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Overlayer-induced resonant electronic states: A theoretical study

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By using a simple model, we show that the density of states of a metallic overlayer deposited on a metallic substrate contains resonances (size quantization peaks) that do not broaden as an effect of the overlayer-substrate coupling, but remain well-defined features for different values of the coupling parameter. Instead, these modes become sharper by increasing the thickness of the overlayer. We also investigate the influence of the work function on the localized and resonant states associated with the overlayer. This effect, which, in general, is not considered in tight-binding models, is most significant for the highest localized or resonant mode, which becomes a surface mode of the overlayer.

The investigation of the structures and growth modes of overlayers and their related electronic, chemical, or magnetic properties has attracted much interest in recent research activities. The electronic structure of thin metallic films adsorbed on a substrate or sandwiched between two metals has been studied by spectroscopic techniques [photoemission,[1-17] low-energy electron diffraction (LEED),[17,18] and Auger[18]] as well as theoretically.[19-23] In the case of epitaxial metallic overlayers, quantum-well-like states induced by the adsorbate have been observed[13-16] around some particular points of the two-dimensional Brillouin zone of the surface, where there is a local gap in the band structure of the substrate. The appearance of these modes is intimately related to the quality and thickness of the overlayer.

Besides the possible localized modes that may exist in an energy gap of the substrate, resonant states induced by the overlayer appear as well-defined peaks in the spectral density inside a bulk band. The purpose of this paper is to study qualitatively such resonant electronic states associated with an overlayer. We show that, surprisingly, the latter modes do not become very broad as an effect of the substrate-adsorbate coupling, and sharpen when the thickness of the overlayer increases. We use a very simple semianalytical model, namely an s-band tight-binding Hamiltonian, in crystals having a simple-cubic structure and an orientation along the [001] direction. In this model, which gives a qualitative description of a transition metal's band structure, for example, the local densities of states can be calculated in a closed form. Such a model has already been used for the study of metallic surfaces,[24,25] interfaces,[26] superlattices,[27] and quantum wells.[28] Our calculation is performed within the formalism of interface-response theory,[29] which is an efficient method for calculating the Green function in systems with several interfaces. From the knowledge of the Green response operator and the densities of states, we shall discuss the characteristics of the new states as a function of the overlayer thickness.

Another interesting question we address in this paper is the modification of the overlayer-state energies that occurs when we take into account the influence of a finite work function in the system, in contrast to usual tight-binding calculations. In the case of a surface without an adsorbate, this problem has already been discussed[30] and an even more realistic potential with a tail representing the image potential was considered,[31] giving rise to image states at a free surface or at a tunnel junction. However, we shall limit our discussion in the overlayer system to the case of a step barrier potential at the surface (Fig. 1).

Let us first define the parameters involved in the calculation. The substrate is characterized by a hopping integral β_1 and an intra-atomic energy ε_1. The bulk energy band of the infinite substrate is then defined by

$$E(\mathbf{k})=\varepsilon_1-2\beta_1(\cos k_1a_0+\cos k_2a_0+\cos k_3a_0)\ , \tag{1}$$

where k_1, k_2, and k_3 are the components of a three-dimensional wave vector $\mathbf{k}$ and a_0 is the lattice parameter. Therefore, in the (001)-surface problem considered here, for a given value of the wave vector, $\mathbf{k}_\parallel=(k_1,k_2,0)$,

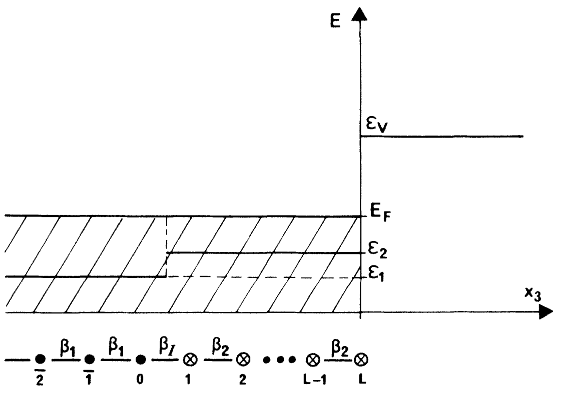

FIG. 1. One-dimensional representation of the geometry and of the model of the overlayer-substrate system. The hatched area represents the occupied electronic levels. E_F and ε_V are the Fermi energy and vacuum level, respectively.

parallel to the surface, the energy band (Fig. 2) extends from $\varepsilon_1 - 2\beta_1(\cos k_1 a_0) + \cos k_2 a_0 + 1)$ to $\varepsilon_1 - 2\beta_1(\cos k_1 a_0 + \cos k_2 a_0 - 1)$.

The hopping integral inside the overlayer and at the substrate-adsorbate interface (Fig. 2) are denoted, respectively, β_2 and β_I, and, in the following applications, β_I is taken to be an average of β_1 and β_2. Near the substrate-adsorbate interface, as well as inside a very thin overlayer, the intra-atomic matrix elements vary slightly from site to site and need, in principle, to be calculated in a self-consistent way—for example, by using the idea of local charge neutrality.[24] In our qualitative approach, which, moreover, is mainly concerned with overlayers thicker than a few atomic planes, we assume a uniform intra-atomic energy ε_2 in the adsorbate; then, we adjust the difference $\varepsilon_1 - \varepsilon_2$ in order to align the Fermi energy E_F in two semi-infinite metals made of the substrate and the adsorbate, respectively. Finally, the thickness of the overlayer is La_0, where L is the number of atomic adsorbed planes.

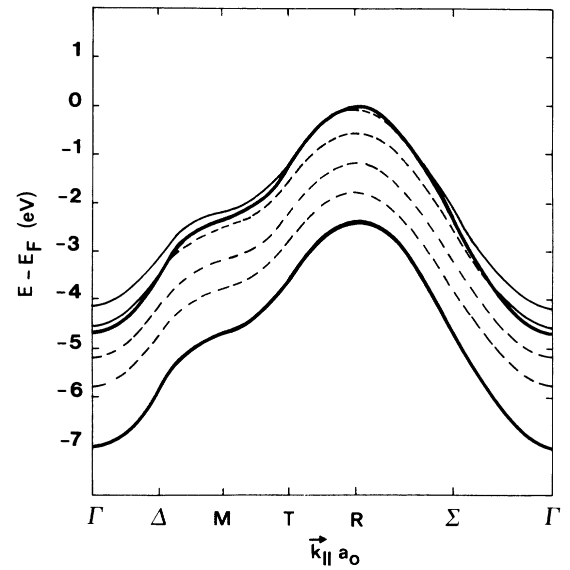

FIG. 2. Dispersion within the two-dimensional Brillouin zone of the surface, and of localized (thin solid curves) and resonant states (dotted curves) induced by an overlayer composed of $L=4$ atomic planes. The thick solid curves give the limits of the substrate bulk band. The origin of energy is taken at the Fermi level, which is assumed in this example to be situated at the top of the bulk bands of both the substrate and the adsorbate. The horizontal axis represents the wave vector $\mathbf{k}_{\parallel}$, which starts from the center Γ of the Brillouin zone, going to point $M(\pi/a_0, 0)$ along the axis Λ $[\mathbf{k}_{\parallel} = (k_1, 0)]$, then to the point $R(\pi/a_0, \pi/a_0)$ along the axis $T(\pi/a_0, k_2)$, and finally back to Γ along the axis $\Sigma(k_1, k_1)$.

Let l_3 be the index number of the atomic planes in the direction perpendicular to the surface: $1 \le l_3 \le L$ for the adsorbate and $l_3 \le 0$ for the substrate. By using the formalism of interface-response theory,[29] the Green operator $g(\mathbf{k}_{\parallel}; l_3, l_3; E)$ can be obtained in closed form; the local density of states $n(\mathbf{k}_{\parallel}, l_3, E)$ is then

$$n(\mathbf{k}_{\parallel}, l_3, E) = -\frac{1}{\pi} \operatorname{Im}[g(\mathbf{k}_{\parallel}; l_3, l_3; E)] \ . \tag{2}$$

Here,

$$g(\mathbf{k}_{\parallel}; l_3, l_3; E) = \frac{1}{\beta_2 W(\mathbf{k}_{\parallel}, E) \sinh(q_2)} \left[\cosh[q_2(L+1-2l_3)] - \cosh[q_2(L+1)] + \frac{\beta_I^2}{\beta_1 \beta_2} \exp(q_1) \{ \cosh(q_2 L) - \cosh[q_2(L+2-2l_3)] \} \right] , \tag{3a}$$

and the quantities involved in Eq. (3a) are given by

$$\cosh(q_i) = \frac{\varepsilon_i - E}{2\beta_i} - \cos k_1 a_0 - \cos k_2 a_0 \ , \tag{3b}$$

$$W(\mathbf{k}_{\parallel}, E) = \sinh[q_2(L+1)] - \frac{\beta_I^2}{\beta_1 \beta_2} \sinh(q_2 L) \ . \tag{3c}$$

The energies of the localized modes in the band gaps of the substrate are obtained as solutions of $W(\mathbf{k}_{\parallel}, E) = 0$, whereas the resonant modes correspond to well-defined peaks in the local densities of states inside the bulk band.

Figure 2 gives an example of the dispersion curves of localized and resonant states within the two-dimensional Brillouin zone. For the sake of clarity in the figure, we have considered a thin adsorbate containing only $L=4$ atomic planes. In this example, we have assumed that the substrate is a full d-band metal, and then set $\varepsilon_1 - \varepsilon_2 = -0.5$ eV, $\beta_1 = \frac{7}{12}$ eV and $\beta_2 = \frac{6}{12}$ eV; the latter values for β_1 and β_2 were proposed for the 5d and 4d transition-metal series, respectively,[24] from a comparison of their measured cohesion energies with those predicted by the model. We notice that at a given value of $\mathbf{k}_{\parallel}$ the band structure presented in Fig. 1 roughly reproduces the situation at the L point of the Brillouin zone in the Ag/Au(111) system.[14–16]

In Fig. 2 the bulk band of the substrate is limited by the thick solid curves. There are four branches induced by the overlayer that appear either as localized or resonant states, depending on the value of $\mathbf{k}_{\parallel}$; they all belong to the bulk energy band of the adsorbate. The connection between the localized and resonant modes in this figure is noticeable.

In order to show that resonant states remain well-defined features and that they be detected experimentally, we present in Fig. 3 the local density of states on the surface atom ($l_3 = L$) at $\mathbf{k}_{\parallel} = 0$, namely $n(\mathbf{k}_{\parallel} = 0, l_3 = L, E)$, for $L = 10$ atomic adsorbed layers. We obtain a total of 10 localized and resonant states; however, it should be noted (see Fig. 4) that if one of the localized modes becomes very close to the upper edge of the bulk band, then the density of states contains an extra peak near this edge inside the band. By increasing the number of adsorbed layers, the resonant modes become sharper, and we find a situation similar to that of a free slab where the density of states is composed of L delta peaks, whose energies are given by $\sinh[q_2(L+1)]=0$ (the peak positions are slightly modified due to the interaction with the substrate). However, the sharpness of the peaks is not related to a particular choice of the coupling parameter β_I at the substrate-overlayer interface; actually, the peaks in the surface local density of states become more pronounced—not only for small values of β_I, but also by increasing β_I from its value in Fig. 3. A similar behavior is observed for the variation of the total density of states $\Delta n(\mathbf{k}_\parallel,E)$, i.e., the difference between the density of states of the overlayer-substrate system and the substrate alone.

The sharpness of the peaks in Fig. 3 suggests that experimental observation of them should be possible, and this is mostly a function of the crystallographic quality of the deposited layers and of the energy resolution of the experimental apparatus.

The local densities of states on other atoms of the overlayers display the same features as in Fig. 3, except that the intensities of the peaks are different in each case due to the spatial distribution of each mode.

Now, we shall discuss the influence of the work function on these localized and resonant modes, i.e., the modifications of the above results when the electrons are allowed to penetrate into the vacuum whose lowest electronic level is noted ε_V such that $\Phi=\varepsilon_V-E_F$ is the work function. The calculation of the Green function can be performed as in Refs. 30 and 31. Figure 4 gives an example of this density of states at $\mathbf{k}_\parallel=0$, for $L=10$ adsorbed layers. The numerical values used in this calculation are $\Phi=4.3$ eV and $a_0=4.09$ Å. From a comparison of Figs. 3 and 4, one can observe that the general effect of the solid-vacuum coupling is to raise the energy of the overlayer states. Although this increase is equally important for every mode when the adsorbate is very thin, it only becomes significant for the highest localized mode when the thickness of the overlayer goes beyond a few atomic planes. The energy of the latter mode is almost independent of the overlayer thickness and is found to be the same as the energy of a surface state when the overlayer becomes a semi-infinite solid (let us again stress that this state, whose energy is above the bulk band of the overlayer, only appears due to the finite value of the work function). This mode is localized at the surface of the overlayer and, thus, is very different from the corresponding mode when the solid-vacuum coupling is not taken into account. As a consequence of this localization, the influence of this state on the surface atom is

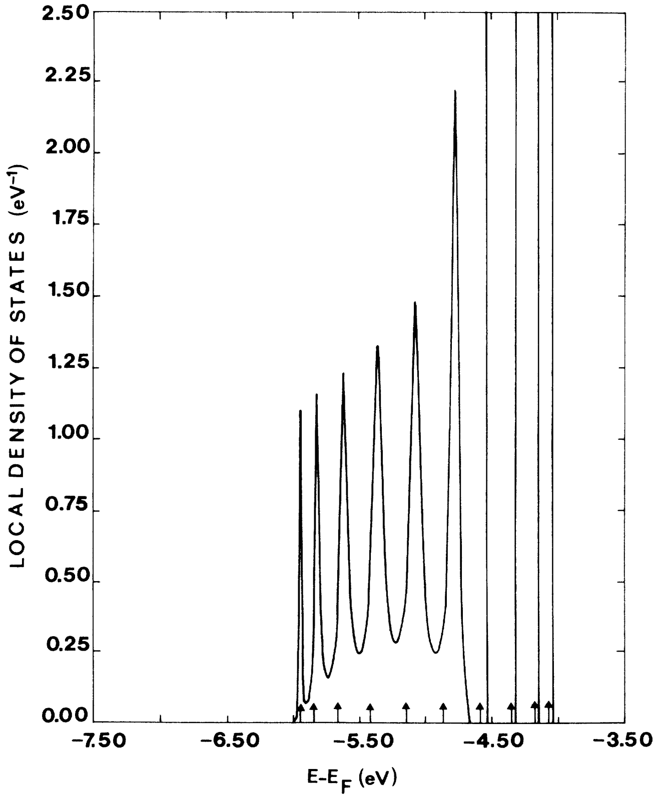

FIG. 3. Local densities of states at $\mathbf{k}_\parallel=0$, on the surface atom, in the case of an overlayer composed of $L=10$ monolayers. The localized states are indicated by vertical bars. The energies of the electronic levels in a free slab of the same thickness are also marked by arrows.

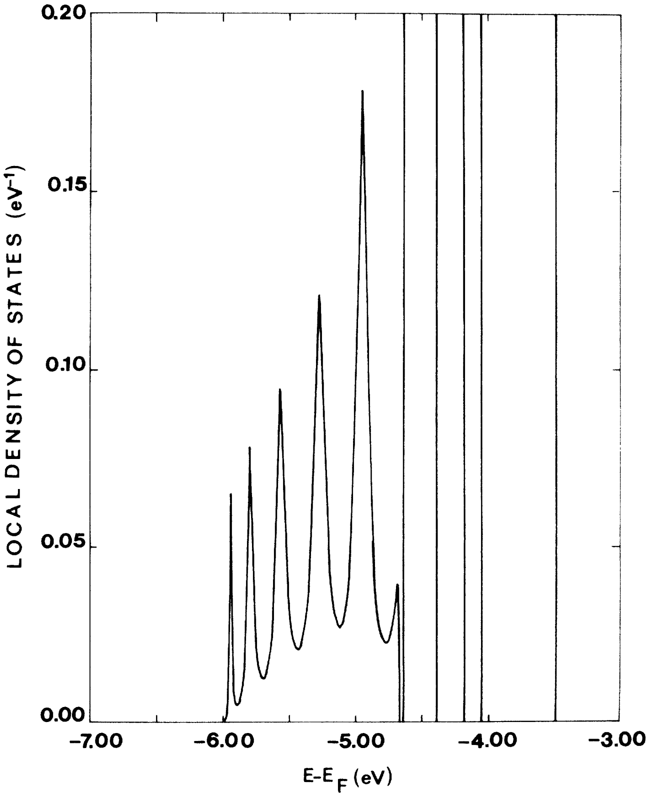

FIG. 4. Same as in Fig. 3 when we take into account the effect of a finite work function.

more important in Fig. 4 than in Fig. 3 and, consequently, the other resonant and localized modes have a smaller weight on the surface atom in the former case; this explains the difference between the scales of the vertical axes in these two figures. Finally, a comparison of Figs. 4 and 3 shows that one of the resonant modes in the latter case has become localized in the former; due to the proximity of this localized state to the edge of the substrate bulk band, an extra peak also appears in the density of states below the edge.

In conclusion, the simple model used in this paper shows that overlayer-induced resonant states remain well-defined features of the density of states, even when the thickness of the overlayer increases. This qualitative result is believed to be independent of the model and we hope that it will be corroborated by more realistic models and by experimental investigations.

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