Investigación *Revista Mexicana de Física* **37** *No. 3 (1991) 503–511*

The Mo/Ta (100) interface

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(Recibido el 29 de noviembre de 1990; aceptado el 2 de mayo de 1991)

Abstract. We have calculated the interface local density of states (ILDOS) formed by the transition metals Mo/Ta using a tight-binding Slater-Koster description and the Green's function matching method together with quickly converging algorithms to compute the transfer matrices. We obtain the surface LDOS as a byproduct. Our result is a useful tool to analyze experimental results and to check models as a function of the value of the tight-binding parameters either of the bulk or at the interface itself. We consider the (100) direction. We compare the interface to the bulk and to the surface and comment on some recently found experimental results for this interface.

PACS: 72.20.Dx; 71.20.Cf

1. Introduction

The study of the physics of surfaces, interfaces and superlattices of transition metals is the object of a new and increasing interest nowadays. At the origin of the deep understanding of the experimental results on these systems is an accurate description of its electronic band structures and its phonon spectra. In this paper we use an empirical tight-binding [1] description of the electronic structure of the transition metals Mo and Ta to calculate the ILDOS using the Green Function Matching Method [2]. Our study is analogous to the recent calculation by Baquero *et al.* [3] for other transition metals. The LDOS for the surfaces is obtained as a byproduct.

We consider ideal interfaces. This is not a limitation anymore for metallic systems. Recent advances in thin-film deposition technology [4] have allowed the fabrication of overlayers on surfaces, interfaces and superlattices under more strict control of the parameters entering the process of production and samples with a high degree of structural coherence are now possible.

Metallic interfaces are relatively seldom studied. The electronic structure of the Ni-Al interface was recently studied experimentally by Bonnelle *et al.* [5] by electron stimulated X-ray emission spectroscopy and the results analyzed theoretically by the recursion method [6] using tight-binding hamiltonians. Farquhar and Inglesfield have calculated, very recently, the interface electronic structure by the embedding method [7]. A tight-binding analysis of the cohesive properties of this interface can be found in Ref. [8]. Also, the growth and modification of the Al/Ta(100) interface was studied by photoemission [9]. There is no previous study of Mo/Ta interface known to us.

Artificially prepared superlattices of transition metals are a relatively new class of materials and their electronic, magnetic and superconducting properties are being studied quite intensively [10]. The Mo-Ta superlattice has been studied recently [11].

2. The method

As stated above, to describe the interface between two transition metals we make use of empirical tight-binding hamiltonians. Since the Green's function matching method takes into account the perturbation caused by the surface or the interface exactly, at least in principle, we can use the tight binding parameters for the bulk. This does not mean that we are using the same tight-binding parameters for the surface, or the interface and for the bulk. their difference is taken into account through the matching of the Green's functions. We use the method in the form cast recently by García-Moliner and Velasco [2]. They make use of the transfer matrix approach first introduced by Falicov and Yndurain [12]. This approach became very useful due to the quickly converging algorithms of López Sancho *et al.* [13]. Following the suggestions of these authors, the algorithms for all transfer matrices needed to deal with surfaces, interfaces, quantum wells and superlattices can be found in a straightforward way [14]. The mathematical details of the method are described in the appendix.

3. Results and discussion

This is the first calculation of the interface local density of states (ILDOS) for the Mo/ta interface.

In Figs. 1 and 2, we show our result for the ILDOS. These were obtained with a two center, orthogonal empirical tight-binding description of the *s*, *p*, and *d*-bands. The tight-binding parameters were taken from the work of Papaconstantopoulos [16].

In Fig. 1, we can see the LDOS projected at the interface on the Ta atomic layer compared to the surface and bulk LDOS. In Fig. 2, we present the analogous result for the projection on the Mo side.

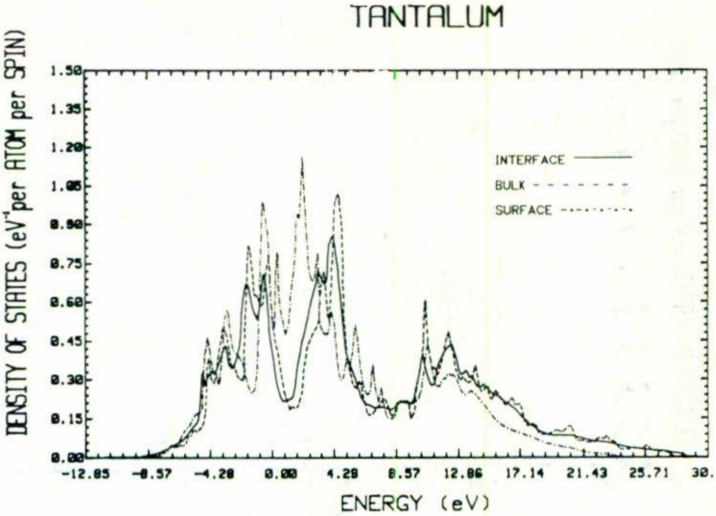

FIGURE 1. The tantalum SLDOS, BLDOS and the ILDOS for the Mo/Ta interface.

In general, the bulk LDOS (BLDOS) for the *bcc* elements shows two peaks separated by a minimum. The Fermi level, E_f, is found usually around this minimum. The surface LDOS (SLDOS), in contrast, presents a very strong peak around the position of the minimum in the BLDOS. The surface becomes very active when E_f occurs around the maximum in the SLDOS. The states at these energies for the transition metals are predominantly *d*-like and therefore very localized. This fact can lead to special properties of transition metal surfaces. A known general characteristic of these LDOS is that the width of the bands is approximately the same for the interface and the bulk but for the surface it is narrower.

Let us concentrate on Fig. 1, where the Ta sides of the ILDOS is compared to the BLDOS and SLDOS for Ta(100). Notice first that the general characteristics mentioned above hold for this case. The BLDOS presents two peaks of high intensity and two minor ones at the lower and higher energies respectively. The Fermi level occurs below the minimum in the BLDOS. The SLDOS is very different from the bulk and from the ILDOS. The two high maxima come closer to each other and the Fermi level occurs in the quickly varying part of the spectrum showing that any charge transfer of whatever origin to this surface can change its properties. This can occur when overlayers are grown onto the surface. The ILDOS, the new result, turns out to be quite similar to the BLDOS but the Fermi level occupation is lower. Sometimes, interfaces have characteristics similar to surfaces of the same material and therefore should share some of their properties. A well known case is V(100) [3].

Our figures have their origin at the Fermi level. When the bottom of the *s* band is taken as the origin, the values for E_f are for the tantalum side: 11.2 for the

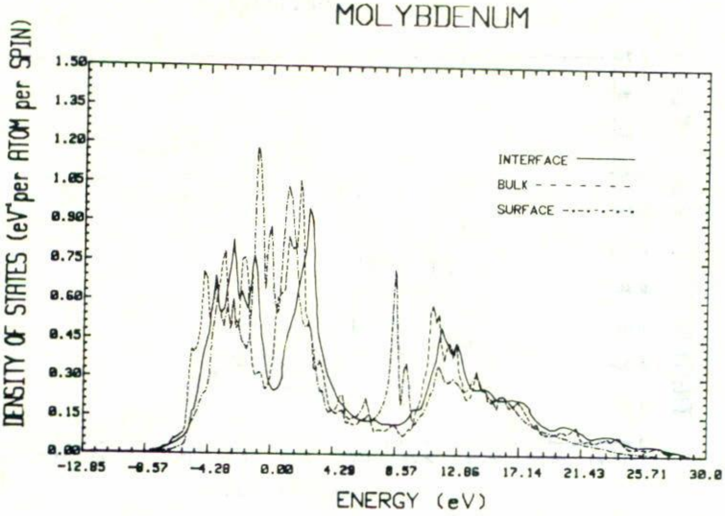

FIGURE 2. The molybdenum SLDOS, BLDOS and the ILDOS for the Mo/Ta interface.

surface, 9.4 for the bulk and 9.6 for the interface and for the molybdenum side: 11.1 for the surface, 10.8 for the bulk and 10.2 for the interface in eV.

In order to keep the highest energy level at the same energy on both sides we have added to the diagonal matrix elements of the hamiltonian in the Ta side, 0.8 eV following the procedure of Refs. [3] and [5].

Let us now concentrate in Fig. 2. The first thing to notice is that the ILDOS resembles the BLDOS again which is not the general case. When looking carefully we see that the Mo ILDOS is slightly shifted towards higher values of the energy. The Fermi level is right at the minimum and therefore any charge transfer will have consequences in the behavior of the interface. The density of states at the Fermi level is quite lower on this side of the interface than on the other side. This is the real sharp discontinuity at the interface. The ILDOS in the Mo side resembles the BLDOS much more than the SLDOS and no similarities between the interface and the surface behavior can be inferred from these results. The Mo(100) surface does reconstruct and it is believed that the surface states are responsible for it. The density of states at the Fermi level is very big for the surface case when compared to the bulk or to the interface case.

A last point concerns the Mo/Ta (100) superlattice. In the study of the superconducting properties of this superlattice of Ref. [11], the superconducting critical temperature, T_c, of samples with different layer thickness, Λ ($d_1 = d_2 = \Lambda/2 = d$) were measured. The have obtained a monotonical decrease of T_c with Λ which they could account for within the Gennes-Werthamer theory [11,17] on the proximity effect in the region where d is larger or comparable to the superconducting coherence length, $\mathcal{E}$. To fit the data at $d < \mathcal{E}$ they needed an additional mechanism reducing the intrinsic T_c of the superconductors. They have related this effect to the smearing of the density of states $N(E)$ and a lowering of $N(E_f)$. It is interesting to notice in this respect that in our study of the Mo/Ta interface, we get a reduction of the Fermi level population with respect to the bulk value only on the Ta-side of the interface.

4. Conclusions

We have calculated the interface local density of states (ILDOS) for the transition metal interface Mo/Ta in the (100) direction by using an empirical tight-binding hamiltonian and the Green's function matching method to calculate the interface Green function.

As a general feature we get that the ILDOS in both sides of the interface looks similar as the bulk projected LDOS which is very different from the surface local density of states in the same direction. Also, we get a local density of states at the Fermi level smaller than the bulk value for the Ta side but which is the same in the Mo side. It is possible that this is related to the measured dependence of Tc with respect to Λ, the layer thickness of the superlattice.

Appendix

We describe the electron bands with the tight-binding method of Slater and Koster [1]. To set up the hamiltonian for the interfaces we assume ideal truncation.

With this hamiltonian we obtain the Green's function from

$$(\omega - H)G = I, \tag{1}$$

where ω is the energy eigenvalue and I is the unit matrix. We adopt the customary description in terms of principal layers. We label them with positive numbers and zero for the surface atomic layer. Let $|n\rangle$ be the principal layer wave function describing the n^{th} principal layer. It is a LCAO wave function with five d-like, three p-like and one s-like atomic functions per spin on each atom and two atomic layers, *i.e.*, it is a 18-dimensional vector. If we take matrix elements of Eq. (1) in the Hilbert space generated by this system of wave-functions $|n\rangle$, we get

$$\langle n|(\omega - H)G|m\rangle = \delta_{mn}. \tag{2}$$

The identity operator (from the definition of principal layer) can be cast as

$$I = |n-1\rangle\langle n-1| + |n\rangle\langle n| + |n+1\rangle\langle n+1| \tag{3}$$

since there are only nearest neighbour interactions between principal layers and therefore $H_{m,m+i} \equiv 0$ for $i \geq 2$. By inserting (3) in (2) we get

$$(\omega - H_{nn})G_{nm} - H_{nn-1}G_{n-1m} - H_{nn+1}G_{n+1m} = \delta_{mn}. \tag{4}$$

The matrix elements of the hamiltonian, H_{nm}, that appear in this formula are 2×2 supermatrices (each principal layer contains two atomic layers) each of whose elements is a 9×9 matrix (since we are using a 9-wave functions basis for each atom). For example:

$$H_{01} = \begin{pmatrix} h_{0-2} & h_{0-3} \\ h_{-1-2} & h_{-1-3} \end{pmatrix}. \tag{5}$$

Notice that the rows are labeled with the index of the surface principal layer zero (containing atomic layers 0 and -1) while the columns are indexed with the first principal layer (atomic layers -2) and -3). We label principal layers with positive numbers and atomic layers with negative numbers. The surface is labeled with zero in both cases. We shall adopt the hypothesis of an ideal, non reconstructed surface and then $H_{00} = H_{nn}$ for any n. Also $h_{0-2} = h_{-1-3}$ and $h_{-1-2} = h_{0-1}$. For second-nearest neighbour interactions $H_{0-3} = 0$. To calculate H_{00} and H_{01} we need to know only h_{00}, h_{0-1} and h_{0-2} which are 9×9 matrices as stated before. These three matrices are readily written in a tight-binding language and can be calculated with the bulk parameters mentioned above. They depend on the energy, ω, and on the wave vector $\mathbf{k}$.

Using (4) for $m = n$ it is straightforward to get the surface Green's function

$$G_s^{-1} = \omega I - H_{00} - H_{10}T \tag{6}$$

and the principal-layer-projected bulk Green's function

$$G_b^{-1} = G_s^{-1} - H_{01}^{\dagger}\tilde{T}. \tag{7}$$

The principal-layer-projected Green's function on the layers next down from the surface is given by

$$G_{nn} = G_b + T^n(G_s - G_b)\tilde{S}^n. \tag{8}$$

It is customary to define the transfer matrices as

$$G_{k+1p} = TG_{kp}, \qquad G_{k+1p} = G_{kp}S, \quad k \geq p \geq 0, \tag{9.a}$$

$$G_{ij+1} = \tilde{T}G_{ij}, \qquad G_{ij+1} = G_{ij}\tilde{S}, \quad j \geq i \geq 0. \tag{9.b}$$

These matrices can be calculated by the quick algorithm of López-Sánchez *et al.* [13]

and Baquero [14]. They get

$$T = t_0 + \tilde{t}_0 t_1 + \cdots + \tilde{t}_0 \tilde{t}_1 \cdots \tilde{t}_{i-1} t_i + \cdots \tag{10.a}$$

$$\tilde{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + \cdots + t_0 t_1 \cdots t_{i-1} \tilde{t}_i + \cdots \tag{10.b}$$

$$S = s_0 + s_1 \tilde{s}_0 + \cdots + s_i \tilde{s}_{i-1} \cdots \tilde{s}_1 \tilde{s}_0 + \cdots \tag{10.c}$$

$$\tilde{S} = \tilde{s}_0 + \tilde{s}_1 s_0 + \cdots + \tilde{s}_i s_{i-1} \cdots s_1 s_0 + \cdots \tag{10.d}$$

where,

$$t_0 \equiv (\omega - H_{00})^{-1} H_{01}^{\dagger}, \qquad \tilde{t}_0 \equiv (\omega - H_{00})^{-1} H_{01}, \tag{11.a}$$

$$t_i \equiv M_{i-1} t_{i-1}^2, \qquad \tilde{t}_i \equiv M_{i-1} \tilde{t}_{i-1}^2, \tag{11.b}$$

with $M_{i-1} = (1 - t_{i-1}\tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1}$,

$$s_0 \equiv H_{01}^{\dagger} (\omega - H_{00})^{-1}, \qquad \tilde{s}_0 \equiv H_{01} (\omega - H_{01})^{-1}, \tag{11.c}$$

$$s_i \equiv s_{i-1}^2 N_{i-1} \qquad \tilde{s}_i \equiv \tilde{s}_{i-1}^2 N_{i-1}, \tag{11.d}$$

with $N_{i-1} \equiv (1 - s_{i-1}\tilde{s}_{i-1} - \tilde{s}_{i-1} s_{i-1})^{-1}$.

The i-th term in (10) is of the order of $2^{i+1} - 1$ in H_{01} and it vanishes rapidly. Thus, a good approximation is obtained for the transfer matrices. Once they are known we can compute the G_s, G_b and G_{nn} in an straightforward way from the formulae given above.

In the case of interfaces the matrices double in size. The algebra is the same. One gets

$$G_I^{-1} = G_{S(A)}^{-1} + G_{S(B)}^{-1} - I_B H^i I_A - I_A H^i I_B, \tag{12}$$

which is the analogous formula to (6) above. G_I^{-1} is the interface Green's function. In (12) $G_{S(A)}^{-1}$ and $G_{S(B)}^{-1}$ are the surface Green's function of medium A and B respectively in the doubled space of the interface.

$$G_{S(A)}^{-1} = \begin{pmatrix} G_{(A)}^{-1} & 0 \\ 0 & 0 \end{pmatrix}, \tag{12.a}$$

where $G_{(A)}^{-1}$ is the surface Green's function for the medium A calculated from the formula (6). It is a 18 × 18 matrix while $G_{S(A)}^{-1}$ is a 36 × 36 matrix. $I_B H^i I_A$ and

$I_AH^iI_B$ are also 36×36 matrices of the same form of (12.a)

$$-I_BH^iI_A - I_AH^iI_B = \begin{pmatrix} 0 & -\mathcal{J}_AH^i\mathcal{J}_B \\ -\mathcal{J}_BH^i\mathcal{J}_A & 0 \end{pmatrix} \qquad (12.B)$$

They describe the interaction between the two media. $-\mathcal{J}_AH^i\mathcal{J}_B$ and $-\mathcal{J}_BH^i\mathcal{J}_A$ are 18×18 matrices. In our simple model they take the form of the surface hamiltonian H_{01} and $H_{01}^{\dagger}$ respectively but with tight-binding parameters being the average of those for the two media. This is a reasonable approximation when both sides of the interface have the same crystallographic structure and we take the same basis of wave functions.

From the knowledge of the Green's functions we can calculate the local density of states (LDOS) projected at an atomic layer either at the interface or at any of the two media through the usual formula

$$N_i(\omega) = -\frac{1}{\pi}\sum \mathrm{Im}\int G_{I_{ii}}(\kappa,\omega)\,d\kappa \qquad (13)$$

where the integration is made in the two-dimensional first Brillouin zone by the method of Cunningham [18]. The index i refers to the layer where the LDOS is projected. Each of the four groups of five elements on the diagonal of G_I, gives the LDOS projected at an atomic layer (the interface and the first atomic layers on both sides).

Acknowledgements

We acknowledge the technical help of Mrs. Celia Ayala to this work.

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Resumen. Presentamos el cálculo de la densidad local de estados electrónicos (ILDOS) de la interfaz formada por los metales de transición Mo(100)/Ta(100). En este cálculo describimos nuestro sistema por medio de hamiltonianos "tight-binding" en el esquema de Slater-Koster y empleamos el método de empalme de funciones de Green para obtener la densidad local de estados a cada lado de la interfaz. Como un resultado adicional, obtenemos la densidad de estados de la superficie (SLDOS). En este trabajo, comparamos la densidad de estados de la interfaz con la densidad de estados del "bulto" y con la densidad de estados de la superficie y hacemos algunos comentarios sobre resultados experimentales reportados recientemente sobre esta interfaz. Nuestros resultados pueden ser una herramienta útil para analizar resultados experimentales.