

## Two-State Systems and the Electronic Structure of Metal-Semiconductor Interfaces: A New Unifying Mechanism

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A self-consistent theory of metal-semiconductor electronic structure is presented. We discover that this structure is formed out of two-state systems; these include metal-like states and metal-induced semiconductorlike states. This dual aspect may provide a new unifying mechanism for existing models of metal-semiconductor electronic structures. We discuss the relevance of the discovered two-state character to the Fermi-level pinning. Finally, the local density of states is calculated.

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The metal-semiconductor (M-S) interface is an important heterostructure with respect to its technological involvement in many areas of microelectronics. A plethora of studies have been devoted to this system to explain the origin of Schottky-barrier heights. Despite the tremendous effort made in this field and the production of many very interesting models<sup>1-3</sup> and theories,<sup>4,5</sup> it seems that there is no general theory which gives a unified view of the elementary mechanism, if one exists. This is probably due to the complexity of this structure. A semiconductor surface is a system very sensitive to external perturbations: It may reconstruct under cleavage or surface segregation conditions while its perturbation by foreign incoming atoms may produce intrinsic point defects. In this Letter, I investigate the specific electronic properties induced by metallization and I emphasize their relevance to Fermi-level pinning.

The idea of the involvement of semiconductor defect states<sup>6-9</sup> is probably due to results showing a very weak sensitivity of the barrier to the metal deposited<sup>10,11</sup> for the more covalent semiconductors. Recently,<sup>12</sup> the surface position of the Fermi level in M-S structures has been analyzed in terms of two different types of electronic states. These include adatom-related states and the continuum of adsorbate-induced interface states corresponding, respectively, to the metal-submonolayer regime and the metallic-island or continuous-metallic-film regime. A new insight into this problem, based on simple considerations of local charge neutrality, has been gained.<sup>13</sup> On this basis, it is argued that the metal-induced gap states (MIGS) separate into two categories: occupied states having a valencelike character and unoccupied states having a conductionlike character. The interface Fermi level  $E_F$  is pinned at  $E_B$ , the "midgap energy" at which the character of MIGS switches from a valencelike to a conductionlike character.

In this Letter, I present a self-consistent study of the electronic structure of the M-S interface which considers the evolution of this structure as a function of the metal thickness. I show that two kinds of electronic states are

induced by metallization: metalliclike and semiconductorlike states which form a related two-state system. This two-state system provides a basic mechanism which may unify the existing models concerning Fermi-level pinning in both thin and bulk metallic adsorbates.

Generally speaking, any theory which concentrates only on the calculation of the electronic interface states cannot show the basic mechanism which is invoked in this Letter. In order to give evidence of such a mechanism, we need a theory which shows how the metal band is built up during metallization and which then gives an account of the perturbation of the semiconductor bands in this process. In what follows, I present the basic elements of the theory; more details will be given elsewhere.<sup>14</sup>

The electronic-structure calculation is made within the framework of a tight-binding Hamiltonian. A simple one-band model is used to describe the bulk-metal electronic structure and a two-band model is used for the bulk-semiconductor electronic structure. The quantity relevant to our problem is the Green's function for the entire M-S structure, which may be calculated within the following scheme: (i) Use the Green's functions for the separated bulk materials (metal and semiconductor) as reference quantities. This will result in a two-block Green's-function matrix  $\mathbf{G}_0$  which gives the decoupled metallic and semiconductor bulk electronic structures. (ii) Create a metallic film and a semi-infinite semiconductor by introducing a cleavage operator  $\mathbf{V}_S$  which will extract these systems from the corresponding bulk materials. (iii) Create the M-S interface by introducing interfacial hopping integrals between atoms in the metal and in the semiconductor surfaces (operator  $\mathbf{V}_i$ ). In order to take into account the charge flow across the interface, we introduce Coulomb repulsion potentials  $U_M$  and  $U_S$ , respectively, on the metal and on the semiconductor atoms. In fact, this is equivalent to the Hartree-Fock approximation on the Coulomb interaction site. If we assume the same linear dependence of  $U_M$  and  $U_S$  on charge transfer, and because of the translational symme-

try parallel to the interface, we obtain  $U_M = -U_S$  ( $=U$ ). Finally,  $U$  and the M-S Fermi level  $E_F$  are related by the Friedel<sup>15</sup> sum rule, ensuring that the charge-neutrality condition is satisfied,

$$\Delta N(E_F, U) = 0. \quad (1)$$

In this Letter, we use the following method to carry out the numerical calculations: For a given Fermi level, we determine the self-consistent potential by using the charge-neutrality condition and we then calculate the M-S electronic structure.

One can summarize all of these perturbations within the same perturbation matrix  $\mathbf{P}$ . In this way, the electronic structure of the M-S system can be determined once we know the corresponding Green's-function matrix  $\mathbf{G}_p$ , given by Dyson's equation:

$$\mathbf{G}_p = \mathbf{G}_0 + \mathbf{G}_0 \mathbf{D}^{-1} \mathbf{P}, \quad (2)$$

where  $\mathbf{D}^{-1}$  represents the inverse matrix of  $\mathbf{D} = \mathbf{I} + \mathbf{P}$ . The originality of our method is such that by solving the equation

$$\det(\mathbf{D}) = 0 \quad (3)$$

we obtain the dispersion relations of all electronic structures induced by the metal. These include metal-like states, semiconductorlike states, and interface states.

The local density of electron states, in any atomic plane within the M-S structure, may be calculated from the imaginary part of  $\mathbf{G}_p$  by using standard procedures. Two such procedures are the double summation over all values of the two-dimensional wave vector  $k_{\parallel}$  within the irreducible part of the two-dimensional Brillouin zone and the use of an appropriate sampling of values of  $k_{\parallel}$  (special-points method).

Let us now give the main results which establish the basic unifying mechanism invoked in this Letter. A typical example is presented in Fig. 1. This corresponds to a semiconductor substrate terminated by acceptorlike atoms (surface atoms are of anion type) on the top of which metallic layers are adsorbed. For the chosen system,  $E_F = -0.1$  eV (the zero of energy is chosen midway in the semiconductor gap), one can notice that the metal band overlaps the semiconductor valence and conduction bands. We can clearly see that the electronic features specific to the M-S heterostructure are present in the form of a two-state system. By a two-state system, we mean that each metal-like state, created during the metallization process, is "attached" to an associated metal-induced state (MIS). This latter set of levels may be thought of as specific to the semiconductor and to the interface. This shows the local metallic character of the semiconductor near the interface. The first set of states follows the asymptotic shape of the bulk-metal electronic band. The second set is formed out of states extracted from the semiconductor bands. The energy levels of this set may fall within the overlapping parts of bulk-

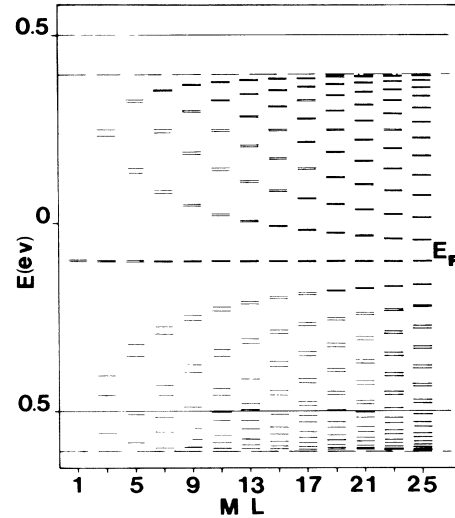


FIG. 1. Energy and number of two-state structures as a function of metal thickness (ML denotes number of monolayers). The dash-dotted lines represent the limits of the metallic bulk band while the solid lines represent the top of the semiconductor valence band (lower) and the bottom of the semiconductor conduction band (upper). The chosen example corresponds to  $E_0 = 0.2$  eV,  $E_F = -0.1$  eV, and to a 1-eV-wide semiconductor gap. The states are calculated for wave vector  $k_{\parallel} \cong 0.63\pi/a$ .

semiconductor and bulk-metal bands (resonant-state regime) as well as within the semiconductor gap (metal-induced-gap-state regime). Strong evidence of the metallic character of the first set is given by analyzing the M-S-associated Bloch waves and their corresponding eigenstates at the bidimensional (interfacial) Brillouin-zone edges. It is very well known that at this limit ( $k_{\parallel} \sim \pi/a$ ;  $a$  is the lattice parameter), microscopic electronic features associated with the atomic species present may appear. Indeed, our results show that the metal atomic level  $E_0$ , the energy at the middle of the metallic band, appears as an eigenstate belonging to the first set (Fig. 2, curve 1). It is also worth noting that the difference in energy between two associated levels decreases as the metal thickness increases. At the same time, the number of such double states increases, approaching a quasicontinuumlike state distribution (Fig. 1).

It is this dual aspect of M-S electronic features which, I believe, may provide a basic mechanism for a unifying theory of existing models of M-S electronic structures. This will concern the most popular models, namely (i) defect models<sup>6-9</sup> and (ii) the midgap energy model.<sup>13</sup>

(i) *The two-state mechanism and defect models.*—First of all, the consequences of such a mechanism are meaningful for intrinsic-defect models of Schottky-barrier formation.<sup>6-9</sup> Indeed, the unifying mechanism establishes that as soon as the metallization process starts, not only do adsorbate-like states appear, but also

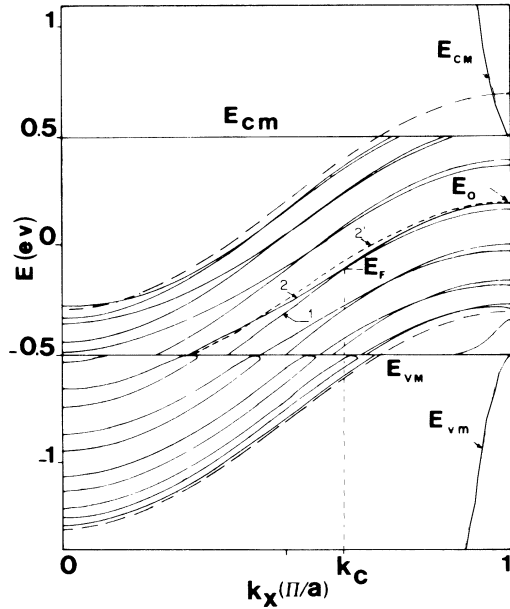


FIG. 2. Electronic structure of an M-S system along the (10) direction of the interfacial Brillouin zone. This shows the two-state character of M-S electron dispersion relations and the intersection of curves 1 and 2 at  $E_F$ . The metal atomic level  $E_0$  is "caught" by a metal-like state. The non-self-consistent treatment moves curve 2 upwards ( $2 \rightarrow 2'$ ) while the metallic level (curve 1) remains unchanged.  $E_{vm}$ ,  $E_{VM}$ ,  $E_{cm}$ , and  $E_{CM}$ , represent, respectively, the limits of valence and conduction bands. The dash-dotted curves represent the bulk-metal band limits. The metallic film is seven layers thick. The same parameters as in Fig. 1 have been chosen.

adatom-induced perturbations of the semiconductor bands are initiated, leading to the creation of tied double states. Those of metallic character will form the continuum of bulk-metal electronic states, while those of semiconductor character provide a set of metal-induced states. These latter may act as precursor states in accommodating defect levels resulting from the metal-semiconductor interaction, especially when this interaction is exothermic. In our model, the number of these precursor states increases as the number of adsorbed metal atoms increases.

(ii) *The two-state mechanism and the midgap energy theory.*—Second, our results show a fundamental behavior of the two-state system which may enlighten our understanding of the basic nature of Fermi-level pinning in M-S structures. This clearly appears in Fig. 2, where the dispersion curves of each doublet intersect one another at a certain value  $k_c$  of the bidimensional wave vector. Of special interest is the result showing that the dispersion curve associated with the metal atomic level  $E_0$  (Fig. 2, curve 1) intersects the semiconductorlike level of the doublet (curve 2) exactly at the Fermi level  $E_F$ . We have checked that this interesting feature is not specific to the choice of parameters we have made, as different sets of parameters give the same feature. Figure 1 shows

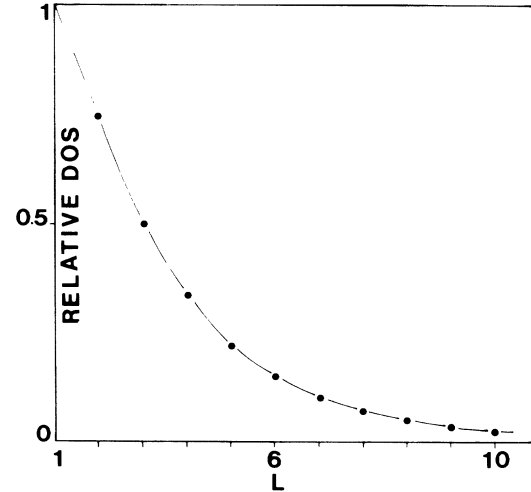


FIG. 3. Variation of the relative local DOS as a function of the position  $L$  of the semiconductor atoms.  $L=1$  corresponds to a surface layer where the relative density is equal to 1.

that the Fermi-level pinning mechanism presented in this Letter works even at one-metal-monolayer coverage, in agreement with other data reported in the literature.<sup>16,17</sup>

Let us now analyze the physics behind such a result and try to draw a possible analogy with existing models of the electronic structure of the M-S system.

It is worthwhile to mention that the intersection between curves 1 and 2 at  $E_F$  is related to self-consistency, as a non-self-consistent treatment shifts the MIS upwards by  $\approx 0.03$  eV (curve  $2 \rightarrow 2'$ ; curve 1 unchanged). As it is the charge neutrality which fixes the position of the Fermi energy, we can say that the intersection at  $E_F$  is a direct consequence of the charge neutrality. Arguments have been presented that because of the charge-neutrality concept, the results concerning the M-S electronic structure are not strongly parameter dependent.<sup>16</sup> Moreover, it may be seen (Fig. 2) that a non-self-consistent treatment will destroy the semiconductor band origin of the MIS. This is because the corresponding dispersion relation (curve  $2'$ ) reaches the metal atomic level  $E_0$  at the zone boundary. This undoubtedly stresses the universally acknowledged role of interface dipoles at M-S interfaces. The doublet (1,2) separates the metal band into two regions where an equal number of two-state electronic structures appear. It thus plays the role of a mixed midstructure associated with the metallic band and the semiconductor gap (mid-band-gap two-state structure) for those parts of the semiconductor gap (and bands) overlapping the bulk-metal bands. In the unifying mechanism, it is this mid-band-gap two-state structure which may represent the analog of the midgap occupied-unoccupied states, as far as the position of  $E_F$  is concerned.<sup>13</sup> In our approach, this two-state structure is indeed related to metallic and semiconductor features.

We have also calculated the variation of the local density of states when one moves from the semiconductor

surface towards its inner (bulk) part. Our results, represented in Fig. 3 for an energy equal to the Fermi energy, show a sensitive drop in this density for semiconductor atoms a few monolayers from the metal. This is in agreement with another calculation<sup>4</sup> which shows that the Fermi-level position corresponds to a minimum in the density of states within the semiconductor.

In conclusion, I have presented a theory which shows that the entire electronic spectrum of an M-S system consists of two-state structures. Each structure is formed out of a metalliclike state and a semiconductorlike MIS. Among them, a midgap structure plays a dominant role in the determination of the position of Fermi level. This feature presents an analogy with the "midgap-energy" theory.<sup>13</sup> Although I have used in this study simple models to describe the electronic structures of both metal and semiconductor materials, I believe that the discovered two-state structure provides a new basic mechanism which may enlighten and hopefully unify the existing models on the electronic structure of M-S interfaces.

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