Band mapping by photoemission: analysis of overlayer states in Ag films on Au (111)

LETTER TO THE EDITOR

Band mapping by photoemission: analysis of overlayer states in Ag films on Au(111)

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Abstract. Photoemission spectra for thin overlayers with quantum well states can be used to map out electron energy bands in the direction perpendicular to the surface. The perpendicular component of the wavevector is obtained from the phase condition satisfied by the overlayer states. Here we determine the dispersion for part of the Ag s,p band using previously reported spectra for Ag overlayers on Au(111).

Photoemission, in particular the angle-resolved version, has provided a large amount of information about the electronic structure in the bulk and at the surface of solids. When a photoemission measurement is made with the purpose of mapping out bulk energy bands, one difficulty is that no information is obtained about the wavevector component perpendicular to the sample. The reason is that this quantity does not enter the conservation rules for the photoemission process. In most cases the reported dispersion is obtained after some assumption has been made regarding the electronic structure. One may for example use a trial band structure with parameters that can be adjusted to obtain agreement with the recorded spectra [1, 2] or one may simply assume that the final-state bands are free-electron-like.

Recently a way of determining dispersion, $E(k)$, in the perpendicular direction by photoemission [3] was demonstrated. The method is based on the appearance of discrete valence electron states in thin overlayers. These quantum well states are formed by valence electrons which are forever moving back and forth between the vacuum barrier and the overlayer–substrate interface. Such propagation is possible for energies below the vacuum level if the substrate has a band gap at the energies and wavevectors of interest. Previously, standing-wave states have been resolved by tunnelling spectroscopy and the results of the measurements were used for band determinations [4]. The metal film studied was then evaporated on top of an insulating layer and served as an electrode in the tunnelling sandwich. For metallic systems overlayer states have been observed for Na, Ba and Cs on Cu(111) [3, 5, 6] and for Ag on Au(111) [7]. In all of these cases the observations were made using photoemission. Recently an oscillatory thickness dependence was found for the resistivity of Pb films deposited on a Au-covered Si crystal, a behaviour that was ascribed to standing-wave states in the film [8].

Due to the confinement of the electrons in a thin film the perpendicular component of the wavevector, k, can have only a discrete set of values which are determined by the phase condition satisfied by the overlayer states, $\Phi_B + \Phi_C + 2\Phi_D = 2\pi m$, $m = 0, 1,$
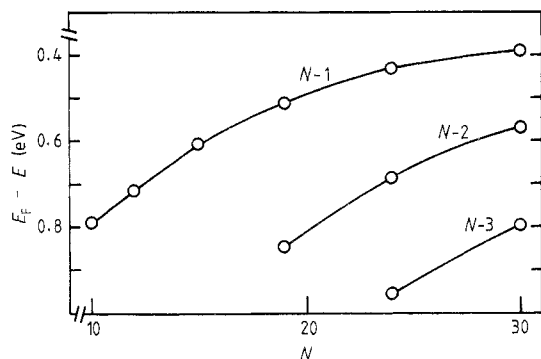
Figure 1. The overlayer-state energy, E, relative to E_F, versus thickness for Ag overlayers on Au(111). The energies have been obtained by reading off the peak positions of spectra shown in [7]. The quantum numbers, m, assigned to the various states are given on the curves. N is the number of atomic layers of Ag.

$2, \ldots$, where $\Phi_D = kNa$ is the phase change across a film consisting of a stack of N atomic layers each with thickness a. Φ_B and Φ_C are the phase changes at the vacuum barrier and at the substrate–overlayer surface respectively. The dispersion can now be obtained by measuring the energies of overlayer states using photoemission and determining the wavevector from the phase condition. Loly and Pendry have pointed out some advantages of using overlayer samples in photoemission experiments [9].

Since the phase condition, apart from the quantum number m, contains two unknown quantities, namely k and $\Phi_B + \Phi_C$, it is obvious that some approximation has to be made before k can be determined. So far the method has been used only for Cs [3]. The purpose of the present Letter is to apply the method to Ag, a substance for which overlayer states were recently observed in photoemission measurements on Ag-covered Au(111) [7]. A second purpose is to point out one additional advantage of using overlayer states for bulk band studies. This is the possibility that arises, given a certain range of available photon energies, of obtaining information about parts of the band structure that cannot be probed by photoemission from conventional samples. As will be discussed further below the possibility of reaching new regions of the Brillouin zone is well illustrated by the results obtained by Miller and co-workers [7].

As a first step in the determination of k we assign a quantum number m to each of the observed states. The assignment is shown in figure 1 where the energies of the overlayer states relative to the Fermi level are plotted against the thickness given by the number of atomic layers, N. The states have been divided into three different groups. For the first group $m = N - 1$, for the second $m = N - 2$ and for the third $m = N - 3$. It is straightforward to arrive at this assignment. The energies, and hence, the k-values, of the states in one of the three groups do not change very much when another atomic layer is added. The easiest way to achieve this is to let m and N change in unison. No experimental information is available about the $m = N$ states except for the $m = N = 0$ state, which is the Au(111) surface state at around 0.5 eV below E_F. The assignment of quantum numbers to surface states has been discussed extensively for Cu(111) [10].

The second step in obtaining k is to assume that the barrier phase shifts do not depend on the thickness. For the thicknesses of more than ten atomic layers, which is the thickness range of present interest (figure 1), this is certainly a very good approximation. The final step in the procedure for determining k is to eliminate the barrier phase shift sum, $\Phi_B + \Phi_C$, from the phase condition. Since this quantity depends only on the energy it can be eliminated if we find two overlayer states with the same energy. Let us assume that one of the states has quantum number m_1 and appears at a thickness corresponding to N_1 atomic layers while for the other state these quantities are m_2 and N_2 respectively.
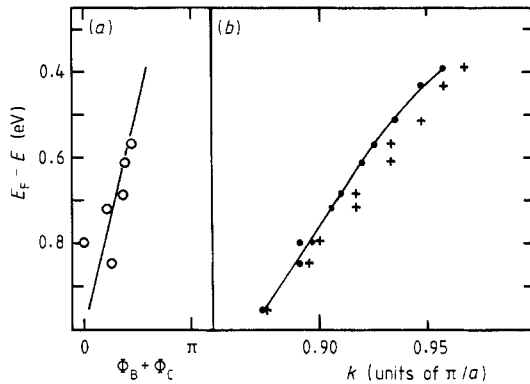
Figure 2. (*a*) The barrier phase shift sum, $\Phi_B + \Phi_C$, obtained from the energies, quantum numbers and thicknesses in figure 1. (*b*) The dispersion obtained when $\Phi_B + \Phi_C$ is assumed to be zero (crosses). Also shown (full circles) is the dispersion obtained with $\Phi_B + \Phi_C$ values given by the straight line in (*a*).
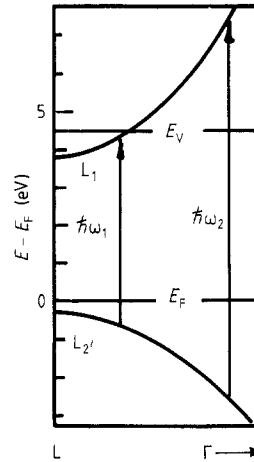
Figure 3. A schematic drawing of the s,p band structure of Ag near L and the initial and final states involved in transitions at a photon energy of around 5 eV and at a photon energy of 10 eV.

By applying the phase condition to these two states one obtains after subtraction $k = \pi(m_2 - m_1)/a(N_2 - N_1)$. The thickness can be varied only in steps of one atomic layer. It is then unlikely that we will find two states with the same energy. To be able still to use the simple expression for k we draw smooth curves through the data points in figure 1 and assume that these curves would give the overlayer-state energies for the overlayer if its thickness could be varied in a continuous manner. For each state the k-value can now be obtained from the above expression after measurement of the horizontal separation between the curves drawn through the points.

With thicknesses ranging between 10 and 30 atomic layers the barrier phase shift sum $\Phi_B + \Phi_C$ can be regarded as a correction when the wavevector is determined. If $\Phi_B + \Phi_C$ is taken to be zero one obtains $k = \pi m/aN$. The dispersion obtained with these k-values is shown by the crosses in figure 2(*b*). When the barrier phase shifts are included in the analysis one obtains the dispersion shown by the full circles in figure 2(*b*). In the present case the k-values have been determined by first plotting the values for $\Phi_B + \Phi_C$ obtained from the phase condition, namely $\Phi_B + \Phi_C = 2\pi(m_1N_2 - m_2N_1)/(N_2 - N_1)$ and then using phase shift values read off from a straight line fitted to the points (figure 2(*a*)).

The barrier phase shift shows a considerable variation in the measured region. This is due to the fact that the energy is close to the low-energy edge of the s,p conduction band gap of Au at the L point of the Brillouin zone [7]. Across this gap the phase shift is expected to vary from zero at the low-energy edge of the gap to π at the high-energy edge with most of the variation near the band edges [11]. The vacuum barrier phase shift of Ag(111) is expected to have a relatively small negative value in the energy range of interest. This is obvious from the fact that Ag(111) has a surface state of around 0.1 eV below E_F [12]. At this energy for Ag(111) therefore, $\Phi_B + \Phi_C = 0$, which is the phase condition satisfied by surface states. The surface state is located around 0.2 eV above the low-energy edge of the s,p conduction band gap in Ag. At this energy Φ_C for Ag(111) will have a relatively small positive value and Φ_B thus a small negative value. The barrier

phase shift varies rather slowly between the Fermi level and the energy range of present interest. This means that Φ_B is expected to have a relatively small negative value in this energy range also. The conclusion of this is that the barrier phase shift sum obtained from the data recorded by Miller and co-workers [7] is in good agreement with expectations.

Also, the band energies obtained by the present analysis are in good agreement with previous work. The photoemission data discussed here indicate that the $L_{2'}$ band edge is 0.3 eV below E_F and that the band mass here is around $0.14m$. The edge energy agrees well with a previous determination using photoemission [1] and with the tunnelling results [4]. The band mass obtained from the tunnelling spectra was $0.17m$ [4]. The fact that the result agrees with the expected dispersion for Ag is encouraging, since it means that the present method, which earlier had been applied only to Cs [3], appears to be useful for other solids too.

What is even more interesting, with the data obtained by Miller and co-workers [7], than the fact that the band structure obtained is in agreement with expectations is the fact that this part of the band structure can be studied at all by photoemission at the low photon energies used. Photoemission measurements on a thick, clean Ag(111) sample give no information about the s,p band states in the vicinity of the L point of the Brillouin zone. The relevant part of the band structure is shown in figure 3. To study transitions near the L point one would have to use photon energies near 5 eV (see figure 3) and at these photon energies none of the excited electrons can overcome the vacuum barrier. Miller and co-workers [7] used a photon energy, $\hbar\omega_2$ in figure 2, of 10 eV. In a photoemission experiment on a thick sample one would then obtain an emission peak due to initial s,p band states around 3 eV below E_F with little information about the s,p band states much closer to E_F discussed here.

This important difference between a thick sample and an overlayer can be understood as follows. The photoemission peak from the thick sample has a considerable width which is determined by the dispersion of the bands involved in the optical transition and by the final electron- and hole-state lifetimes [2]. The peak obtained for the thick sample can be regarded as an envelope to the many-peaked structure obtained for the overlayer. As the thickness is increased the individual overlayer states can no longer be resolved and the emission spectrum is the same as for a thick sample. For the thick sample the tails of the emission peak provide no information about the band structure. However, for a thin film if one can resolve overlayer states in these tails one can obtain the detailed band-structure information available from the data reported in [7]. The present comments are based on the assumption that the emission peaks are due to bulk-like optical transitions in the interior of the overlayer. It should be pointed out, however, that in the present case the emission could be due to the surface photoelectric effect. Normally for the noble metals bulk-related emission dominates, but the surface emission could have an intensity comparable to the intensity far out in the tails of the bulk-derived emission peaks.

In previous photoemission work one way used for obtaining information about the states near L has been to reduce the work function by using an alkali deposit [1]. Another procedure is to use photon energies that are high enough to excite the electrons into the next higher final band [13]. The authors point out, however, that there are difficulties with this measurement due to the small escape depth at the high final-state energies and the reduced amplitude near the surface of the s,p states in the vicinity of the L point. For the two substances studied so far by the present photoemission method, Cs and Ag, low photon energies have been used and it has not been necessary to make any assumption regarding the final states.

In summary, bulk band structure can be determined via photoemission from thin overlayer films in which the valence electrons form discrete, quantum-well-type states. Energies and wavevectors may be determined for states about which it has been difficult to obtain information from measurements on a conventional sample.

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