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Schottky-barriers for clean, etched and reactive metal-semiconductor junctions

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Résumé. — Nous proposons un modèle simple et général pour les jonctions métal-semiconducteur propres, décapées ou bien chimiquement actives. Pour les jonctions propres, nous considérons également la possibilité d'une relaxation ou de la présence d'une couche physisorbée. En ce qui concerne les deux autres cas, le paramètre crucial du modèle est la charge électrique liée aux états électroniques de surface qui réagit soit avec l'agent décapant, soit avec le métal. Nous analysons de manière self-consistante la redistribution de cette charge à la jonction ainsi que la densité d'états correspondante. Dans ce modèle nous incluons les résonances induites par les états liés ou les liaisons libres (caractéristiques des interfaces inactives chimiquement) ainsi que les nouveaux états à l'interface créés par réaction chimique. La densité d'états à l'interface est utilisée pour trouver le niveau de charge neutre qui est un concept fondamental pour la description du comportement des jonctions métal-semiconducteur. Dans ce contexte nous discutons les données expérimentales concernant les jonctions non réactives avec des semiconducteurs ioniques ou covalents ainsi que les jonctions décapées et actives de Si(111). Bien que, dans la plupart des cas, seule une comparaison qualitative entre la théorie et les données expérimentales soit possible, nous montrons comment ce modèle peut être utile à la compréhension des différents facteurs inhérents au comportement de la jonction.

Abstract. — A unifying simple model for clean, etched and reactive metal-semiconductor junctions is proposed. For clean junctions the possibility of some relaxation or a physisorbed layer at the interface is also considered. As regards the other two, the crucial parameter of the model is the amount of charge located in the semiconductor surface states that reacts either with the etching agent or the metal. The selfconsistent redistribution of charge at the junction and its density of states are analysed as a function of the interface conditions. Virtual states or dangling bond derived resonances (characteristics of non reactive interfaces) and new interface states induced by the chemical reactions are embodied in the theory. The interface density of states is used to obtain the charge neutrality level, a central concept to explain the behaviour of metal-semiconductor junctions. The available data for ionic and covalent semiconductor non reactive junctions, and etched and reactive Si(111) junctions, are discussed within this context. Although in most cases only a qualitative comparison between the theory and experiment can be done, the model is shown to be helpful for improving our understanding of the different factors governing the junction behaviour.

1. **Introduction.** — The mechanism of Schottky-barrier formation at metal-semiconductor junctions has been the subject of many different interpretations [1-11]. All these theories have assumed a chemically abrupt interface in which, at most, there was some kind of relaxation [10, 11] or a physisorbed dielectric layer [3, 11] at the interface. Leaving appart the many-body theories [5, 6], the interface behaviour has been interpreted in terms of either semiconductor surface states [2, 3] or virtual states originated by the tails of the metal wavefunctions tunnelling into the semiconductor optical gap [4, 7-9]. More recently a case

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intermediate to those two has been considered, namely that of dangling bond derived resonances [10, 11], in which the semiconductor surface states are broaden by the presence of the metal; this broadening being possibly due to either a relaxed interface [10, 11] or the presence of a physisorbed dielectric layer [11]. The case of semiconductor surface states can be simply considered as the limit of very thick layers.

None of these theories fit into the very rich experimental information recently obtained [12-16]. In these experiments a novel feature of metal-semiconductor junctions has been put forward, namely, the eventual reactivity between the metal and the semiconductor. An immediate consequence of this reactivity is the formation of a chemical compound at the interface, whose electronic structure is not, in principle, related to those of the metal and the semiconductor [15]. It is clear that when extended reaction has occurred, a proper description of the electronic structure of the chemical compound being formed [15] is needed. Nonetheless it might be reasonable to think that the changes occurring in the junction behaviour during the first stages of the reaction can be described by considering the charge rearrangement at the interface without caring about the actual electronic structure of the compound. A kind of junctions which could be considered by means of a similar scheme are those in which the semiconductor surface has been etched before the junction is made [17]. In these junctions a rearrangement of the charge at the semiconductor surface is promoted by the reactant and then the metal is deposited on this etched surface.

To summarize, the experimental and theoretical studies performed up to now [1-21] suggest that the metal-semiconductor junctions can be classified into three broad groups : i) non reactive interfaces, for which no chemical compound is formed between the metal and the semiconductor — including those in which some relaxation or a physisorbed dielectric layer is present —; ii) etched interfaces, for which the semiconductor surface has been previously treated with a reactant, leaving an oxide layer between the metal and the semiconductor; and iii) reactive interfaces, for which the metal and semiconductor form a new chemical compound. Notice that under the heading of non reactive interfaces we include both the covalent (Bardeen-like) and ionic (Schottky-like) [20] junctions, as the differentiation made by Andrews and Phillips [12] in terms of the strength of the interface bonds, could be described by the relaxation at the interface [10] mentioned in i).

The purpose of this paper is to present a theory which might treat under the same footing either the virtual states or the dangling bond derived resonances characteristics of non reactive junctions, and the new interface states originated through the interface reactions taking place in etched or reactive junctions.

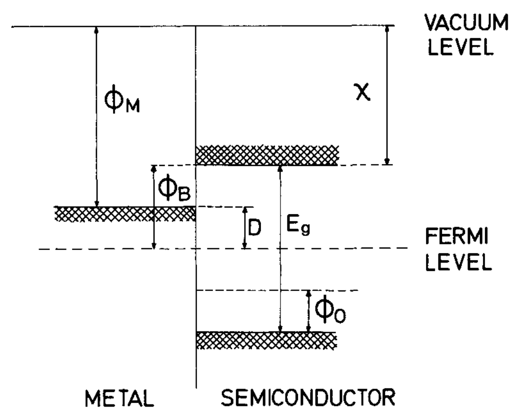

Fig. 1. — Energy diagram in the metal-semiconductor junction. The meaning of the symbols is as follows : χ semiconductor electron affinity; φ_M metal work function; E_g semiconductor band gap; φ_0 charge neutrality level; D interface induced dipole; φ_B barrier height.

As pointed out above, we will discuss the first stages of the interface reactions. To this end we shall follow the lines of the theory presented by Cowley and Sze [3, 8], whereby the properties of the junction are explained in terms of the dipole layer built up at the interface. According to this theory the barrier height for a n-type junction (φ_{bn}) can be written as (Fig. 1) :

$$\varphi_{bn} = \varphi_M - \chi + D = \frac{1}{1+\alpha N_{ss}}(\varphi_M - \chi - E_g + \varphi_0) + E_g - \varphi_0 , \quad (1)$$

where φ_M and χ are the metal workfunction and the semiconductor affinity respectively, and E_g is the semiconductor band gap. The dipole induced at the interface is represented by D. The parameter α is related to some many-body interface properties [8], and the remaining parameters of the theory are φ_0, the neutral level [18] (also called charge neutrality level [3]) — which can be defined as the energy level up to which the interface density of states in the gap have to be filled in order to compensate the defects of states in the semiconductor valence band induced by the interface — and N_{ss} the interface density of states.

According to this theory, in order to discuss the three types of junctions mentioned above, we must determine both quantities, the density of interface states and the neutral level. The latter requires a careful analysis of the whole spectrum of electronic states. We shall perform in depth this analysis not only for the rather simple case of non reactive interfaces, but also for the more involved of reactive and etched junctions. The physics contained in the two latter junctions will be modelled by assuming that, as the chemical reaction proceeds, some electronic charge at the interface is removed from the semiconductor, to form a chemical compound. In fact this amounts to the description of the microscopic redistribution of the charge at the interface [13] promoted by the

chemical reaction taking place. Although this is a rather simplified model it will turn out a helpful tool to improve our understanding of these complicated interfaces.

The rest of the paper is organized as follows. In section 2 we discuss in detail a one-dimensional model which might be used to describe the three types of junctions. This 1-dimensional model will allow us to discuss some of the more prominent features of the junctions. The 3-dimensional analysis is presented in section 3. In this part of the paper we focus on Si(111) junctions for which there is a wealth of experimental data for all the different junctions. The 2-dimensional Brillouin zone is treated by considering a single representative point [8, 22, 23]. Then, the results obtained for the different junctions are discussed and used to analyse the available experimental information. Finally some concluding remarks are included in section 4.

2. **The model.** — For non reactive junctions in which there is an intimate contact between the metal and the semiconductor, a simple model has been proposed by different authors [4, 8, 22, 23], whereby the metal was treated in the jellium model and the semiconductor within a narrow gap approximation. Moreover, recently similar simple models have been suggested to handle relaxed interfaces and physisorbed dielectric layers at the interface [10, 11]. In this paper we shall use a rather similar model. In figure 2 we show schematically the model used in the present work. The electronic charge in the junction is neutralized by the ionic charge which in our model is simulated by two uniform charges extending up to the crystal edges. When there is any relaxation or a physisorbed layer the thickness T is non zero, while for non reactive interfaces d is always zero (Fig. 2).

For an etched interface, an electronegative atom reacts with the semiconductor surface forming a

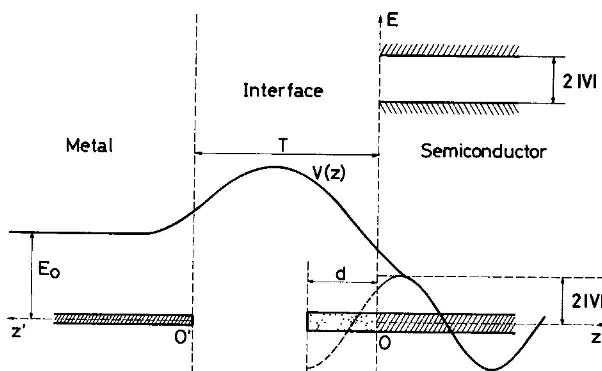

Fig. 2. — 1-dimensional model for clean, etched or reactive metal-semiconductor junctions depending upon the values of the thickness of the dielectric layer (T), and the charge removed from the semiconductor (described by d). For $d = 0$ an intimate contact junction ($T = 0$) or one relaxed or with a physisorbed layer ($T \neq 0$) are represented. In the cases of etched or reactive interfaces T and d are both $\neq 0$. $|V|$ stands for the absolute value of the effective Fourier component of the semiconductor pseudopotential.

chemical compound. Then the metal is deposited upon this etched surface. If there is a large electronegative difference between the etching atom (O, Cl, ...) and the semiconductor, we might assume that, during the etching process, the electronic charge in the surface states characteristic of the semiconductor free surface, are transferred to the absorbate in order to complete its partially filled configuration. The crucial difference between this case and the previous one is the whole electronic charge at the interface. In the etched interface we assume that the electronic charge playing a role in the barrier formation, is that defined subtracting to the charge of the clean metal and semiconductor surfaces, the charge transferred from the semiconductor surface states to the absorbate. In figure 2 this is schematically represented by the dotted region in the positive homogeneous charge of the semiconductor, in such a way that the rest of the positive charge cancels the electronic charges in the metal and semiconductor bands. The effect of the oxide layer is described not only by removing the above mentioned charge but also by considering a new interface potential between both crystals.

An intermediate case between clean and etched interfaces appears for etched junctions in which not all the semiconductor dangling-bonds are saturated by the absorbate. For instance this occurs in ageing junctions in which ionic diffusion allows a dangling bond saturation along the time [17, 18]. For these interfaces we can propose a model in which the electronic charge transferred to the absorbate is only a fraction of the charge located in the semiconductor surface states.

Reactive junctions are more involved. As remarked in the introduction, the reactions can be very extensive in such a way that very thick layers of the chemical compound can be formed at the interface, either by rapid Si diffusion or by metallic diffusion [24, 25]. It is clear that the present model have to be restricted to the first stages of the reaction, as when a thick layer of chemical compound is built up at the interface, a proper description of the electronic structure of the compound which in some cases turns out to be a metal [15] might be needed. According to this we shall consider only reactive interfaces in which extensive reaction has not occurred. To these junctions a model similar to that described for etched or partially etched junctions can be applied.

The model shown in figure 2 can be handled as follows. First we notice that the metal and the semiconductor are connected through the interface region, where some selfconsistent potential is created by the interface electronic charge as well as the oxide (or chemical compound) layer, if any, formed between the metal and the semiconductor. The whole free electronic charge is neutralized by the homogeneous positive charges denoted by dashed regions in figure 2, whereas the dotted region of width d defines the positive charge, and therefore the electronic charge,

transferred from the semiconductor to the chemical compound (or oxide). For a non reactive junction the edge of the homogeneous semiconductor charge coincides with the minimum of the semiconductor pseudopotential ($d = 0$). The semiconductor wavefunctions will be described within a narrow gap approximation and the interface selfconsistency will be introduced in two steps : i) first we shall assume that the interface potential behaves as in the metal-metal junction (described within the jellium model) and solve this selfconsistently; ii) in a second step we shall switch on the semiconductor pseudopotential and assume that it does not perturb appreciably the interface potential; the consistency of this procedure will be also discussed. This procedure will allow us to calculate the interface density of states and the neutral level for all the different cases.

2.1 THE 1-DIMENSIONAL METAL-METAL INTERFACE. — This interface can be described as the limit of the metal-semiconductor interface (see Fig. 2) for $|V| \to 0$, V being the effective pseudopotential Fourier component which originates the semiconductor optical gap. For the metal-metal junction at a given energy $E > E_0$ [26] ($E = 0$ and E_0 being the average potentials at the semiconductor ($z > 0$) and the metal ($z' > 0$) sides respectively) and far away from the interface, we have the following wavefunctions

$$\psi \sim \sin(\lambda z + \eta) \quad \text{for} \quad z \gg 0 \tag{2a}$$

$$\psi' \sim \sin(\lambda' z' + \eta') \quad \text{for} \quad z' \gg 0\,, \tag{2b}$$

where λ, λ' and η, η' are the momenta and the phase-shifts. Notice also that we have used different spatial origins for the two media (see Fig. 2).

For an energy $E < E_0$, we only have one wavefunction propagating away from the interface. This is given by

$$\psi \sim \sin(\lambda z + \eta) \quad \text{for} \quad z \gg 0 \tag{3}$$

since for $E < E_0$ and $z' \gg 0$ the wavefunction ψ' decays exponentially.

To simplify the task of counting states we hereafter work with finite media by placing two infinite barriers at $z = L$ and $z' = L'$, L and L' being as large as needed. Then if we place two infinite barriers at $z = 0$ and $z' = 0$ and assume that the potential is constant up to these barriers, we have $\eta' = \eta = 0$, and the whole density of states is given by

$$N(E) = N_L(E) + N_{L'}(E) + N^{\text{I}}(E)\,, \tag{4}$$

where $N_L(E)$ ($N_{L'}(E)$) is the density of states of a jellium metal extending from $z = 0$ ($z' = 0$) up to $z = L$ ($z' = L'$) and the density of interface states $N^{\text{I}}(E)$ is given by

$$N^{\text{I}}(E) = -\tfrac{1}{4}\,\delta(E) - \tfrac{1}{4}\,\delta(E - E_0) \tag{5}$$

with the typical defects of 1/4 of state [22, 23] coming from each band edge.

Now if the infinite barriers at $z = 0$ and $z' = 0$ are removed, matching through the interface allows us to obtain, for $E > E_0$, a relation between the two phase-shift η and η', which for a general interface potential can be written in the following general form

$$f(\eta, \eta') = 0\,. \tag{6}$$

In Appendix I it is shown that taking $\eta = \eta'$ in equation (6) gives two solution $\eta^{(1)}$ and $\eta^{(2)}$ from which the density of interface states can be obtained as follows :

$$N^{\text{I}}(E) = \frac{1}{\pi}\frac{\mathrm{d}\eta^{(1)}}{\mathrm{d}E} + \frac{1}{\pi}\frac{\mathrm{d}\eta^{(2)}}{\mathrm{d}E} \quad \text{for} \quad E > E_0\,. \tag{7}$$

Furthermore it is also shown in Appendix I that the two wavefunctions associated with $\eta^{(1)}$ and $\eta^{(2)}$ are given by

$$\psi^{(1)} \sim \begin{cases} \dfrac{a}{\sqrt{\lambda}}\sin(\lambda z + \eta^{(1)}) & \text{for} \quad z \gg 0 \\[2ex] \dfrac{b}{\sqrt{\lambda'}}\sin(\lambda' z' + \eta^{(1)}) & \text{for} \quad z' \gg 0 \end{cases} \tag{8}$$

$$\psi^{(2)} \sim \begin{cases} \dfrac{b}{\sqrt{\lambda}}\sin(\lambda z + \eta^{(2)}) & \text{for} \quad z \gg 0 \\[2ex] -\dfrac{a}{\sqrt{\lambda'}}\sin(\lambda' z' + \eta^{(2)}) & \text{for} \quad z' \gg 0 \end{cases} \tag{9}$$

with the relation $a^2 + b^2 = 2$. A second relation between a and b can only be found by considering each particular case. Two limits are worth of discussing : i) first we assume that both media are decoupled, ii) in the second limit we consider an interface potential varying very slowly through the interface, in such a way that the WKB solutions for the wavefunction are valid.

In the first case the two wavefunctions given by equations (8) and (9) behave in the same way, and therefore

$$\eta^{(1)} = \eta^{(2)}\,, \qquad a = b\,. \tag{10}$$

In the second case we find

$$\eta^{(1)} = \eta^{(2)} + \frac{\pi}{2}\,, \qquad a = b\,. \tag{11}$$

These two cases show that, depending on the interface conditions, $\eta^{(1)}$-$\eta^{(2)}$ varies between the extreme values 0 (decoupled metals) and $\pi/2$ (WKB). Moreover, considering the relation between a and b given in equations (10) and (11) we use for the metal-metal junction the wavefunctions of equations (8) and (9) with $a = b = 1$.

Once defined the interface properties for $E > E_0$, we turn to consider the case $E < E_0$. In this case the interface density of states can be obtained from the phase-shift of equation (3)

$$N^{\text{I}}(E) = \frac{1}{\pi}\frac{\mathrm{d}\eta}{\mathrm{d}E} \quad \text{for} \quad E < E_0\,. \tag{12}$$

This equation is in fact equivalent to equation (7) considering that in Appendix I it is shown that

$$\eta^{(2)} \to 0\,, \quad \eta^{(1)} \to \eta\,, \quad \text{for} \quad E \to E_0\,; \qquad (13)$$

this also shows that $\psi^{(1)}$ of equation (8) tends to the wavefunction of equation (3) when $E \to E_0$.

With this in mind we can finally write the expression for the whole density of states as

$$N(E) = N_L(E) - \frac{1}{4}\,\delta(E) + N_{L'}(E) - \frac{1}{4}\,\delta(E - E_0) + + \frac{1}{\pi}\frac{\mathrm{d}\eta^{(1)}}{\mathrm{d}E} + \frac{1}{\pi}\frac{\mathrm{d}\eta^{(2)}}{\mathrm{d}E}. \qquad (14)$$

Finally it is worth remarking that equation (14) allows us to obtain a Friedel-type sum rule for the values of $\eta^{(1)}$ and $\eta^{(2)}$ at the Fermi level, namely, $\eta_{\mathrm{F}}^{(1)}$ and $\eta_{\mathrm{F}}^{(2)}$. To this end we use equation (13) and consider that for $E \to 0$, $\eta^{(1)} \to 0$; then, requiring overall charge neutrality, we finally obtain

$$\eta_{\mathrm{F}}^{(1)} + \eta_{\mathrm{F}}^{(2)} = \frac{\pi}{2}. \qquad (15)$$

A second relation is needed to determine $\eta_{\mathrm{F}}^{(1)}$ and $\eta_{\mathrm{F}}^{(2)}$. However, it can only be obtained once the particular interface potential is known. For instance for decoupled metals $\eta_{\mathrm{F}}^{(1)} = \eta_{\mathrm{F}}^{(2)}$, while for a slowly varying interface potential $\eta_{\mathrm{F}}^{(1)} = \eta_{\mathrm{F}}^{(2)} + \pi/2$. In general the interface conditions can be characterized by defining a parameter A as

$$A = \eta_{\mathrm{F}}^{(1)} - \eta_{\mathrm{F}}^{(2)}\,, \qquad (16)$$

which varies between $\pi/2$ (WKB case) and zero (decoupled metals). Notice that in the last case $\eta_{\mathrm{F}}^{(1)} = \eta_{\mathrm{F}}^{(2)} = \pi/4$, a well known result for a free metal surface [23]. The parameter A is in fact similar to the one introduced by Mele and Joannopoulos [10] to describe the broadening of the dangling bond states which they assume to appear in the metal-semiconductor junction.

2.2 THE 1-DIMENSIONAL METAL-SEMICONDUCTOR INTERFACE. — Once the metal-like wavefunctions have been obtained at the interface, we proceed to analyse the interface density of states for the metal-semiconductor junction, by switching on the crystalline pseudopotential and assuming that the interface potential is not perturbed. If we assume further that the narrow gap approximation is valid, we will only need to focus our attention in the energy region around the optical gap (or the Fermi level) as for energies well below (or above) it the metal-metal solutions will be still valid.

To study the 1-dimensional model drawn in figure 2, we start by considering the case of two infinite barriers at $z' = 0$ and $z = -d$ with the crystalline potentials (a constant for the metal) extending up to these barriers. Then the whole density of states is given by

$$N_{\infty}^{\mathrm{M-S}}(E) = N_L^{\mathrm{S}}(E) + N_{L'}^{\mathrm{M}}(E) + N_{\infty}^{\mathrm{I,M-S}}(E)\,. \qquad (17)$$

In equation (17), $N_L^{\mathrm{S}}(E)$ is the bulk density of states for a semiconductor of length L extending from $z = -d$ up to $z = (-d + L)$, with $L = na$, n being an integer and a the lattice constant, $N_{L'}^{\mathrm{M}}(E)$ the density of states for a jellium metal of length L' extending from $z' = 0$ up to $z' = L'$, and finally $N_{\infty}^{\mathrm{I,M-S}}(E)$ is the interface density of states which, for energies below the optical gap [22], takes the form

$$N_{\infty}^{\mathrm{I,M-S}}(E) = -\tfrac{1}{4}\,\delta(E) - \tfrac{1}{4}\,\delta(E - E_{\mathrm{V}}) - \tfrac{1}{4}\,\delta(E - E_0)\,, \qquad (18)$$

with the typical defects of 1/4 of state associated with the band edges [22, 23] $E = 0$, E_{V}, E_0 [26], the bottom and top of the semiconductor valence band and the bottom of the metal band respectively.

We now remove the infinite barriers at $z' = 0$ and $z = -d$ and proceed to discuss this case by differentiating two energy regions, namely, inside and outside the optical gap.

a) Over the range of energies inside the semiconductor gap, the interface density of states can be obtained by matching the metallic and the semiconductor wavefunctions through the interface. The metallic wavefunction can be written as

$$\psi^{\mathrm{M}} \sim \sin(\lambda'_{\mathrm{F}}\, z' + \eta') \quad \text{for} \quad z' \geqslant 0\,, \qquad (19)$$

where η' is a phase-shift so far undefined and, as we work in the narrow gap approximation, we can approximate the momentum by a constant equal to the Fermi momentum.

For the semiconductor wavefunction we write within the narrow gap approximation

$$\psi^{\mathrm{S}} \sim \exp(-\,qz)\sin\left[\tfrac{1}{2}\, g(z + d) + \tfrac{1}{2}\,\varphi\right], \qquad (20)$$

where

$$\exp(i\varphi) = -\left[\varepsilon + i\sqrt{V^2 - \varepsilon^2}\right]/V\,, \quad V(<0)$$

being the effective pseudo-potential Fourier component which creates the optical gap and g its associated reciprocal lattice vector; ε is the energy referred to the midgap and $q = \frac{2}{g}\sqrt{V^2 - \varepsilon^2}$, in such a way that $q \ll g$ since $V \ll g^2$. Notice also that $g/2 = \lambda_{\mathrm{F}}$.

Now the wavefunctions given by equations (19) and (20) have to be matched to the wavefunctions coming from the interface. Within our model these wavefunctions can be expressed as linear combinations of those given in equations (8) and (9) — with $a = b = 1$ —, as follows

$$\psi^{\mathrm{I}} \sim \begin{cases} k_1 \sin(\lambda'_{\mathrm{F}} + \eta_{\mathrm{F}}^{(1)}) - k_2 \sin(\lambda'_{\mathrm{F}}\, z' + \eta_{\mathrm{F}}^{(2)}) \\ k_1 \sin\left(\dfrac{g}{2}\, z + \eta_{\mathrm{F}}^{(1)}\right) - k_2 \sin\left(\dfrac{g}{2}\, z + \eta_{\mathrm{F}}^{(2)}\right). \end{cases} \qquad (21)$$

The equation obtained by marching these wavefunctions can be written as

$$\tan \eta' = \frac{\cos A - \tan\left(\frac{\varphi}{2} + \frac{\delta}{2}\right)}{1 - \cos A \tan\left(\frac{\varphi}{2} + \frac{\delta}{2}\right)}, \quad (22)$$

where we have made use of equations (15) and (16). Equation (22) gives η' as a function of ε-note the dependence of φ on ε. The interface properties are included through A and $\delta = gd$ (Fig. 2). The first parameter (A) describes the interface potential (it can be related to the interface thickness T, see Fig. 2), while the second (δ) specifically accounts for the charge removed from the semiconductor (related to d in figure 2).

Finally the interface density of states inside the optical gap can be obtained from equation (22) as follows :

$$N_{\mathrm{V}}^{\mathrm{I,M-S}}(E) = \frac{1}{\pi}\frac{\mathrm{d}\eta'}{\mathrm{d}\varepsilon}(|\varepsilon| < |V|). \quad (23)$$

b) As regards the range of energies outside the fundamental gap, we have to match the metallic wavefunction (19) to the interface wavefunction (21), and this one to the semiconductor wavefunction in the valence band, namely,

$$\psi^{\mathrm{S}}(z) = \sin\left[\left(-\frac{g}{2} + \lambda\right)(z + d) - \eta\right] + a \sin\left[\left(\frac{g}{2} + \lambda\right)(z + d) - \eta\right], \quad (24)$$

where

$$\lambda = \frac{2}{g}\sqrt{\varepsilon^2 - V^2} \ll g, \quad a = (\varepsilon + \sqrt{\varepsilon^2 - V^2})/V,$$

and η is a phase-shift so far undefined. The matching of these wavefunctions gives a relation between η and η'. Using now the results obtained in Appendix I for the metal-metal interface, we can take $\eta = \eta'$, and then, the following equation for η is obtained

$$\tan^2 \eta - \frac{2}{1+a}\tan\eta \frac{1 + a\tan\frac{\delta}{2}\cos A}{\tan\frac{\delta}{2} + \cos A} - \frac{a-1}{a+1}\frac{-\tan\frac{\delta}{2} + \cos A}{\tan\frac{\delta}{2} + \cos A} = 0, \quad (25)$$

where we have also made use of equations (15) and (16). From equation (25) we obtain two solutions, $\eta_{\mathrm{I}}^{(1)}$ and $\eta_{\mathrm{I}}^{(2)}$; then the interface density of states is given by

$$N^{\mathrm{I,M-S}}(E) = \frac{1}{\pi}\frac{\mathrm{d}\eta_{\mathrm{I}}^{(1)}}{\mathrm{d}\varepsilon} + \frac{1}{\pi}\frac{\mathrm{d}\eta_{\mathrm{I}}^{(2)}}{\mathrm{d}\varepsilon} \quad (|\varepsilon| > |V|). \quad (26)$$

Equations (23) and (26) allows us to obtain the whole interface density of states as a function of the interface properties brought in by A and the charge removed from the semiconductor described by δ ($= gd$). Then we write

$$N^{\mathrm{M-S}}(E) = N_L^{\mathrm{S}}(E) + N_{L'}^{\mathrm{M}}(E) - \tfrac{1}{4}\delta(E) - \tfrac{1}{4}\delta(E - E_{\mathrm{V}}) - \tfrac{1}{4}\delta(E - E_0) + N^{\mathrm{I,M-S}}(E) \quad (27)$$

for $E < E_{\mathrm{c}}$ (the conduction band edge) with $N^{\mathrm{I,M-S}}(E)$ given either by equations (23) or (26), depending on the energy.

We can now calculate the neutral level by recalling that it is the energy level up to which the interface states are filled when the interface is neutral, namely,

$$\int_{-\infty}^{\varphi_0} N^{\mathrm{M-S}}(E)\,\mathrm{d}E = \text{whole charge in the two media}, \quad (28)$$

which leads to

$$-\frac{3}{4} + \int_{-\infty}^{\varphi_0} N^{\mathrm{I,M-S}}(E)\,\mathrm{d}E + \frac{\delta}{2\pi} = 0, \quad (29)$$

where the contribution $\delta/2\pi$ ($\delta = gd$) represents the electronic charge per spin participating in a chemical reaction at the interface (the charge removed from the semiconductor, see Fig. 2). Using now equations (23) and (26) we can rewrite equation (29) as follows

$$\frac{1}{\pi}[\eta'(\varphi_0) - \eta'(E_{\mathrm{V}})] = \frac{3}{4} - \frac{1}{\pi}[\eta_{\mathrm{F}}^{(1)}(E_{\mathrm{V}}) + \eta_{\mathrm{F}}^{(2)}(E_{\mathrm{V}})] - \frac{\delta}{2\pi}. \quad (30)$$

Moreover, using equation (25) we can easily see that at $E = E_{\mathrm{V}}$, $a = 1$ and the phase-shifts are given by

$$\eta_{\mathrm{I}}^{(2)}(E_{\mathrm{V}}) = 0$$

$$\tan \eta_{\mathrm{I}}^{(1)}(E_{\mathrm{V}}) = \frac{1 + \tan\frac{\delta}{2}\cos A}{\tan\frac{\delta}{2} + \cos A}, \quad (31)$$

and finally

$$\frac{1}{\pi}[\eta'(\varphi_0) - \eta'(E_{\mathrm{V}})] = \frac{3}{4} - \frac{\delta}{2\pi} - \frac{1}{\pi}\tan^{-1}\frac{1 + \tan\frac{\delta}{2}\cos A}{\tan\frac{\delta}{2} + \cos A}, \quad (32)$$

which together with equation (22) gives the charge neutrality level (φ_0) as a function of δ and A.

Let us now discuss the results which emerge from the previous analysis.

i) *Ideal metal-semiconductor junction* ($A = \pi/2$). — This is the case of an intimate contact first discussed by

Heine [4]. In this case we obtain an interface density ($N^{I,M-S}$) of states which is symmetric with respect to the midgap, the charge neutrality level (φ_0) lying in the middle of the gap. This density of states is originated by the tails of the metal wavefunctions tunnelling into the semiconductor gap. We notice that Heine [4] and other authors [27] obtained for an abrupt potential a non symmetric density of states rather than a symmetric one. Our result is a consequence of treating the actual selfconsistent interface potential within the WKB approximation, a procedure which should be specially valid if the metal and the semiconductor forming the junction have similar densities. On the other hand, Heine's original calculation for such a junction would have also lead to a symmetric density of interface states. A further consequence of the WKB approximation is that φ_0 and $N^{I,M-S}$ are independent of δ. Finally it is also worth noting that the whole density of states in the gap (1/2) is compensated with two defects of 1/4 located at the band edges.

ii) *Decoupled media* ($A = 0$). — This is the other limiting case. Again well known results are rescued. For instance, if $\delta = 0$ we have a covalent semiconductor free surface, for which a surface state appears in the midgap with an occupancy of 1/2 [22, 23, 28]. For $\delta \neq 0$ we recover the case of an ionic semiconductor with the surface state displaced with respect to the midgap and no longer half occupied [28, 29].

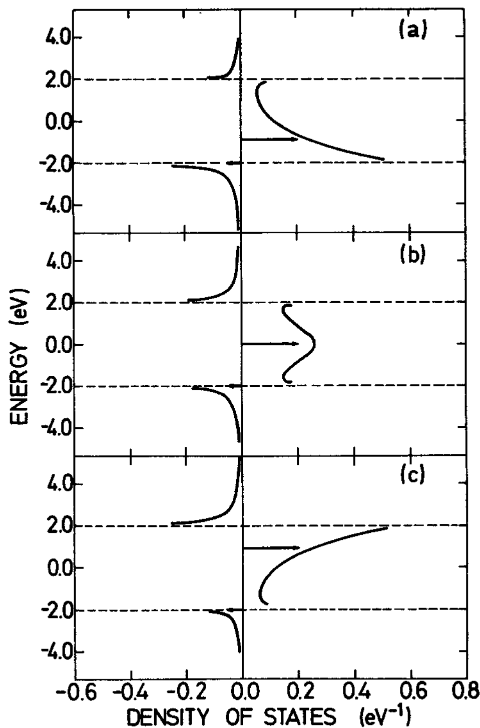

Fig. 3. — Density of interface states for the metal-semiconductor junction within the one-dimensional model described in the text. The horizontal broken lines bound the semiconductor band gap. The defect of 1/4 of state in the band edges is also indicated. The dielectric layer is very thin ($A = 1.0$, see text). a, b and c correspond to three different values of $\delta = gd$ (see Fig. 2 and text), namely $-\pi/2$, 0 and $\pi/2$, respectively.

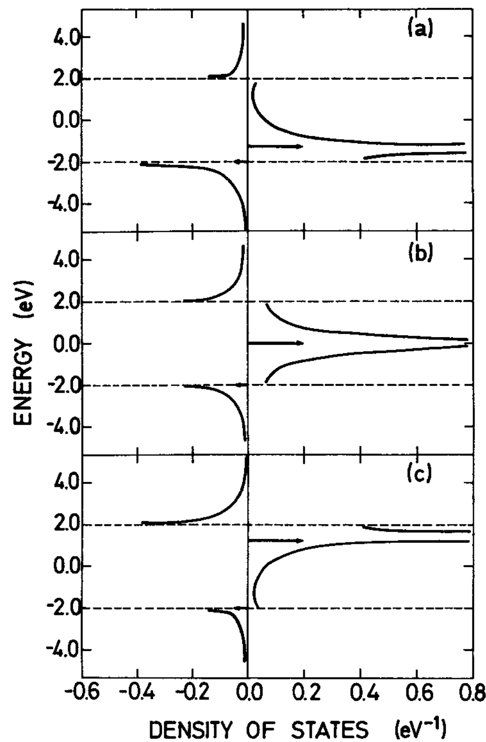

Fig. 4. — Same as figure 3 for a thicker dielectric layer ($A = 0.6$).

iii) *Intermediate cases* ($0 < A < \pi/2$). — In order to illustrate the kind of results which are obtained in this case, we show in figures 3 and 4 two sets of calculations for a semiconductor like Si. In figure 3 we report the results for a value of A close to $\pi/2$ ($A = 1.0$) and different values of δ. The density of interface states is no longer independent of δ and so is φ_0. For a lower value of A (Fig. 4) the density of states becomes more similar to that of the semiconductor free surface. In both figures we also show the density of states in the bands. In all cases we have an exact compensation between the density of states in the gap and in the bands. Note that cases (a) and (c) are symmetric of each other with respect to the mid-gap.

Some consequences of the above results should be remarked. First we consider the case of $\delta = 0$. In this case the density of states evolves from the featureless density of states of the ideal metal-semiconductor junction ($A = \pi/2$) to a bound state ($A = 0$) characteristic of the semiconductor free surface. We notice that for intermediate values of A we obtain the dangling bond derived resonances already discussed by Flores [11], and Mele and Joannopoulos [10]. The latter authors introduced a parameter (Γ) similar to ours (A).

A novel situation occurs when $\delta \neq 0$. This case can correspond either to a junction built up with an ionic surface (like (111) surfaces of III-V compounds) or to a junction formed with a covalent semiconductor from which some charge has been removed. Let us examine the latter case. In this case « new » states induced either by an etchant or a metal reacting with the

semiconductor, appear. The physics underlying this result is that as electronic charge is removed from the semiconductor, the centre of the density of states in the gap shifts and so does φ_0, to preserve overall charge neutrality. The relevance of these results in improving our understanding of reactive or etched interfaces will be discussed in the next section.

3. **The 3-dimensional metal-semiconductor interface.** — Let us now discuss how the previous scheme can be extended to 3-dimensional semiconductors. Here we limit our discussion to the (111) face of covalent semiconductors (diamond structure). In this case we have shown elsewhere [22] that a reasonable average of the different points of the 2-dimensional Brillouin zone can be achieved by taking the corner point as a representative one. Moreover, a narrow gap approximation seems to be a reasonable approach for discussing, even quantitatively, the surface properties of covalent semiconductors [8, 22, 23]. Within this approximation, the analysis of the interface can be shown to be equivalent to three 1-dimensional cases [22, 30], each one having the following pseudopotential for the semiconductor :

$$\begin{aligned} V^{(1)}(z) &= -\,|\,V\,|\,(e^{igz} + e^{-igz}) \\ V^{(2)}(z) &= -\,|\,V\,|\,(e^{igz}\,\omega^2 + e^{-igz}\,\omega) \\ V^{(3)}(z) &= -\,|\,V\,|\,(e^{igz}\,\omega + e^{-igz}\,\omega^2)\,, \end{aligned} \tag{33}$$

where

$$\omega = \exp\left(-\,i\,\frac{2\,\pi}{3}\right).$$

Then, the 3-dimensional metal-semiconductor junction can be approximately analysed by simultaneously considering three 1-dimensional cases, and using for each case the results of paragraph 2.

Note that now we have, in principle, three different problems with their corresponding phase-shifts, density of states, etc..., at the interface. However, the sum rule has to be considered for the full 3-dimensional problem; this means that is has to be rewritten as

$$\langle\, \eta_F^{(1)} \,\rangle + \langle\, \eta_F^{(2)} \,\rangle = \frac{\pi}{2}, \tag{34}$$

where $\langle\, \eta_F^{(i)} \,\rangle$ are the averages of $\eta_F^{(i)}$ for the three 1-dimensional problems. In the approximation we are using, we take the three values of $\eta_F^{(1)}$ and $\eta_F^{(2)}$ identical and equal to their mean value $\langle\, \eta_F^{(1)} \,\rangle$ and $\langle\, \eta_F^{(2)} \,\rangle$. This comes from the fact that although the potentials in equation (33) are shifted between them by the complex constant ω, and therefore with respect to the jellium edge, their Fourier components and their associated reciprocal lattice vectors are the same for all the three 1-dimensional problems. In fact it can be shown that the interface potentials for each 1-dimensional problem are also the same [22].

On the other hand, the three 1-dimensional cases are characterized by the same values of A and δ ($\delta = gd$, g being the reciprocal lattice vector associated with the periodicity perpendicular to the interface and d is the quantity shown in figure 2); the properties of the junction as a function of the two parameters of our model can be obtained by using the analysis described in section 2.

Here we should comment on the consistency of the procedure we used to achieve selfconsistency. In relation to this it is an important result that the whole cancellation between the occupied density of states in the gap and the valence band holds locally too; this is an exact result for $\delta = 0$ and it is very approximately true for $\delta \neq 0$. This means that when the pseudopotential is switched on at the metal-metal interface, a density of states appears at the interface in such a way that there is no new contribution to the interface potential. This result justifies our procedure to obtain selfconsistency at the interface and therefore all the magnitudes characteristic of it, namely, interface density of states, neutral level, etc.

In the following paragraph we shall discuss the metal-semiconductor junctions mentioned in the Introduction by means of this simple approach.

3.1 NON REACTIVE INTERFACES ($\delta = 0$). — In this section we consider two different interfaces i) junctions in which there is an intimate contact between the metal and the semiconductor, and ii) metal-semiconductor junctions with some relaxation or a physisorbed layer at the interface.

Here we have $\delta = gd = 0$ (see Fig. 2), since we have no electronic charge of the semiconductor sharing any chemical bond at the interface. The different junctions are described by the parameter A; for an intimate contact $A = \pi/2$, while for decoupled surfaces $A = 0$. When some relaxation or a physisorbed layer is present at the interface $0 < A < \pi/2$.

As regards the density of interface states in the fundamental gap, the following results are worth of comment; i) For an intimate contact ($A = \pi/2$, $\delta = 0$) we have the ideal metal-semiconductor junction with the same typical density of states (symmetric respect the midgap) for each 1-dimensional problem (see Section 2). ii) For decoupled media (either by a very wide layer or large relaxation), $A \to 0$, and a surface state, associated with the first 1-dimensional problem [22, 30] appears located in the midgap. iii) For intermediate cases ($0 < A < \pi/2$) we have obtained the density of interface states shown in figure 5. A peak evolves at the midgap for the first 1-dimensional case, while for the other two cases the densities of states are each one the symmetric of the other and decrease as A tends to zero. This peak is nothing but the surface state characteristic of the semiconductor free surface broaden by the presence of the metal, the half-width of the peak being related to the amount of relaxation or the width of the physisorbed layer at the interface. Notice that this resonance is the same that those previously discussed by Mele and Joannopoulos [10] and Flores [11], and

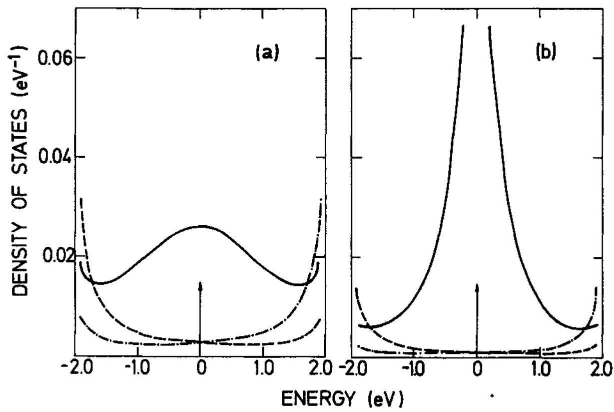

Fig. 5. — Density of interface states (eV^{-1}), for a metal-semiconductor junction with a physisorbed layer, in the semiconductor gap for the three 1-dimensional problems at the corner point of the 2-dimensional Brillouin zone of (111) faces. The charge neutrality point always lies in the middle of the semiconductor gap (vertical arrow). The densities of states for two different thickness of the physisorbed layer are shown : *a*) 0.5 Å, and *b*) 1 Å.

fortunately called by the former authors [10] dangling bond derived resonances. On the other hand, an important result which is deduced from the given density of states is that the charge neutrality level (φ_0) remains always in the midgap. Moreover, the interface density of states around φ_0 increases as $A \to 0$, i.e., as the interface changes from an intimate contact to decoupled surfaces.

The main conclusions for non reactive covalent junction are : *a*) the neutral level φ_0 is independent of any relaxation or physisorbed layer at the interface, and *b*) moreover, the interface density of states around φ_0 is always high giving in any case a junction behaviour closed to the Bardeen limit. This result is in line with many experimental data [18, 25].

It is worth to comment here that the reason for the last conclusion (b) is that, in both the free surfaces and the junctions of covalent semiconductors, there is a high density of states around φ_0. This may not be the case for ionic crystals. For instance, ZnS seems to have a very low density of surface states around E_F at its free surface [31], while in its ideal junctions with metals there is a non negligible density of interface states [7, 9, 32]. This is the kind of reasoning underlying the model used by Mele and Joannopoulos [10] in trying to explain the covalent-ionic transition in metal-semiconductor junctions reported by Kurtin *et al.* [20]. Nonetheless those authors [10], artificially introduced some relaxation at the interface without giving any sound reason for doing that. Considering the results obtained in this paper, we can suggest two ways to justify a model similar to that of Mele and Joannopoulos [10] : 1) following Andrews and Phillips we might think that the bonds between the ionic crystal and the metal are weaker than those between the covalent semiconductor and the metal. This would justify the assumption of relaxations in the junctions formed with insulators, and 2) considering that the experimental data collected by Kurtin *et al.* [20] were obtained in the sixties, it might be plausible to assume the existence of physisorbed layers in the junctions studied. Both suggestions would tend to explain the covalent-ionic transition reported by Kurtin *et al.* [20], a field which is still definitely open.

3.2 Etched junctions ($\delta = \pi/3$). — These junctions are prepared by allowing an electronegative atom, i.e., O, Cl, etc., to react with the semiconductor surface. We assume that only the charge in the surface states takes part in the reaction ; this amounts to one electron per surface atom. In our model this is equivalent to take $\delta = \pi/3$.

The interface density of states for this case is shown in figure 6, where two values of A have been chosen. Notice that the density of states for the first 1-dimensional case decreases as A decreases, i.e., for wider oxide layers, while for the other two cases two peaks evolve near the edges of the gap. When the two media are decoupled these resonances become bound states, this case being that of an etched semiconductor free surface or, equivalently, a monolayer of an electronegative atom chemisorbed on a covalent semiconductor surface. It is indeed very satisfactory that with our simple model we recover the results of Schlüter and Cohen [33] for Cl chemisorbed on Si(111) at the corner of the 2-dimensional Brillouin zone. On the other hand, the total density of interface states (the sum of the three 1-dimensional cases) is symmetric with respect to the midgap, and again the neutral level (φ_0) lies in the midgap for any A.

Thus our main results for an etched interface are the following : i) The neutral level φ_0 is independent of the oxide layer thickness, its position being the same that in the case of non reactive interfaces, ii) the density of states around φ_0 decreases as the layer thickness increases, in opposition with the previous case, and iii) new interface states are induced by the

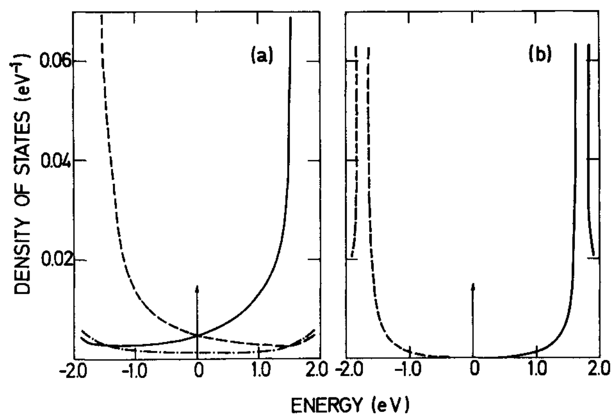

Fig. 6. — Same as figure 5 for an etched metal-semiconductor junction. Here again the charge neutrality point remains in the middle of the semiconductor gap (vertical arrow). It has been assumed that all the charge in the surface states of the semiconductor has been removed. The results for two layer thicknesses (T) are shown : *a*) 0.8 Å and *b*) 2.0 Å. Notice the strong decrease of the interface density of states at the charge neutrality level, as T increases.

Table I. — *Theoretical values for the density of states* N_{vs} *and for the slope* S *(see text) as a function of the effective* (*T*) *of the oxide layer for metal-semiconductor junctions prepared from etched semiconductor surfaces* (see § 3.2).

T (Å)	0.0	0.8	2.0	2.4	3.0	4.0
$N_{vs} \times 10^{-14}$ ($cm^{-2}\,eV^{-1}$)	7.57	3.31	0.22	0.09	0.02	0.002
S	0.07	0.08	0.46	0.66	0.87	0.98

etchant, not related to the free surface neither to the ideal (intimate contact) metal-semiconductor junction.

These results are very important as regards the junction behaviour. In fact as the density of states around φ_0 decreases, the slope of the straight line relating the barrier height and the metal workfunction should increase (see Eq. (1)). In table I we show the slope S of this straight line as obtained for different values of the effective widths of the oxide layer in an etched metal-Si(111) junction. It should be remarked here that in order to relate A with the layer thickness (T), we have described the oxide layer by a simple square barrier, its width being that of the layer (T) and its height being defined by the vacuum level. In this model A is given by

$$A = \tan^{-1}\left[\sqrt{\frac{\omega}{\omega'}}\coth\left(\frac{T}{2}\sqrt{\omega}\right)\right] - \tan^{-1}\left[\sqrt{\frac{\omega}{\omega'}}\tanh\left(\frac{T}{2}\sqrt{\omega}\right)\right], \quad (35)$$

where $\omega = E_{vac} - E_F$ and $\omega' = E_F$, E_F being the Fermi level and E_{vac} the vacuum level [26]. This formula has been used to determine A in figures 5-7. It should be noticed in table I that when $T = 4$ Å, S is very near 1; this is, therefore, the minimum width of the oxide layer to decouple the metal and the semiconductor.

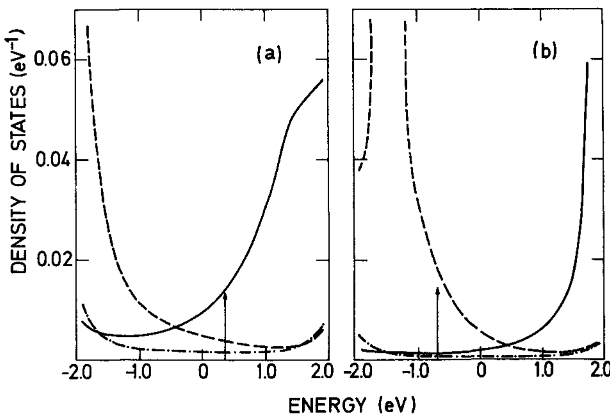

Fig. 7. — Same as figure 5 for a reactive metal-semiconductor junction. Two cases in which a different amount of electronic charge has reacted are shown : *a*) 3/4 of electron, and *b*) 5/4 of electron. *T* (Fig. 2) is taken equal to 2 *d* (see text). Notice that the charge neutrality point no longer lies in the middle of the semiconductor gap; see also figure 8.

The above results can be used to discuss the experimental data of Turner and Rhoderick [17, 18] for etched metal-Si(111) junctions. These authors showed how, for these junctions, the slope S increases up to 0.46. According to our analysis, this could be explained by assuming a minimum effective width for the oxide layer of 2 Å (see Table I).

3.3 Reactive interfaces. — In these junctions the metal reacts with an otherwise clean semiconductor surface leaving a chemical compound at the interface. These reactions dominate the interface behaviour, and recently different correlations between the barrier heights and magnitudes such as heats of formation of the chemical compounds [12, 13] or eutectic temperatures for transition metal-silicide-Si systems [25] have been suggested.

As discussed earlier in this paper, in order to obtain qualitative results for these junctions, we use the 3-dimensional model given above for different values of δ. We recall that our results would be valid only for the first stages of the reaction (small δ), as for extended reaction we would need to describe the electronic structure of the compound being formed [13, 15]. Note that this model can be also used to analyse etched interfaces for which only a fraction of the dangling bonds have been saturated (in this case $0 < \delta < \pi/3$).

In figure 7 we have drawn the density of interface states for the three 1-dimensional cases for different values of A and δ. The main feature of these results is that now the whole density of states ceases to be symmetric around the midgap, in such a way that the neutral level φ_0 is also displaced from $\varepsilon = 0$ (midgap). Here we notice that as in the previous case, new interface states induced by the chemical reaction appear. In figure 8 the charge neutrality level is shown as a function of δ; it can be noticed that for $\delta > 2\pi/3$ (two electrons removed), both media are decoupled and the charge neutrality follows that corresponding to the semiconductor free surfaces. Two assumptions have been made in doing these calculations. First we took the effective layer thickness $T = 2d$ (see Fig. 2); this is probably an underestimation of T. Second we calculated A by using equation (35); this means that we are assuming the chemical compound to be a dielectric. We must be aware of the fact that in many instances the silicides are metals, as for example is Pd_2Si [15]; in such cases our model cannot probably be used (see discussion below).

The above results can be firstly applied to study the ageing of etched metal-Si junctions [17, 18]. Notice that in this case our calculation of A by means of equation (34) is correct as the layer being built up at the interface is probably an oxide. Turner and Rhoderick [17] have found that as etched metal-Si contacts are aged, the barrier heights (for Au-Si junctions in particular) increase with time of ageing although the final value is practically insensitive to the method used to prepare the surface. If we made the plausible

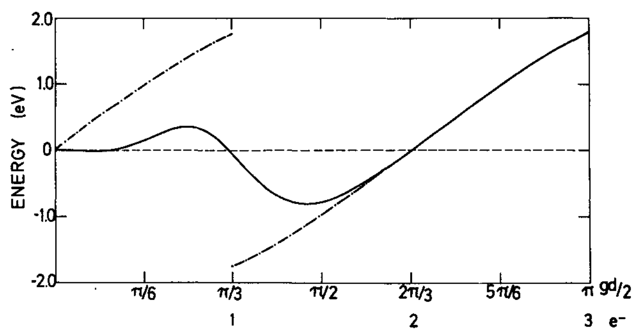

Fig. 8. — The charge neutrality level in reactive metal-semiconductor junctions (full line) as a function of either the electronic charge removed or the quantity gd, g being the reciprocal lattice vector at the Fermi level and d is the distance shown in figure 2. T (Fig. 2) is taken equal to 2 d (see tex)). Notice that for removed electronic charges higher than 2 electrons the charge neutrality level in the metal-semiconductor junctions follows that corresponding to the free semiconductor surface (thick broken line).

assumption that ageing favours the saturation of the dangling bonds, we can interpret those data as follows : the final barrier height for a fully etched junction is obtained when all the charge in the semiconductor dangling bonds has reacted ($\delta = \pi/3$) with the adsorbate (this result being independent of the method used to fully etch the surface). If a less amount of charge has reacted (this can now depend on the method used), $0 < \delta < \pi/3$, the neutral level lies at higher energies (Fig. 8) giving a smaller barrier height, in qualitative agreement with the results of Turner and Rhoderick [17].

The discussion of reactive interfaces is not so clean. Our model can be only used to interpret the first stages of the reaction. Unfortunately, barrier heights changes during those initial stages have not been carefully analysed. Recently Cheng *et al.* [16] have suggested that these measurements have to be performed at low temperatures (170 K) to control the rapid reactions that take place. The present theory predicts that for these initial stages the neutral level would be displaced to higher energies (Fig. 8) giving smaller heights. One might be tempted to compare this result with those of Brillson [13] which indicate that the barrier heights for reactive interfaces are smaller than those of non reactive junctions ; however, a more detailed knowledge of the conditions under which those data were taken and of the properties of the compounds being formed is needed in order to make a comparison with total confidence. We should conclude that to develop a microscopic theory of reactive junctions, more detailed experimental data are needed, in particular there is a need of achieving a sound knowledge of the properties of the silicides being formed.

4. **Concluding remarks.** — The aim of this paper has been to present a theory, which could account for some of the properties of the junctions mentioned in the introduction. To this end we have analysed the interface density of states and the neutral level as a function of the interface conditions. To our knowledge, this is the first time that a rigorous discussion of the neutral level in such a general terms, has been made [18]. The price we have paid for it is the use of a rather simplified model. However we have reached some general conclusions that seem to be at least in qualitative agreement with the experimental evidence. i) For clean covalent junctions, the neutral level is independent of any relaxation or physisorbed layer at the interface ; the junction behaviour, turns out to be always near the Bardeen limit. ii) For ionic junctions we have shown that the rather Bardeen-like behaviour found for intimate contacts [7, 9, 32] can be changed into a Schottky-like behaviour if a physisorbed layer or some relaxation [10] are present at the interface ; we have also pointed out that the latter could be correlated with the Andrews and Phillips suggestion [12] concerning the strength of the metal-semiconductor bonds (weak for the ionic junctions and strong for the covalent ones). iii) For etched covalent interfaces, we have found that the neutral level coincides with the level obtained for non reactive interfaces, although the density of states around φ_0 decreases with the width of the oxide layer ; we have shown that, if the oxide layer is wide enough, the junction behaviour is near the Schottky limit. We have also analysed the ageing behaviour of partially etched covalent interfaces and compared our results with experimental data [17, 18]. iv) Finally we have used our results for reactive interfaces to comment the present state of our knowledge of these complicated system. Following Cheng *et al.* [16] we have remarked the need of performing barrier height measurements at low temperatures, and we have demonstrated that to develop a sound microscopic theory for these junctions, various studies of the electronic structure of the chemical compound being formed are required.

Appendix I. — As stated in section 2, matching wavefunctions like those of equations (2*a*) and (2*b*) through the interface, leads to the general equation

$$f(\eta, \eta') = 0 \qquad \text{(A.1)}$$

that relates the two phase-shifts η and η' of the two wavefunctions given in equations (2). Then, the interface density of states can be obtained from equation (A.1) by using the following argument :

a) Let us consider the system of figure 2 (with $|V| = 0$) and assume that both jellium metals extend up to $z = L$ and $z' = L'$. Then we choose L and L' in such a way that for a given energy E (referred to the average potential in $z > 0$) we have

$$\lambda' L' = m' \pi \qquad \text{(A.2)}$$

$$\lambda L = m\pi \qquad \text{(A.3)}$$

$$\frac{L}{L'} = \left(\frac{\partial E}{\partial \lambda}\right) \Big/ \left(\frac{\partial E}{\partial \lambda'}\right), \qquad \text{(A.4)}$$

where m and m' are integers and λ and λ' are the wavevectors of the wavefunctions given in equations (2*a*), (2*b*). Note that these equations lead to

$$\frac{m}{m'} = \frac{\lambda}{\lambda'} \frac{\partial E/\partial \lambda}{\partial E/\partial \lambda'},$$

a relation that can be satisfied with a given accuracy even though the r.h.s. is an irrational number.

b) Let us now assume that both media have infinite barriers at $z = 0$ ($z' = 0$) and $z = L$ ($z' = L'$) and a constant potential between these barriers. Then, by considering equations (A.2), (A.3) and (A.4) we can prove that both metals have the same spectrum of energy levels around E. In fact equations (A.2) and (A.3) show that we have one electronic state for each metal at the energy E. Moreover, any other level near this one has a momentum given by

$$\begin{aligned} \lambda + \Delta\lambda &= \frac{m\pi}{L} + \frac{\pi}{L}\Delta m \quad \text{for} \quad z > 0 \\ \lambda' + \Delta\lambda' &= \frac{m'\pi}{L'} + \frac{\pi}{L'}\Delta m' \quad \text{for} \quad z' > 0, \end{aligned} \tag{A.5}$$

Δm and $\Delta m'$ being integers. Then the energy of this level will be

$$\begin{aligned} E + \Delta E &= E + \frac{\partial E}{\partial \lambda}\left(\frac{\pi}{L}\Delta m\right) \quad \text{for} \quad z > 0 \\ E + \Delta E' &= E + \frac{\partial E}{\partial \lambda'}\left(\frac{\pi}{L'}\Delta m'\right) \quad \text{for} \quad z' > 0. \end{aligned} \tag{A.6}$$

Taking into account equation (A.4) we finally find that if $\Delta m = \Delta m'$, then $\Delta E = \Delta E'$, and therefore both metals have the same spectrum around the energy E.

c) Now we allow both metals to be connected through the interface (we remove the infinite barriers at $z = 0$ and $z' = 0$), keeping the infinite barriers at $z = L$ and $z' = L'$. In order to obtain the new levels for the junction, we impose the following relations

$$\begin{aligned} (\delta\lambda) L + \eta &= 0 \\ (\delta\lambda') L' + \eta' &= 0 \end{aligned} \tag{A.7}$$

since the wavefunctions (2*a*), (2*b*) must vanish at the infinite barriers $z = L$ and $z' = L'$ respectively.

In equations (A.7) $\delta\lambda$ and $\delta\lambda'$ represent the shift in the wavevectors for the new interface solutions. Accordingly, the energy levels will be shifted to $E + \delta E$, in such a way that

$$\delta E = \frac{\partial E}{\partial \lambda}\delta\lambda = \frac{\partial E}{\partial \lambda'}\delta\lambda'. \tag{A.8}$$

Then equations (A.7), (A.8) and (A.4) lead to the relation

$$\eta = \eta'. \tag{A.9}$$

Then the equation which give the phase-shift η and consequently the new interface energy levels and wavefunctions will be

$$f(\eta, \eta' = \eta) = 0. \tag{A.10}$$

It is important to note that equation (A.10) must have two solutions. In fact for the case of infinite barriers at $z = 0$ and $z' = 0$ we already had two levels, at the same energy, one for each metal. When the two metals are connected through the interface, this degenerate level splits into two states that are given by (A.10).

Finally, the interface density of states $N^1(E)$ can be obtained from the two solutions of equation (A.10), namely, $\eta^{(1)}$ and $\eta^{(2)}$ as follows

$$N^1(E) = \frac{1}{\pi}\frac{d\eta^{(1)}}{dE} + \frac{1}{\pi}\frac{d\eta^{(2)}}{dE}. \tag{A.11}$$

On the other hand, the two wavefunctions can be written as

$$\psi^{(i)} \sim \begin{cases} A_i \sin(\lambda z + \eta^{(i)}) & \text{for} \quad z > 0 \\ B_i \sin(\lambda' z' + \eta^{(i)}) & \text{for} \quad z' > 0 \end{cases} \tag{A.12}$$

for $i = 1, 2$.

Then by using the normalization and orthogonality conditions and equation (A.4) we obtain the following values for the constants in equation (A.12)

$$\begin{aligned} A_1 &= \frac{a}{\sqrt{\lambda}}, \quad B_1 = \frac{b}{\sqrt{\lambda'}}, \\ A_2 &= \frac{b}{\sqrt{\lambda}} \quad \text{and} \quad B_2 = -\frac{a}{\sqrt{\lambda'}} \end{aligned} \tag{A.13}$$

with $a^2 + b^2 = 2$. Introducing these values into equation (A.12) we obtain the form used in equation (18).

Finally, let us discuss the behaviour of $\eta^{(i)}$, $i = 1, 2$ at $E = E_0$ (we recall that $E = 0$, E_0 are the average at $z > 0$ and $z' > 0$, respectively). The general equation (A.1) can be obtained by matching across the interface the wavefunction ψ at $z > 0$ with that at $z' > 0$ given by

$$\psi' \sim \sin(\lambda' z' + \eta') \quad \text{for} \quad E > E_0; \tag{A.14}$$

thus the matching equation is written as

$$\frac{1}{\lambda'}\tan\eta' = \frac{\psi(z' = 0)}{d\psi/dz\,(z' = 0)} \equiv L. \tag{A.15}$$

Now for $E \to E_0$ and $\lambda' \to 0$, equation (A.15) has two solutions, namely,

$$\text{(a)} \ \eta' \to 0 \quad \text{and} \quad \text{(b)} \ L \to \infty. \tag{A.16}$$

The first case (a) corresponds to one of the solutions of equation (A.1), namely $\eta^{(2)} \to 0$, while the second (b) gives a finite value for η' ($\eta^{(1)}$ finite). On the other hand, solution (b) involves a condition ($L \to \infty$) that coincides with the one obtained by approaching $E = E_0$ from $E < E_0$, which means using the wave-function of equation (3). This proves that

$$\text{for} \quad E \to E_0 , \qquad \eta^{(1)} = \eta , \qquad (A.17)$$

as written in equation (13).

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