Atomiclike behavior of the Mo 4d photoionization cross section in Mo islands grown on Al

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The Mo 4d photoionization cross section has been measured, apart from a constant factor, in the photon energy range 63–200 eV from samples consisting of Mo islands grown on Al at 80 K. Within the experimental error the photoionization cross section is in basic agreement with the atomic calculations, in spite of the fact that a considerable d-d interaction between nearby Mo atoms is present. The problems raised by the present results are discussed in connection with the physics of clusters.

The present work is intended to add new relevant information to a previous work[1] on the growth of Mo islands on Al at low temperature (80 K) studied with photoemission and Auger spectroscopy. The new data concern the photoionization cross section of the Mo $4d$-derived valence states. The most relevant features of the Mo/Al system at low temperature are briefly summarized here in order to define the problem and to support the following discussion. The uptake curve, from Ref. 1, in which the Mo MNV Auger intensity is plotted versus coverage, is shown in Fig. 1. The curve shows a plateau in the coverage region between 1×10^{15} and 2×10^{15} atoms/cm^2. These coverages would roughly correspond, in a layer-by-layer growth, to 1 and 2 monolayers (ML) of Mo. The growth of the Mo/Al system, at low temperature, is clearly not uniform, and the plateau in the curve of Fig. 1 was interpreted, in Ref. 1, as due to the formation of Mo islands. The average thickness of these islands was estimated to be up to the order of 2–3 ML. The valence-band spectra taken at 21.2 eV photon energy, and corresponding to the different regions of Fig. 1, are shown in Fig. 2. Curve (a) shows the spectrum of the low-coverage region, in which the lateral interaction between the Mo atoms is negligible. Spectrum (b) was measured from a sample in the island region. Spectrum (c) refers to bulk Mo. As discussed in Ref. 1, the trend shown in Fig. 2 indicates that in the islands a strong lateral d-d interaction between nearby Mo atoms is present (see Ref. 1 for a detailed discussion of this point). The present work is a step forward in the study of this transition from isolated atoms to bulk Mo and reports the experimental values of the Mo $4d$ photoionization cross section in the plateau region of Fig. 1. We anticipate that in this case the cross section shows an intriguing similarity with the isolated atom, in spite of the strong interaction existing between the atoms which form the islands.

Previous investigations[2-5] showed that the $4d$ cross section is very sensitive to the solid environment. A similar effect has been observed in molecules.[6] In the isolated Mo atom the $4d$ cross section shows the so-called Cooper minimum,[7] which is originated by a cancellation effect in the dipole matrix element due to the presence of a node in the initial-state radial wave function. The solid-state effect is not observed when the cross section retains an atomiclike character; this is the case[4,5] of the shallowest $4d$ peak in the valence-band spectrum of the layer compound MoS$_2$. This peak, in fact, is basically due to d_z orbitals oriented normally to the layers which are weakly interacting with the environment.[8,9] On the contrary, in bulk bcc Mo the severe modification of the $4d$ states washes out the Cooper minimum.[2,3] In the present study we investigated the presence, if any, of a solid-state effect on the Mo $4d$ cross section in the islands region of Fig. 1. We prepared two samples, indicated with A and B in Fig. 1, which roughly correspond to the edges of the plateau in the uptake curve.
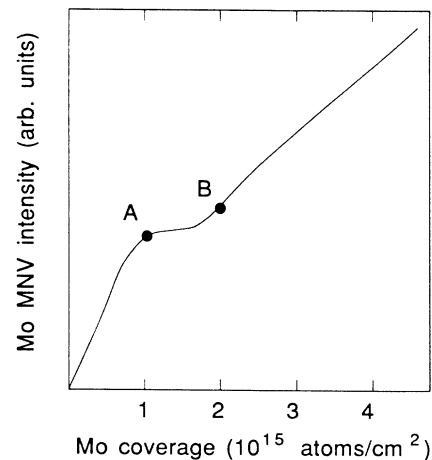

FIG. 1. The uptake curve of Mo (as seen from Mo MNV Auger intensity) vs the number of atoms deposited on Al. The solid line is a best fit of the trend given in Ref. 1. Points A and B refer to the samples used in the present experiment.
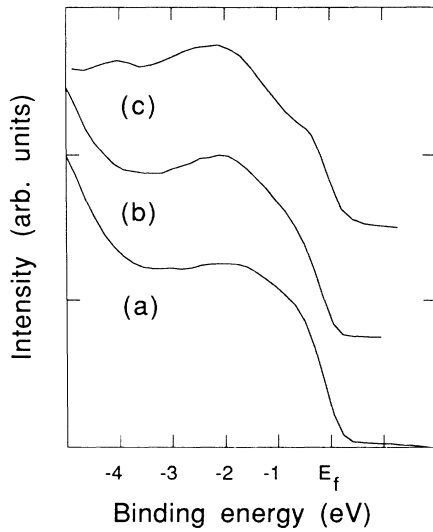
FIG. 2. Angle-integrated photoemission spectra (photon energy 21.2 eV) corresponding to different regions of the curve of Fig. 1. (a) Differential spectrum on passing from 0.1×10^{15} to 0.3×10^{15} atoms/cm^2. (b) Typical spectrum of the plateau region. (c) Bulk Mo; in this case the sample was prepared by evaporating a thick Mo film.

The experiment has been performed at the Standard Synchrotron Radiation Laboratory on beam line 1-I. The base pressure of the vacuum system was 7×10^{-11} Torr. The samples were prepared as described in Ref. 2, with the only difference being that in the present work Mo was thermally evaporated, after long outgassing, from a thin wire wrapped around a W filament. The photoemission spectra were taken with a cylindrical mirror analyzer in the photon-energy range 63–200 eV. The consistency of the sample preparation with Ref. 1 was checked by monitoring both valence spectra and core-line intensities (Al $2p$ and Mo $3d$). The cross section was determined, from the energy-distribution curves, by using the procedure described in Ref. 3. In order to avoid the need for corrections due to the light reflection from the sample,[10] we used light at normal incidence. With this method, the cross section is measured apart from a constant factor and the physical information comes from the shape of the cross section versus energy and not from its absolute value.

The cross section we measured is shown in Fig. 3, lower panel. The points refer to sample A whereas the squares refer to sample B. In order to compare these data with the atomic cross section, we also give, as a solid line in the lower part of Fig. 3, the calculated atomic cross section from Ref. 11. In the upper panel of Fig. 3, the experimental Mo $4d$ cross section is shown as measured from a bulk sample and taken from Ref. 2. The curves of Fig. 3 are arbitrarily normalized in order to allow a better comparison of their shape.

The striking result shown in Fig. 3 is that the Mo $4d$ cross section in the islands retains the Cooper minimum and its shape shows a strong similarity with the atomic calculated cross section. A small difference could be
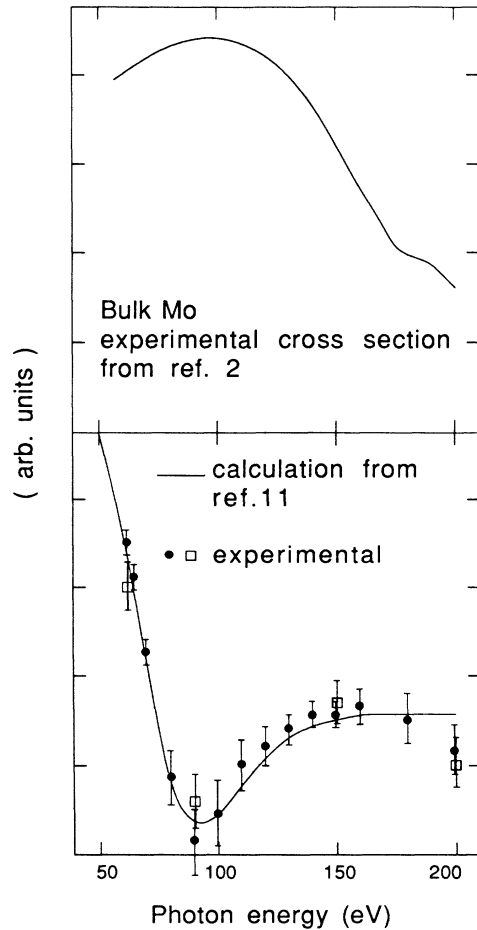

FIG. 3. The energy dependence of the Mo $4d$ photoionization cross section. The dots refer to sample A of Fig. 1, whereas the squares refer to sample B. The solid line is the calculated atomic cross section from Ref. 11. The curves were arbitrarily normalized in order to allow the comparison of their shape.

present at 200 eV but this happens at the upper edge of the investigated energy range, where the statistical noise is stronger and small deviations might be present due to inaccuracies in the escape depth correction (see Ref. 3 for further details). For this reason we will not discuss this marginal difference with respect to the atomic calculation.

The present result can be discussed along the following lines. As already pointed out in Ref. 1, the valence-band spectra in the island regime [curve (b) of Fig. 2] indicate the presence of a strong d-d interaction between nearby Mo atoms. This interaction is responsible for the appearance, in the density of states, of those features typical of bcc refractory metals: a rather large region around E_F which separates the peaks of the occupied and empty states. The effects produced by the d-d interaction on the density of states were predicted by calculating the electronic properties of refractory metal clusters. It has been shown by Zwicknagl[12] that the density of states of a small aggregate of $4d$ atoms in bcc coordination shows the same gross features of the bulk. This is clearly seen in the calculation on Nb clusters (9 and 15 atoms) and by some

partial information on Mo clusters given in the same paper. This effect is basically due to the organization of the d states in the $(xy + yz + zx)$ geometry, which is common to the bcc refractory metals (see, for instance, the calculations for Mo by Zunger et al.[13] and the discussion in Ref. 14). Since the solid-state effect on the photoionization cross section is dramatic in bulk Mo,[2] one might expect to observe a similar effect in the islands, where the d-d interaction is already strong enough to induce significant modifications in the density of states. Moreover, it has been observed that in a wide class of clusters a contraction of the interatomic distance takes place if compared to the bulk:[15] this fact would suggest an even stronger solid-state effect on the cross section in the islands.

On the basis of the above arguments it is clear that the discussion of our results calls for more sophisticated arguments, compared to the cases already published.[2-5] In this connection the consideration of the $4d$ dangling bonds can be useful. It has been shown by calculations[16] that the $4d$ charge at the Mo(100) surface shows a decompression toward the vacuum. This decompression is particularly enhanced for the states closer to the Fermi level. In our experiment a substantial fraction of Mo atoms belongs to the surface of the islands, and therefore it must be expected that charge decompression could play a significant role. However, being our spectroscopical probe is sensitive to the first 2–3 atomic layers of the sample, it is difficult to explain the atomiclike nature of the cross section exclusively in terms of the charge decompression of the surface atoms. Any explanation of this effect must face the fact that also the states internal to the islands give rise to a cross section which is atomiclike. In this connection it must be observed that in bulk polycrystalline Mo the experimental cross section, measured with the same procedure adopted in the present investigation, is completely different with respect to the atomic case, in spite of the high sensitivity of the measurement to the surface and to the subsurface. Thus, the difference between the cross section in the islands and in the bulk must come from tiny differences in the wave function which are relevant for the photoionization cross section and not so important for the density of states. In this respect more detailed calculations of the charge distribution in small aggregates of d metal atoms, and of the corresponding photoionization cross section, could be very useful because, as shown by our data, the information given by the cross section is not a replica of that given by usual photoelectron spectroscopy. A deeper understanding of the differences between these two approaches is important in itself and also for future applications to the study of clusters.

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