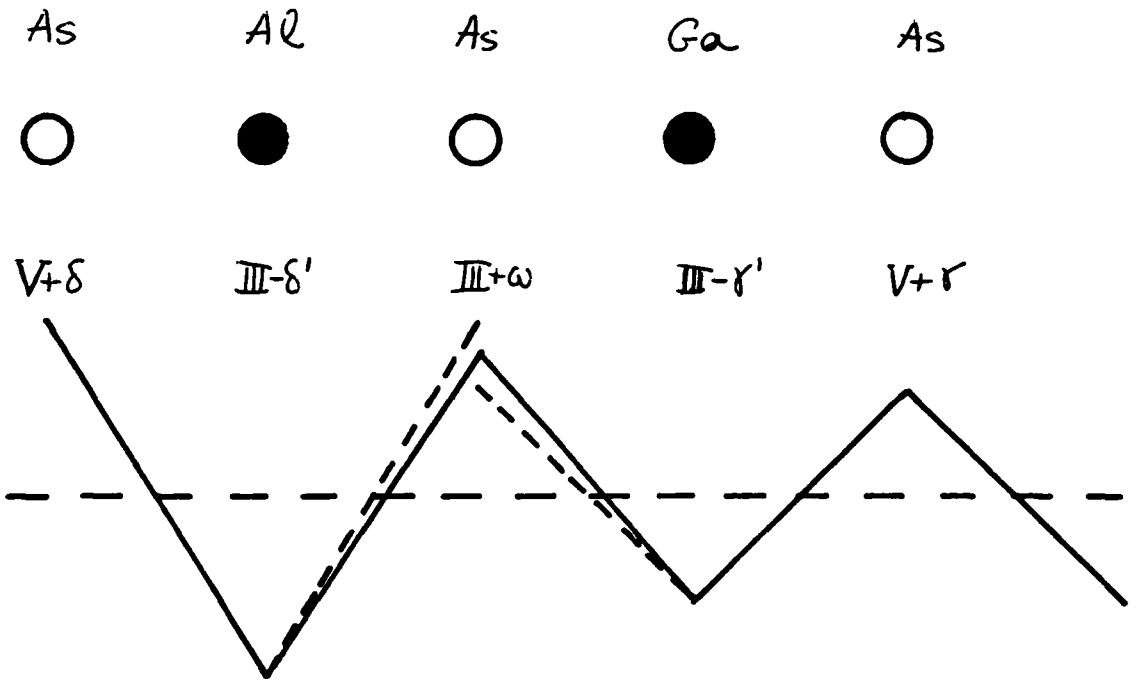

Fig 2

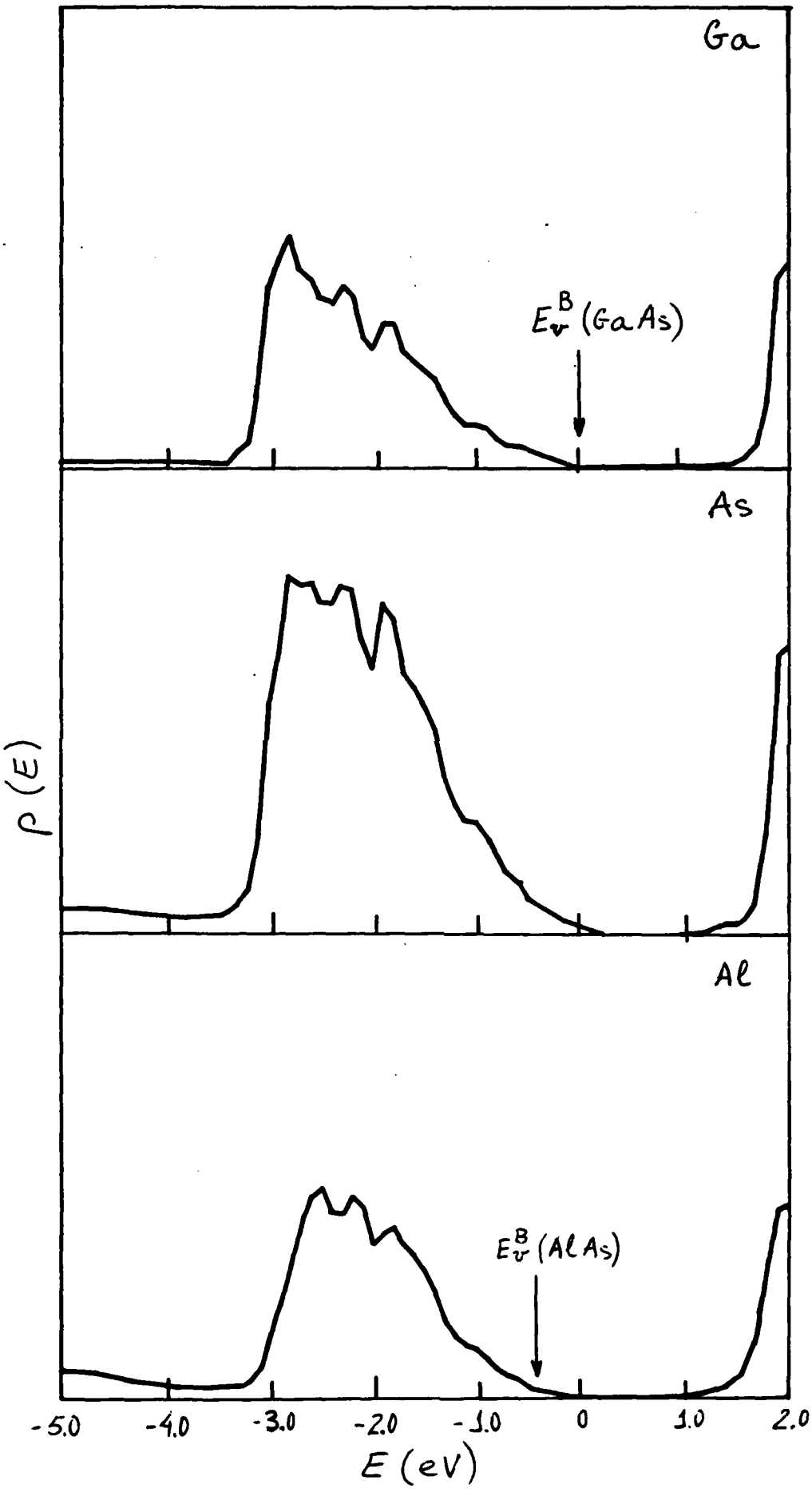

Fig. 3

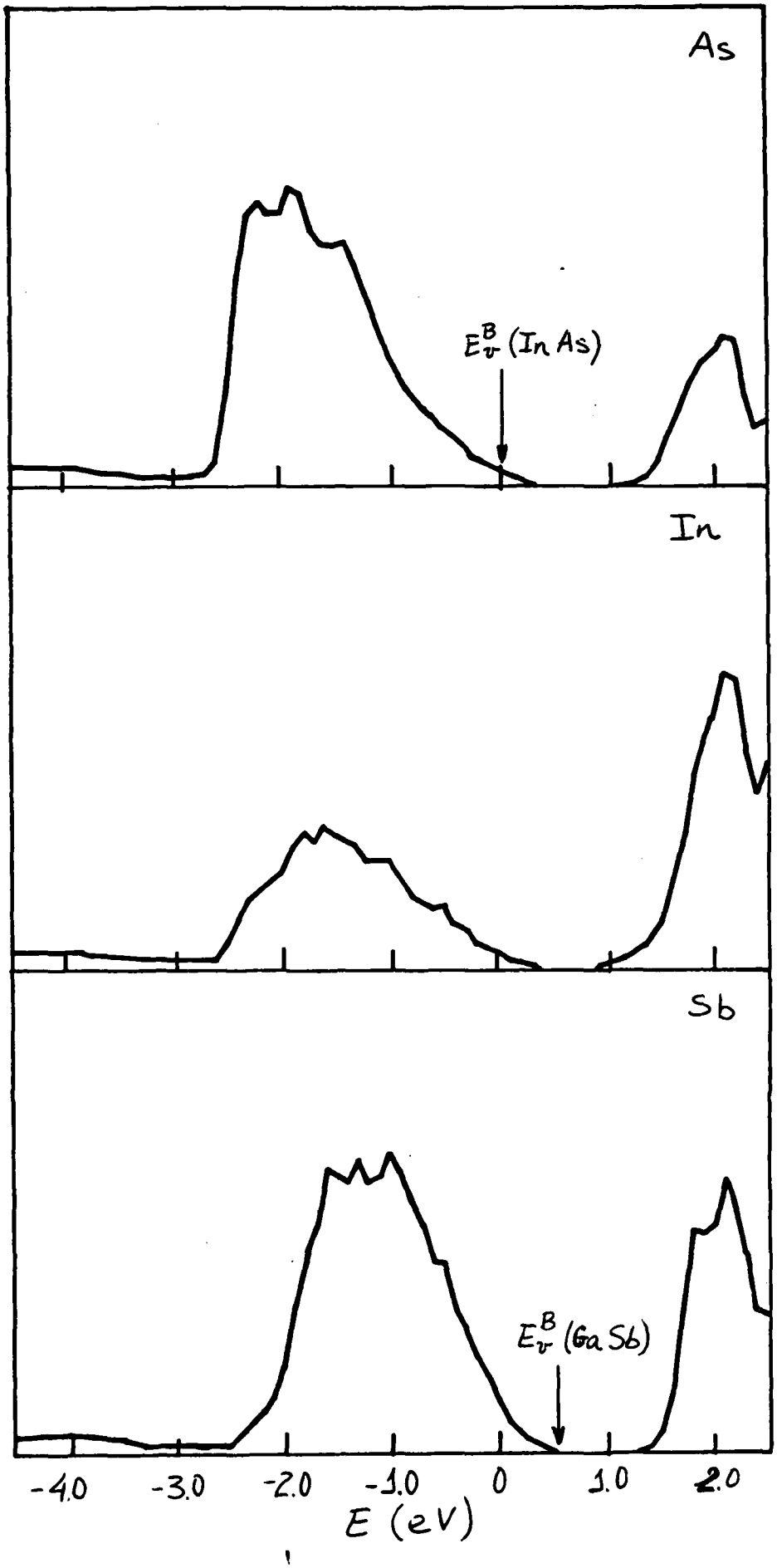

Fig. 4

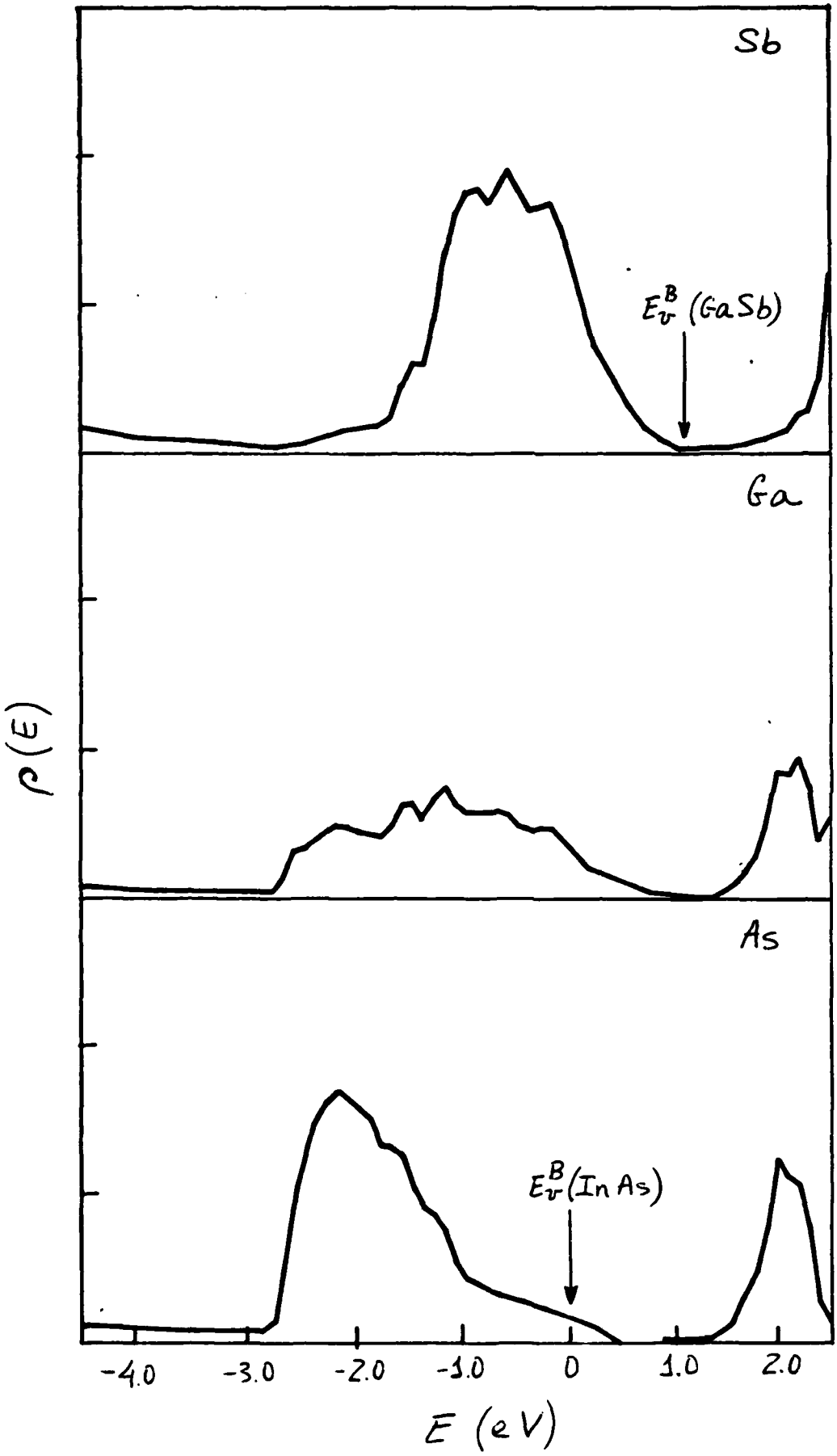

Fig. 5

INITIAL STAGES OF THE SCHOTTKY-BARRIER FORMATION FOR ABRUPT COVALENT INTERFACES

G. PLATERO, J.A. VERGÉS and F. FLORES

Departamento de Física del Estado Sólido, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

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The initial stages of the Schottky-barrier formation for an Al–Si contact are theoretically analysed. Four different geometrical configurations are discussed, and their charge neutrality level, interface Fermi level and local density of states are calculated. We conclude that the Schottky barrier is formed with a monolayer and that the charge neutrality level at the junction is a function of the metal–semiconductor interaction.

The mechanism of the Schottky-barrier formation is a matter of current controversy [1]. Several models have been proposed in the last few years. The defect model [2] seems to be very appropriate for ionic semiconductors; the problem with it is related to the number of defects necessary to pin the Fermi level at the interface. A different mechanism based on the concept of the charge neutrality level at the interface was first proposed by Tejedor et al. [3]; recently Guinea et al. [4] and Tersoff [5] have extended this approach, which seems to be particularly appropriate for abrupt interfaces with a well-defined separation between the metal and the semiconductor. In the mechanism of this model, charge neutrality conditions fix the interface Fermi level at an energy quite close to the Fermi level for a free surface. Detailed calculations using a self-consistent tight-binding method [4, 6] have shown that the Fermi level of the free surface can be slightly shifted in a junction, depending on the interaction between the last layers of the metal and the semiconductor. Experimental results tend to support these findings; thus, Margaritondo et al. [7] have found that for Al, Ga and In on Si, the Fermi level at the interface moves downwards, with respect to the free surface, by 0.2, 0.3 and 0.4 eV, respectively.

In this paper we consider the initial stages in the Schottky barrier formation; in particular, we have analysed the case of a monolayer of Al on Si. This case has been studied experimentally [8], and the evidence seems to indicate that the Schottky barrier is already formed with only a monolayer.

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In previous papers, Chang and Schlüter [9], and Chelikowsky [10] have analysed theoretically the same problem for a monolayer in a Lander substitutional geometry and in other surface configurations. One of these latter configurations corresponds to an Al atom on top of a Si surface atom, another corresponds to an Al atom placed on a three-fold coordinated site. The analysis of Chang and Schlüter [9] tends to support a three-fold coordinated site for the Al atom. However, the theoretical results of these authors show that the Fermi level at the surface is shifted to higher energies with respect to the Fermi level of the free surface by 0.2 eV, this result being in conflict with the fact that, for a full monolayer, the barrier is completely formed and that the Fermi level for the junction is located at lower energies than the Fermi level for the free semiconductor surface.

In this work, we reconsider the problem of a monolayer of Al on Si, and discuss four different configurations: the top position, two three-fold coordinated positions which, following Northrup [11], will be called the T_3 and H_4 configurations (Northrup has shown that the H_4 site, with an Al atom placed in a three-fold site having a Si atom underneath in the second layer, is the most stable for a $\sqrt{3} \times \sqrt{3}$ configuration), and a Lander substitutional model. In our calculations, we have followed ref. [4], and have calculated the electronic density of states by means of a self-consistent tight-binding procedure. In table 1 we give the parameters used to calculate the Si band structure (these parameters are similar to the ones introduced by Pandey and Phillips [12]), the Al–Al interactions (a first-neighbours interaction calculated with an inverse square law) and the Si–Al interactions (calculated by taking a geometrical average between the interactions for the nearest neighbours of Si–Si and Al–Al).

Figs. 1 and 2 show the local density of states projected on the Al layer as calculated with our procedure for the top, H_3, T_4 and the substitutional configurations. For completeness, we have calculated results for a clean surface (in this latter case, the density of states is projected on the last Si layer). Our results show that: (i) in the top position, the local density of states in Al is more localised near the Fermi level, corresponding to a weaker interaction between Al and Si; (ii) the substitutional case is similar to the clean Si surface, but presenting empty surface states; (iii) the H_3 and T_4 positions have similar densities of states corresponding to similar interactions between Al and Si.

These results are in correspondence with the position of the Fermi level at the interface. Table 2 gives the shift of the Fermi level for the different interfaces as measured from its position at the free surface. In table 2 we also show the Fermi level for the case in which no transfer of charge is allowed between the metal and the semiconductor (this latter case defines the charge neutrality level for each interface). Our results show that the charge neutrality level of each interface is different and dependent on the interaction between the metal and the semiconductor. In the top position, the charge neutrality

Table 1
Different parameters defining the Hamiltonian used in the calculation (the Si–Al distance is taken the same in all the cases)

	Si–Si	Si–Al	Al–Al
E_s	−3.30	-	−0.65
E_p	1.10	-	2.65
$(ss\sigma)_1$	−2.08	−1.30	−0.32
$(sp\sigma)_1$	1.77	2.42	1.20
$(pp\sigma)_1$	2.52	2.99	1.28
$(pp\pi)_1$	−0.33	−0.16	0.0
$(pp\sigma)_2$	0.58	-	-
$(pp\pi)_2$	−0.10	-	-

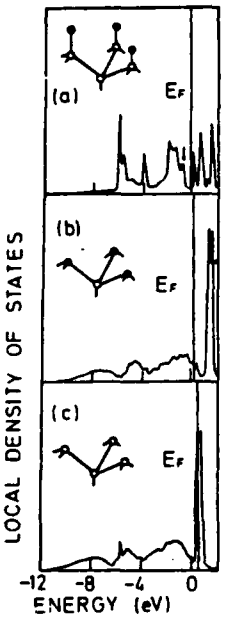

Fig. 1. Local density of states on the last Si layer for (a) the top position, (b) a Lander substitutional, and (c) a clean S surface. E_F = Fermi level. The arrow in (a) shows the specific surface peak found in photoemission experiments [7].

level is shifted downwards in energy, while for larger interactions between the metal and the semiconductor (H_3 and T_4 positions) that level is shifted upwards. Let us remark that the Fermi level does not exactly coincide with the charge neutrality level: the main reason is that for the full solution the charge neutrality case has to be relaxed, allowing for some transfer of charge between the metal layer and the last Si layer.

Let us comment at this point that the absolute values we have calculated for the Fermi level shift at different interfaces are too large due to the Pan-

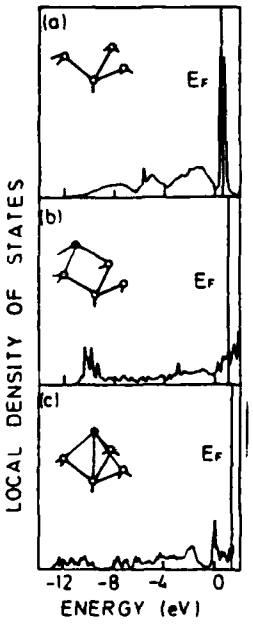

Fig. 2. As fig. 1 for (a) a clean surface, (b) a H_3 position, and (c) a T_4 position.

Table 2
The Fermi level, the charge neutrality level and the Fermi level shift for different geometries (the zero-energy level is located at the top of the Si valence band)

Geometrical position	E_F (eV)	Fermi level shift (eV)	Charge neutrality level (eV)
Si (clean surface)	0.55	-	0.55
Top	0.00	−0.55	−0.12
Substitutional	0.25	−0.30	0.00
H_3	1.10	0.55	0.92
T_4	1.40	0.85	1.60

dey–Phillips model we use for the semiconductor. As discussed in ref. [4], the Pandey–Phillips model yields values of the Fermi level shift which are too large by a factor of two, due to the large value of the thermal gap.

It is also interesting to note that the results calculated here for the Al top position are in good agreement with the ones given in ref. [4], for a semi-infinite metal having the atoms of the last layer located at the top position, too. This shows that the barrier height is practically formed with a monolayer, in agreement with experiments.

Comparing now with the experimental evidence [8], let us comment that (i) the Fermi level is shifted to lower energies for a well-formed contact, and that (ii) the density of states is very low near the Fermi level, showing a specific peak near 0.7 eV below the Fermi level. These results are in reasonable agreement with our calculations for the top position. In this case the Fermi level is shifted by 0.55 eV (a value too large by a factor of two), and the local density of states shows a similar peak to the one found in the experimental results (see fig. 1a).

We conclude that the Al monolayer is completed with the metal atoms located on the top position. Northrup's results suggest that a $\sqrt{3} \times \sqrt{3}$ Al monolayer has the metal atoms in a T_4 position. These two conclusions are not, however, contradictory if we consider the strong interaction operating between Al atoms in the full monolayer case.

Finally, it is worth stressing our results for the charge neutrality level of the junction. As our results have shown, that level is a *function* of the specific interaction between the last layers of the metal and the semiconductor. This is an important point which must be taken into account to explain the barrier heights of different junctions for the same semiconductor.

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References

[1] V. Heine, Proc. Roy. Soc. London 81 (1963) 300;
F. Yndurain, J. Phys. C4 (1971) 2849;
E. Louis, F. Yndurain and F. Flores, Phys. Rev. B13 (1976) 4408.
[2] W.E. Spicer, P.W. Chye, P.R. Skeath, C.Y. Su and I. Lindau, J. Vacuum Sci. Technol. 16 (1979) 1422.
[3] C. Tejedor, F. Flores and E. Louis, J. Phys. C10 (1977) 2163.
[4] F. Guinea, J. Sánchez-Dehesa and F. Flores, J. Phys. C16 (1983) 6499.
[5] J. Tersoff, Phys. Rev. Letters 52 (1984) 465.
[6] J. Sánchez-Dehesa and F. Flores, Solid State Commun. 50 (1984) 29.
[7] G. Margaritondo, J.E. Rowe and S.B. Christmann, Phys. Rev. B14 (1976) 5396.

[8] D. Bolmont, P. Chen and C.A. Sébenne, J. Physique C5 (1984) 419.
[9] H.I. Zhang and M. Schlüter, Phys. Rev. B18 (1978) 1923.
[10] J.R. Chelikowsky, Phys. Rev. B16 (1977) 3818.
[11] J.G. Northrup, Phys. Rev. Letters 53 (1984) 683.
[12] K.C. Pandey and J.C. Phillips, Phys. Rev. B13 (1976) 750.
[13] W.A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980).

INITIAL STAGES OF THE SHCOTTKY BARRIER FORMATION FOR AN ABRUPT Al-GaAs(100) INTERFACE

G.Platero, J.Durán and F.Flores

Departamento de Física del Estado Sólido,

Universidad Autónoma, Cantoblanco, 28049 Madrid,

Spain

A simple consistent tight-binding method is used to analyse the initial stages of the Schottky barrier formation for an abrupt Al-GaAs(100) interface. Two different cases are discussed: (i) firstly, we consider the case of an Al layer with the Al atoms located in the cation position of the ideal continued GaAs(100) structure; (ii) in the second case, we consider a full Al monolayer with twice the number of Al atoms, having a geometry similar to the (100)-face of an Al f.c.c. structure. Our results show that the Schottky barrier is completely formed with the full monolayer, yielding a barrier height of 0.55 ± 0.05 eV. This barrier height is similar to the one calculated for an abrupt metal-GaAs(110) interface.

1. INTRODUCTION

Different models of Schottky barrier formation have been proposed, and it is clear that no model has a universal acceptance since no single model can explain all the experimental data. This is related to the different kind of interfaces appearing in a semiconductor-metal junction; according with the experimental evidence we find: (i) abrupt interfaces [1,2] with a well defined separation between the structures of the metal and the semiconductor, and (ii) reactive interfaces [3-6], with the metal and the semiconductor interdiffusing and/or forming a new chemical compound at the interface.

The different models, related to the two kinds of interfaces commented on above, appear to continue to attract fairly wide support in the scientific community: (i) The defect model [7-11], which assumes that the Schottky barrier formation results from the creation of significant number of defects at or near the interface, and (ii) the intrinsic interface states model [12-16], which attributes the Schottky barrier height to Fermi level pinning by the metal induced density of states near the semiconductor midgap. Both models involve states at the metal-semiconductor interface with properties that are almost independent of the metal, explaining Schottky barrier heights that are virtually independent of the metals.

There is a general agreement in the fact that the mechanism determining the Schottky barrier heights depends on the kind and quality of the interface. Thus, the defect model can be accepted as the mechanism controlling the Schottky barrier height if the number of defects at the interface is

high enough (something between 0.1% and 10% of the surface atoms, a subject of current controversy).

In this paper we analyse the initial stages of the Schottky barrier formation for an abrupt Al-GaAs(100) interface. The quality of this interface, when Al is epitaxially grown in GaAs(100), appears to be very dependent on the temperature of deposition [17,18]. For low enough temperature, the interface is abrupt, and the epitaxy of Al is observed to grow with different orientations on GaAs [18]. For simplicity, in this paper we only consider the case for which Al(100) growth is observed, a case that would be expected on the basis of simple lattice metals arguments (see below). According with the previous discussion, the Schottky barrier formation for this low temperature case can be expected to be controlled by the metal induced density of states near the semiconductor midgap. This is the point of view taken in this paper, and the first stages of the Schottky barrier formation is analysed following this model.

As regards the different theoretical approaches used to analyse the ideal abrupt interfaces and the metal induced density of states at the semiconductor midgap, let us mention: (i) the self-consistent calculations using pseudopotential theory and local density formalism [19], and (ii) the simple models introducing the charge neutrality level at the interface [13,16]. In this last context, a mechanism of Schottky barrier formation based on the concept of charge neutrality level was first proposed in Ref.13. Here, it was shown that for a covalent surface, when the semiconductor and the metal are coupled, the semiconductor density of surface states broadens but keeps its

centre of gravity almost constant. Hence the interface's Fermi level almost coincides with the Fermi level for the free surface. For ionic surfaces, like the (100) of GaAs, things are more complicated: in this case, the centre of gravity of the surface bands does not coincide with the mean level of the optical gap [20]; on the contrary, due to the net charge of the last atomic layer, the centre of gravity of the surface bands is displaced for an anion surface towards the valence band [21]. However, for an intimate metal-semiconductor junction, the surface band of the ionic surface also broadens and the final density of interface states resembles very much that of a covalent case [21]. In line with these comments, Tersoff has suggested recently [22] that the Schottky barrier for the ionic face of a semiconductor can be also obtained by using the same charge neutrality level calculated for a neutral face of the same semiconductor (say, a (110)-surface).

In this paper we have followed an alternative approach, recently used succesfully to analyse Schottky barriers for covalent semiconductors [14,15]. This is a tight-binding method supplemented with an additional consistency associated with charge neutrality conditions. The idea behind this approach is to extend the charge neutrality level concept [13] to a more sophisticated calculation which takes into account the small variations that interface dipoles introduce in the "rule of thumb" associated with the charge neutrality approach.

On the other hand, our calculation is directed to understanding the first stages of the Schottky barrier formation.

In a previous work [23], we found that for Al on Si(111), the barrier height is completely formed for a monolayer of Al; this suggests that a similar case can be found in the actual junction we discuss here. Our final results show that, indeed, for a complete monolayer of Al on GaAs(100) a finite density of states fill the semiconductor gap, suggesting that the barrier is completely formed.

In §2 we discuss our model, our method of calculation and consistency, and in §3 we present and discuss our results.

2. MODEL, METHOD OF CALCULATION AND CONSISTENCY

In this work we consider the problem of a monolayer (and a half of a monolayer) of Al on GaAs(100). Figure 1a shows one of the geometrical configurations we have analysed. Here, one of the Al atoms is located in the Ga position for the ideal continued GaAs structure. For this position, the Al layer forms an ideal (100)-face of the Al metal structure, except for other Al atoms, located in the centre of the elemental face formed by four Al atoms. We consider two structures: (i) the first one only includes Al atoms in the ideal positions of Ga, (ii) the second one, the full monolayer case, has twice the number of Al atoms, and is similar to the (100)-face of the Al f.c.c. structure. For this case, the Al-(110) direction in the (100)-plane is parallel to the GaAs-(010) direction.

The electronic band structure of GaAs is described by means of a tight-binding model, using sp^3s^* hybrids [24] in each atom, and including interaction parameters that extend up to first neighbours. The effect of the interface penetrates up to the third layer of GaAs [25]; accordingly, we introduce diagonal perturbations, V_1 and V_2, in the last two layers of the semiconductor. These perturbations will be calculated consistently as discussed below. As regards Al, we introduce interactions between As and the nearest Al atom according with the parameters of AlAs [24]. The Al-Al interactions are the same used in Ref.23, and they have been calculated using Harrison's prescription and an inverse square law for the dependence on the Al-Al distance. In Table I we give the different parameters defining the interface Hamiltonian.

In our method of calculation we follow the procedure developed in Ref.14. Summarising, our method uses a Green function approach and, by means of a decimation technique, calculates the surface components of the Green function of the system. Thus, we can project the bulk components of the whole Green function onto a few layers of the interface. In our actual case, we have projected all the electronic bulk structure of the semiconductor onto the last three layers, say, the last As layers, and the next Ga and As layers. In this way, we reduce the whole Hamiltonian to an effective one, associated with the Al layer, and the three last layers of GaAs (this yields a 20x20 effective matris for a half monolayer of Al, counting five orbitals per layer and a 25x25 matrix for the

full monolayer. From this matrix, we can analyse the different electronic properties of the interface, once we introduce at each layer (the Al layer included) the diagonal perturbations to be related to the interface consistency,

Let us now consider how to get the interface consistency in our problem. In Figure 2, we show an ideal Al-GaAs interface, after averaging the charges of each atom in the sense parallel to the surface. For GaAs we assume that the charges per atom inside the crystal are $3-\alpha$ (Ga) and $5+\alpha$ (As). The ideal case shown in Figure 2 is defined by assuming that the electrostatic potential near the interface is the same as in GaAs, and that the electrostatic potential between the last layers of Al and As coincides with the one for an AlAs crystal; this means that the charge per atom for the last Al layer is $3-\beta/2$, while the charge per atom for the last As layer is $5+\alpha/2+\beta/2$, β being the transfer of charge between atoms of Al and As in an AlAs crystal. Notice that this ideal case allows us to define the parameters for Al (as given in Table 1) by referring the Al levels to the As ones by means of the parameters of the AlAs crystal.

The ideal situation shown in Figure 1 allows us to define a starting point for which the different interactions appearing in the Hamiltonian are given by the parameters of Table 1. That means that for the charges shown in Figure 2, we expect to have the parameters given in Table 1.

Once we define this initial situation, we now allow for changes in the charges and potentials, V_0, V_1 and V_2 (see Figure 2), of the layers around the interface. Notice that for the initial potentials defined above (for this case we define

$V_0 = V_1 = V_2 = 0$) we can obtain the charges at each layer by solving the total Hamiltonian: in general, the charges at each layer do not coincide with the initial charges shown in Figure 2. In our consistent procedure, we allow for charges in the potentials, V_0, V_1 and V_2. Thus, V_0, V_1 and V_2 are related to the charges of each layer through a kind of consistent equation. This means that V_i is defined as the electrostatic potential created by the charges δn_i, as measured with respect to the ideal case shown in Figure 2. This yields:

$$V_2 = \alpha d \delta n_3$$

$$V_1 = \alpha d \delta n_3 + \alpha d (\delta n_2 + \delta n_3) \qquad (1)$$

$$V_0 = \alpha d \delta n_3 + \alpha d (\delta n_2 + \delta n_3) + \alpha d' (\delta n_1 + \delta n_2 + \delta n_3) \quad ,$$

where d is the interlayer distance in GaAs and d' is the distance between the Al layer and the last As layer; $\alpha = 4\pi/A$, A being the area per surface atom.

Notice that in our actual case

$$\delta n_0 + \delta n_1 + \delta n_2 + \delta n_3 = 0$$

is verified with a very good approximation since the interface perturbation only penetrates three layers in the semiconductor.

Eqs.(1) define our consistent conditions, and allows us to calculate the final perturbations V_i.

3. RESULTS AND DISCUSSION

Table 2 shows the values of V_0, V_1 and V_2 as obtained for the different geometrical configurations. Figure 3 shows the local density of states in the Al layer for a half monolayer. Figure 3a shows the total density of states, while Figures 3b and 3c show the local density of states projected onto the p_x+p_y (bridge bond) and the $s+p_z$ (dangling bond) orbitals of Al. From these figures we see that there is a cation-like surface band in the semiconductor gap; this band is a dangling bond state, which is 3/4th occupied. Notice that these results are similar to the ones obtained for a cation-terminated GaAs(100)-surface [26,27]; the change of Ga by Al introduces rather small differences between the two cases; in particular, we find the Fermi level pinned by a high density of states, and regions of the semiconductor energy gap (outside the surface band) having a zero density of states.

Figure 4 shows the local density of states in the Al atom for a full monolayer. For this case, and comparing with a half monolayer, we can see the evolution of the electronic density of states. In particular, we see that there is a finite density of states anywhere, with electronic states filling the semiconductor energy gap; however, the Fermi level for this case has not changed very much from the half monolayer case: while for this case E_F is 0.84 eV above the valence band top, for the full monolayer we find that E_F is at 1.15 eV. On the other hand, it is worth stressing that results found in other cases [23,28] (Al on Si(111) and Al on Ga(100)) show that the barrier is completely formed for a monolayer, when the surface

density of states fills completely the semiconductor energy gap. Based on these results and in our present calculations, we can conclude that the Schottky barrier for the Al-GaAs(100) junction is completely formed for the full monolayer.

In order to obtain the barrier height of the junction, we note that our calculations yield a shift of the Fermi level, between the full and the half monolayer, of 0.31 eV. For the half monolayer, our results also show that the Fermi level coincides with the one obtained for a cation-terminated GaAs-(100) surface. It is worth stressing that our calculations yield accurate results for the shift of the Fermi level when depositing the metal on the semiconductor [14,15], but do not give so good results for the initial Fermi level (this energy is very much dependent on the semiconductor bulk bands). We can determine, however, the Fermi level at the interface by using other more accurate calculations for the free cation-like GaAs-(100) surface. In Ref.26, it is shown that the Fermi level of that ideal surface is around 0.55 eV above the valence band top. Combining this result with the calculation presented in this paper, we conclude that the Fermi level at the Al-GaAs(100) interface is located at 0.86±0.05 eV above the valence band top, yielding a barrier height of 0.55±0.05 eV.

Let us finally comment that the barrier height calculated in this paper for the (100)-face is similar to the one calculated for the abrupt Ag-GaAs(110) junction [30]. For this case, the barrier height was found to be 0.63±0.05 eV. Since changing from Ag to Al seems to yield small variations in the barrier height [14], we conclude that, to an accuracy of 0.1 eV, the barrier heights

for the Al-GaAs(100) and Al-GaAs(110) are the same.

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REFERENCES

1. A.McKinley, R.H.Williams and A.W.Park, J.Phys.C, 12, 2447 (1979)
2. R.Ludeke, T.C.Chiang and T.Miller, J.Vac.Sci.Technol., B1, 581 (1983)
3. J.M.Andrews and J.C.Phillips, Phys.Rev.Lett., 35, 56 (1975)
4. G.Ottaviani, K.N.Tu and J.W.Mayer, Phys.Rev.Lett., 44, 284 (1980)
5. R.H.Williams, V.Montgomery and R.R.Varma, J.Phys.C, 11, 1989 (1978)
6. L.J.Brillson, C.F.Bruckner, N.G.Staffel, A.D.Katuani and G.Margaritondo, Phys.Rev.Lett., 46, 838 (1981)
7. M.S.Daw and D.L.Smith, Phys.Rev.B, 20, 5150 (1979)
8. W.E.Spicer, I.Lindau, P.R.Skeath and C.Y.Su, J.Vac.Sci. Technol., 17, 1019 (1980)
9. R.H.Williams, J.Vac.Sci.Technol., 18, 929 (1981)
10. R.E.Allen and J.D.Dow, Phys.Rev.B, 25, 1423 (1982)
11. O.F.Saukey, R.E.Allen and J.D.Dow, Solid State Commun., 49, 1 (1984)
12. V.Heine, Phys.Rev., A138, 1689 (1965)
13. C.Tejedor, F.Flores and E.Louis, J.Phys.C, 10, 2136 (1977)
14. F.Guinea, J.Sánchez-Dehesa and F.Flores, J.Phys.C, 16, 6499 (1983)
15. J.Sánchez-Dehesa and F.Flores, Solid State COmmun., 50, 29 (1984)
16. J.Tersoff, Phys.Rev.Lett., 52, 465 (1984)
17. W.C.Marra, P.Eisenberger and A.Y.Cho, J.Appl.Phys., 50, 6927 (1979)

18. G.Landgren, R.Ludeke and C.Serrano, J.Crystal Growth, 60, 393 (1982)

19. S.G.Louie, J.R.Chelikowski and M.L.Cohen, Phys.Rev.B, 15, 2154 (1977)

20. F.Flores, C.Tejedor and A.Martín-Rodero, Phys.Stat.Sol.(b), 88, 591 (1978)

21. E.Louis and F.Flores, J.Physique, 42, 1313 (1981)

22. J.Tersoff, Surface Sci.(1985), Proc.1st.Int.Conf.Formation of Semiconductor Surfaces, Marseille, France (1984)

23. G.Platero, J.A.Vergés and F.Flores, Surface Sci.(1985), Proc. 1st.Int.Conf.Formation of Semiconductor Surfaces, Marseille, France (1984)

24. P.Vogl, H.P.Hjalmaron and J.D.Dow, J.Phys.Chem.Solids, 44, 365 (1983)

25. G.Platero, J.Sánchez-Dehesa, C.Tejedor, F.Flores and A,Muñoz, submitted for publication

26. J.A.Appelbaum, G.A.Baraff and D.R.Hamann, Phys.Rev.B, 14, 1623 (1976)

27. I.Ivanov, A.Mazur and J.Pollman, Surface Sci., 92, 365 (1980)

28. I.P.Batra, J.Vac.Sci.Technol.B, 1, 558 (1983); I.P.Batra and S.Ciraci, Phys.Rev.B, 29, 6419 (1984)

29. W.Mönch, Surface Sci., 132, 92 (1983)

30. J.Sánchez-Dehesa, J.Dow and F.Flores, to be published

TABLE 1.- Parameters defining the Ga-As, Al-As and Al-Al interactions, and the atomic levels.

	Ga-As	Al-As	Al-Al
V_{ss}	-1.613	-1.666	-1.256
$V_{s_a p_c}$	1.940	2.213	1.351
$V_{s_c p_a}$	2.505	2.380	1.351
$V_{p\sigma}$	3.028	2.616	2.112
$V_{p\pi}$	-0.781	-0.604	-0.599
$V_{s_a^* p_c}$	2.097	1.958	1.263
$V_{s_c^* p_a}$	2.082	2.163	1.263

	As	Ga	Al
E_s	-8.343	-2.657	-1.979
E_p	1.041	3.669	3.645
E_{s^*}	8.591	6.739	7.835

TABLE 2.- Diagonal perturbations (in eV) on the Al layer (V_0) and the last two layers of GaAs.

	V_0	V_1	V_2
Half monolayer	-0.367	-0.059	-0.008
Full monolayer	-0.070	-0.445	-0.044

Figure Captions

Figure 1.- Geometry for Al adsorbed on the GaAs-(100) face. Different sizes are related to the depth of the crystal layers. Al-atoms are shown by dashed circles. a) Half monolayer; b) full monolayer.

Figure 2.- Electrostatic potential of an ideal Al-GaAs interface after averaging the charges in the sense parallel to the surface. V_i refers to the diagonal perturbations discussed in text. For the meaning of α and β, see text.

Figure 3.- (a) Total density of states on the Al-layer for the half monolayer case. This density is projected on (b) the $s+p_z$ orbital, and (c) the p_x+p_y orbital. $E_F \equiv$ Fermi level; $E_c \equiv$ conduction band bottom; $E_v \equiv$ valence band top.

Figure 4.- Local density of states on the Al-layer for the full monolayer case. $E_F \equiv$ Fermi level; $E_c \equiv$ conduction band bottom; $E_v \equiv$ valence band top.

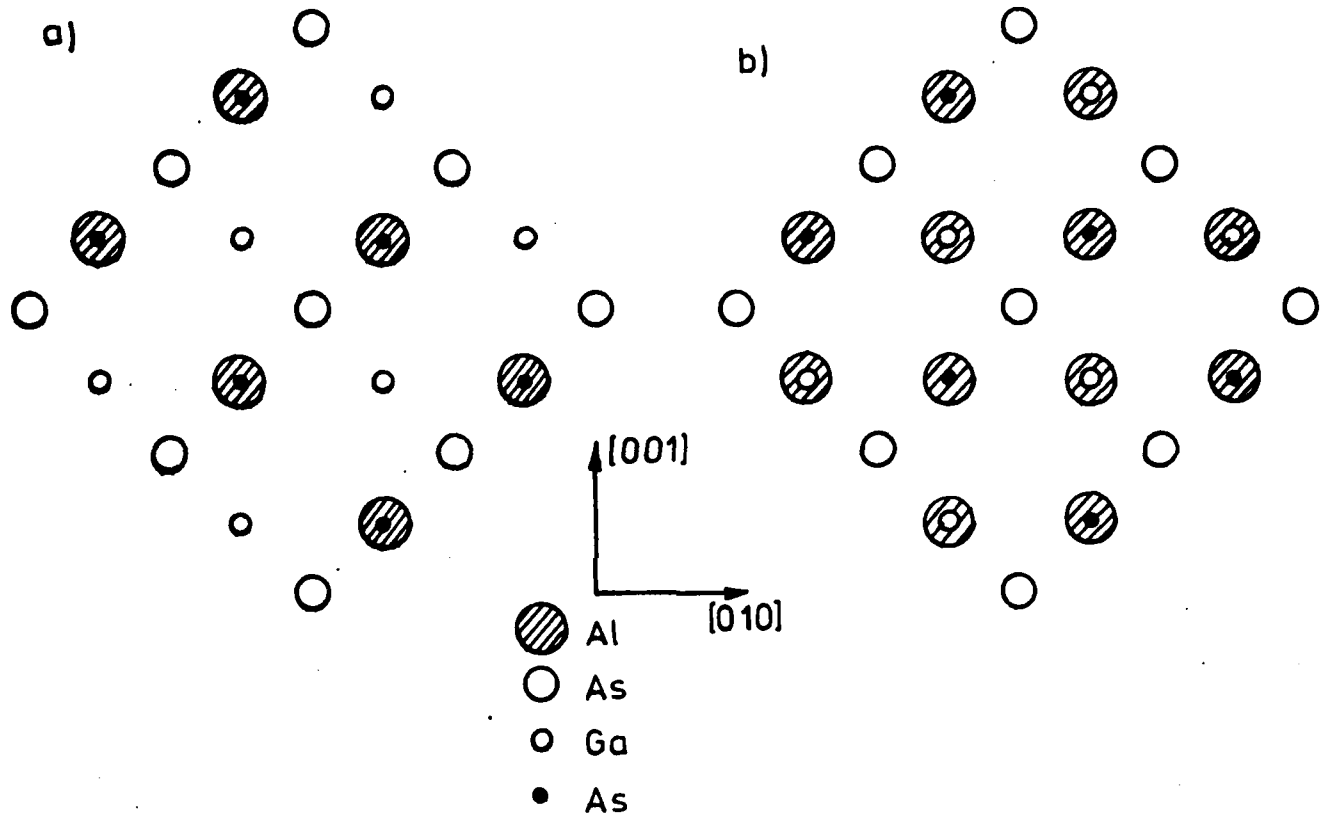


Fig 1

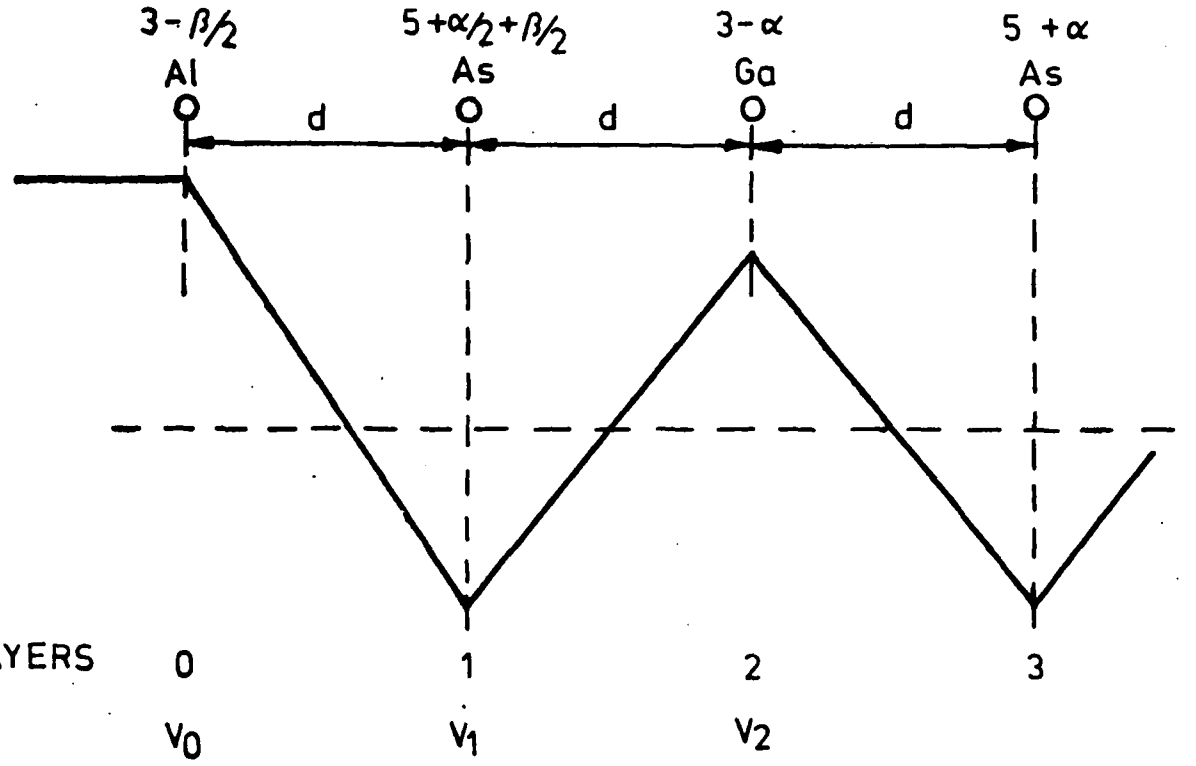
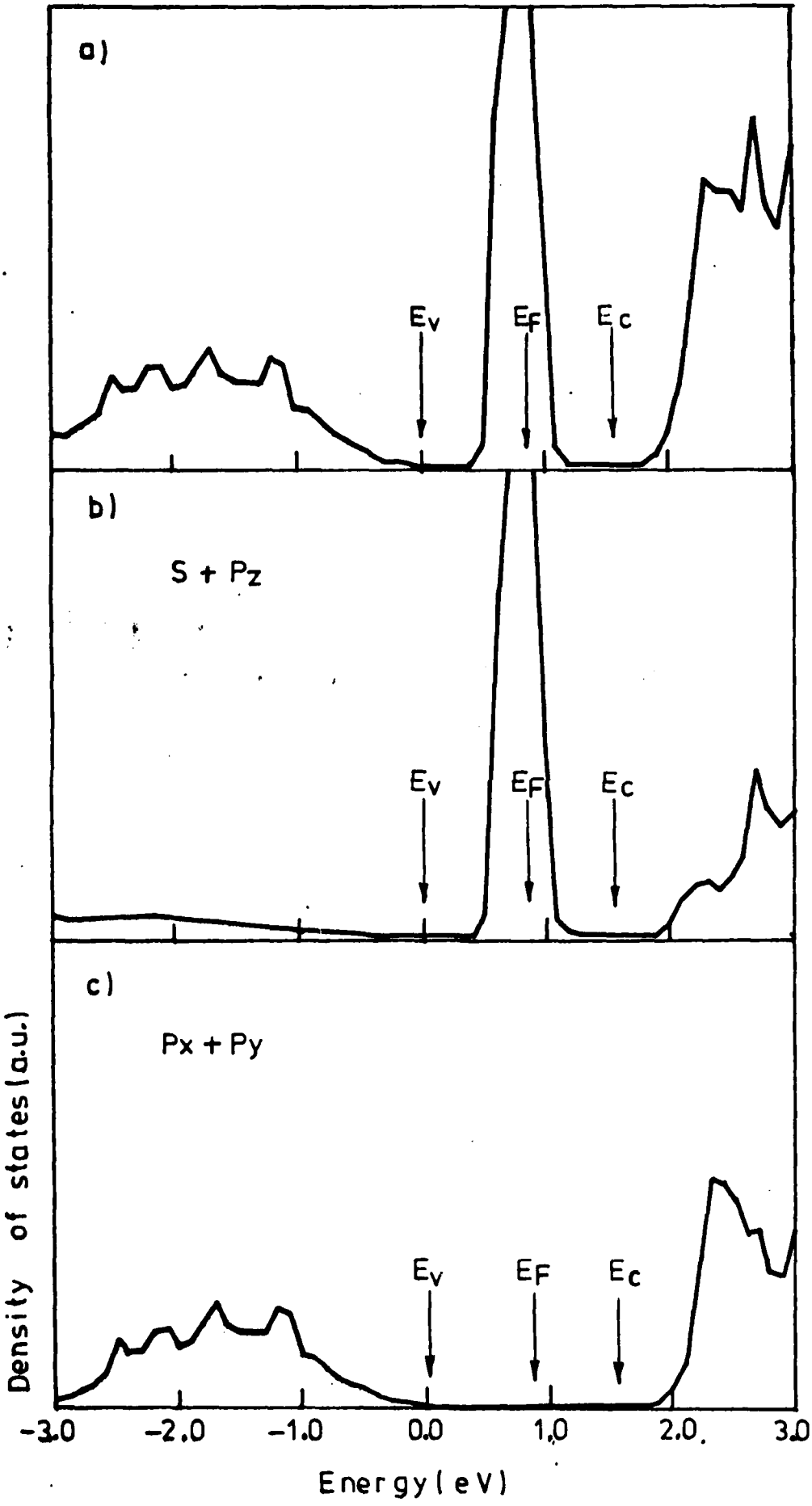


Fig. 2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E_v
E_F
E_c
b)
S + Pz
E_v
E_F
E_c
c)
Px + Py
E_v
E_F
E_c
Density of states (a.u.)
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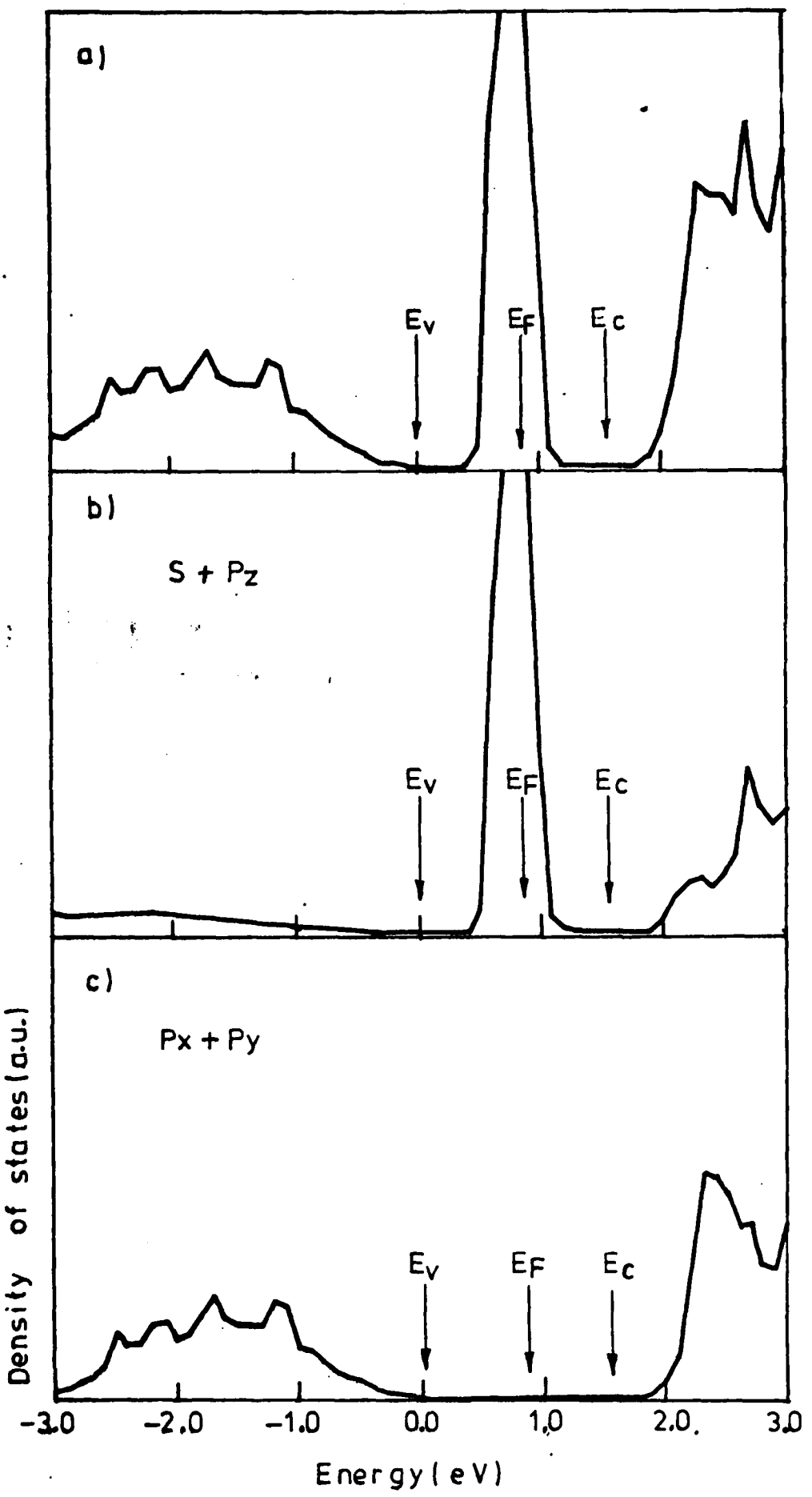
-2.0
-1.0
0.0
1.0
2.0
3.0
Energy (eV)

Fig. 3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b)
S + Pz
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c)
Px + Py
E_V
E_F
E_c
Density of states (a.u.)
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-2.0
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3.0
Energy (eV)

Fig. 3

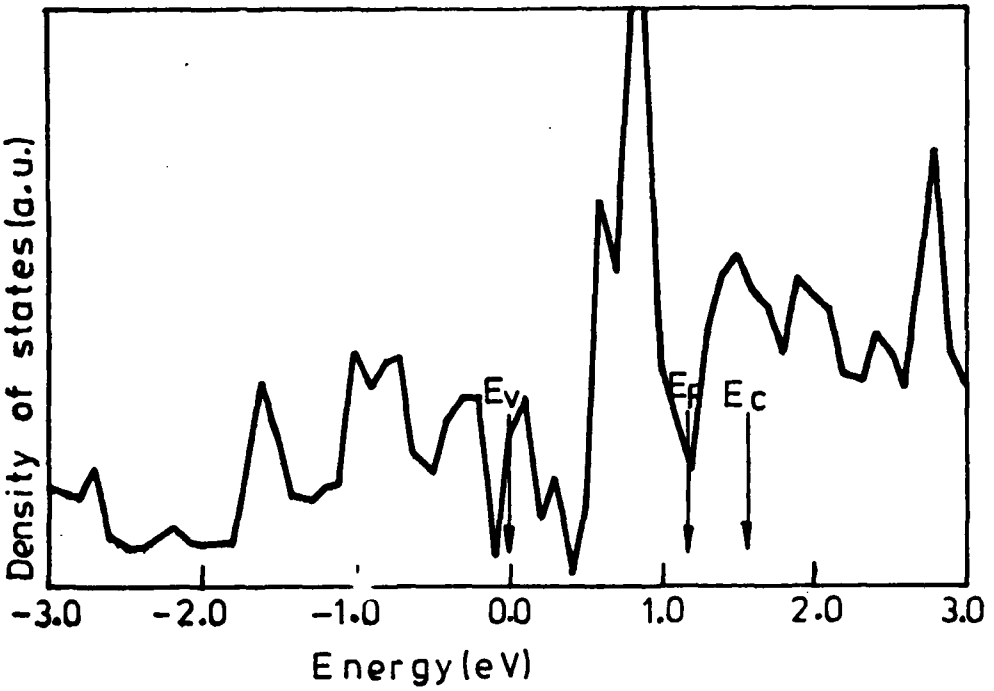

Fig. 4

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