Electron spectroscopy study of the growth of Mo on Al at low temperature: Relevance for cluster physics

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A spectroscopic investigation of the initial overgrowth of Mo (up to 8×10^{15} atoms/cm^2) onto Al at low temperature (~ 80 K) is presented. Angle-integrated valence photoemission ($h\nu = 21.2$ eV), Mo $3d$, Al $2p$ x-ray photoemission spectroscopy ($h\nu = 1253.6$ eV), and Mo MNV and Al LVV results are reported. The overgrowth takes place with the formation of islands whose valence states strongly support recent calculations for small bcc clusters of refractory metals. Significant differences with respect to bulk metals are attributed to surface d states.

A typical feature of the electron states of bcc refractory metals is the opening of a rather extended region around the Fermi level (E_F) having a low density of states and separating the peaks of occupied and empty states.[1-3] This feature comes from the organization of d orbitals in the bcc coordination with a large energy gain in the formation of strong (d-d) bonds having basically $d_{xy+yz+zx}$ nature.[1] An interesting point is to establish experimentally if and how this property is retained in small clusters; in this connection we note also that in the case of density of states essentially determined by local coordination, this is not obvious because a small cluster has a great fraction of nonbonding "surface" states. This is relevant because the discussion of the relative importance of local and long-range order becomes impossible without clarifying this point.

One of the good candidates for this research is Mo, whose bulk electron states have been well established theoretically and experimentally with photoemission[4,5] and with optical measurements;[6] on the other hand, calculations of the electron density of states by Zwicknagel[7] on cluster of a related system [Nb$_9$ (bcc) and Nb$_{15}$ (bcc)] show an interesting similarity with the bulk density of states [also calculations for Mo$_{15}$ (bcc) of the density of states at the Fermi level show a similar trend]. Moreover, contradictory results have been given in other related cases: the calculations for vanadium by Adachi, Tsukada, Yasumori, and Ouchi[8] give a high density of states at E_F, and those by Salahub and Messmer[9] a low density of states at E_F, in qualitative agreement with the bulk (see also Refs. 10 and 11).

In this connection we present experimental results on Mo which shed some light onto this problem, although the present experiment is not a typical cluster research. This fact, far from being an inconvenience, is relevant because it can extend the variety of experimental approaches to cluster physics. The experiment is essentially a photoemission and Auger study of the overgrowth of Mo onto an Al substrate held at low temperature (≈ 80 K). We have found that around 1-2 monolayers the Mo atoms rearrange in small islands; we report the evidence of this process and we discuss the photoemission spectra from the islands in connection with cluster physics. Significant differences with respect to bulk Mo are pointed out, which can be attributed to "surface" Mo states.

The measurements were carried out with the apparatus used in Ref. 12, where a double-pass cylindrical mirror analyzer was installed. Valence photoemission was excited with a He I beam perpendicular to the spectrometer axis and with incidence onto the sample at 55°. Core level photoemission (Al $2p$ and Mo $3d$) excited with Mg K_α (1253.6 eV) radiation were measured; due to the rather high kinetic energy of photoelectrons this is a low surface-sensitivity measurement. High surface sensitivity was obtained by measuring the low-energy Auger signals of Al (LVV, around 62 eV) and of Mo (MNV, around 180 eV) in the spectra excited with x rays. We have not used an electron beam to excite Auger transitions in order to avoid putting energy onto the sample with possible modifications of the overgrowth mechanism. On the other hand, we have found that the use of a substrate at low temperature is essential to eliminate the interdiffusion which causes nonstationary Mo signals already at room temperature. The Al substrate was prepared by evaporation from a bead and Mo was evaporated from an e gun with good focusing so that the pressure remained below 1-2×10^{-9} Torr during evaporation (base pressure 10^{-10} Torr); in these conditions Mo evaporates as isolated atoms.[13] All data were acquired by means of a computer with sequences optimized for noise rejection. No contamination was seen in the spectra.

A first insight into the overgrowth of Mo comes from the intensities of the Mo and Al signals as a function of the number of deposited atoms. In Fig. 1 the intensities of Mo $3d$ and Al $2p$ photoemission and of Mo MNV and Al LVV are given. The surface-sensitive measurements are particularly significant. The Mo MNV Auger intensity increases with the deposited atoms up to $n \simeq 10^{15}$ atoms/cm^2 (region I) [one monolayer (100) of Mo in the bcc crystal corresponds to 10^{15} atoms/cm^2], while the intensity becomes flat from $n \simeq 1 \times 10^{15}$ to $n \simeq 2 \times 10^{15}$ atoms/cm^2 (region II) and starts to increase again beyond this point (region III). The occurrence of some peculiar behavior in this flat region is confirmed by departure of Al Auger signal from the initial exponential behavior as shown by the semilog plot of Fig. 1(c). Also the low surface-sensitivity measurements confirm this trend. These results show clearly that the overgrowth is not of the uniform type. On the other hand, it is impossible to figure out an interdif-
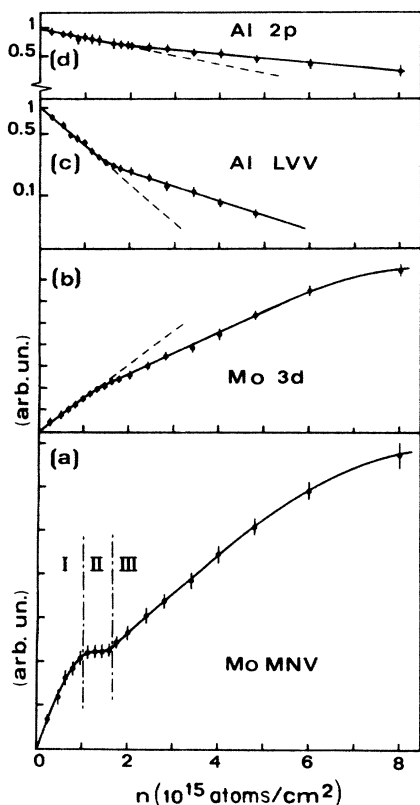
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FIG. 1. Coverage dependence of the Mo and Al signals indicated in the figure for the overgrowth of Mo onto Al. The Auger measurements are highly surface sensitive, while the photoemission ($h\nu = 1253.6$ eV) results have lower surface sensitivity.

fusion mechanism at low temperature, able to produce an intensity of Mo MNV as that of Fig. 1(a). The most natural and obvious interpretation is a nonuniform overgrowth with the formation of islands.

The region II is particularly interesting to our discussion, since at low coverages the smaller islands are likely to be formed, and these are the most interesting for cluster physics. The photoelectron spectra up to the end of the second region are summarized in Fig. 2(a). (The spectra are normalized to the same height in order to compare the shapes.) We omit the spectra at higher coverages which become increasingly similar to bulk Mo and are not interesting in the present discussion. We add that the intensity of the photoemission spectra depends on the number of deposited atoms in a way analogous to the Mo MNV intensity. In region III the increase of the intensities of photoemission spectra and of Mo MNV is obviously due to the increase in dimensions of the islands so that the spectra are dominated by the islands. In region II one cannot assume a Stransky-Krastanov growth with the formation of islands having negligible transverse dimensions being on top of the previously deposited Mo; in this case one should also have a plateau in the curve of Al LVV. Thus, the valence photoemission spectra contain prevalent information from the islands already in region II. We add also that a Stransky-Krastanov mechanism is implausible in a growth at low temperature where the lateral surface diffusion is very
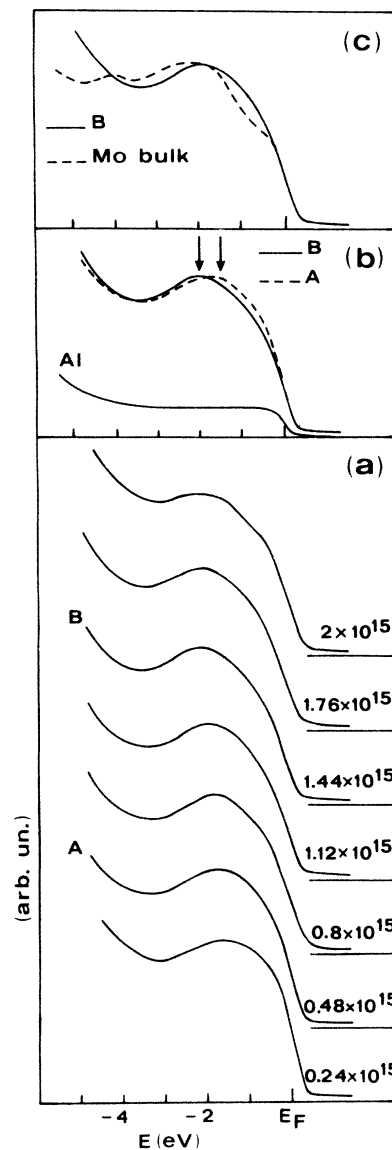

FIG. 2. Angle-integrated valence photoemission data ($h\nu = 21.2$ eV) in the overgrowth of Mo onto Al as a function of the coverage: panel (a). Comparison between the two spectra (A) and (B) at different coverages: panel (b). Comparison with bulk polycrystalline Mo: panel (c). All spectra were normalized to the same height.

inefficient. The fact that the spectra in the plateau region (II) are dominated by the islands implies that the majority of Mo already deposited is rearranged to form these islands. This happens around one monolayer and is consistent with the fact that this rearrangement at low temperature requires a considerable lateral adatom-adatom interaction to be triggered. When the lateral interaction becomes sufficiently strong the system gains energy rearranging the Mo atoms in islands: This process is sustained by the energy gained in this clustering and is in some sense analogous to what was suggested theoretically by Zunger[14] for the overgrowth of Al on GaAs. This process is also consistent with the well-known fact that Mo deposited as a thin film tends to crystallize spontaneously in the bcc form

already at liquid He temperature.[15] The bcc arrangement of the atoms in the islands is reflected in the modification of the valence photoemission spectra on passing from region I to region II. This is shown in Fig. 2(b) where the spectrum at $n = 0.48 \times 10^{15}$ atoms/cm^2 (region I) is compared with that at $n = 1.44 \times 10^{15}$ atoms/cm^2 (region II); the depletion of the shallow states and the considerable shift of the maximum to higher binding energy (~ 0.6 eV as indicated by the arrows) is evident. It is also clear from Fig. 2(b) that the difference between the two curves cannot be due to a small contribution from the Al substrate whose spectrum is also given in Fig. 2(b) with the same normalization of the spectrum at the lower coverage (curve A).

In order to connect the photoemission spectra from the islands with cluster physics it is necessary to have at least a qualitative indication of the dimensions of the islands and, in particular, of their thickness. It is intuitive that these islands are very small (no more than few monolayers thick) since they are formed at very low coverages, i.e., around a value of n corresponding to 1 monolayer. A qualitative evaluation can be easily obtained from the Mo MNV intensities versus n of Fig. 1(a). In a rough model the intensity of Mo in the first region, by assuming for simplicity a flat substrate surface, is given by $I_1 = I_\infty [1 - \exp(-z/\lambda)]$, where λ is the escape depth, and z is the thickness of the deposited layer. After the agglomeration the intensity is given (in region II) by $I_2 = I_\infty [1 - \exp(-s/\lambda)] f_i$, where f_i is the fraction of the sample surface occupied by the islands and s is their average thickness. The mass balance requires that the volume sf_i contains the number of deposited atoms. If one imposes that I_2 and I_1 fit the curve one obtains a value of s and f_i for each coverage. A similar model can also be used to fit with obvious modifications the decrease of Al LVV signal. Whatever the accuracy in the escape depth,[16] in region II one always obtains values between thicknesses of 2 and 3.5 Å and f_i around 0.5–0.6, thus indicating that the islands are very thin [remember that the lattice parameter of Mo (bcc) is 3.14 Å]. These are only qualitative indications which must not be overused but are sufficient to point out that the photoelectron spectra of region II refer to small islands having

a lot of surface states. Note that this conclusion can be arrived at independent of the knowledge of the lateral dimension of the islands. Obviously, future work with lateral resolution will be of great help in this connection.

For these reasons the comparison between the present valence spectra and the calculated density of states of small bcc cluster is significant. The main result of the calculations by Zwicknagel quoted above[7] is that the local bcc coordination forces the density of states to decrease in the Fermi level region but in a less pronounced way than in a bulk bcc crystal. The presence of dangling surface states is one of the origin of the difference. These arguments are strongly supported by the present results. In fact, upon clustering, the density of states evolves towards a more bcc-like shape as already discussed [see Fig. 2(b)]. Moreover, the comparison between the spectra in region II and that of bulk Mo [Fig. 2(c)] shows a similarity in the E_F region, but there are still significant differences at higher binding energies, in qualitative agreement with the argument by Zwicknagel.[7] Once the spectra are normalized to the same height the photoemission is lower in bulk Mo in the region between ~ -0.5 and -1.5 eV. This effect can be attributed tentatively to the surface states of the islands, since in this region the d emission is more important for Mo atoms isolated onto Al, i.e., having a substantial fraction of d-dangling bonds. This is pointed out by the d contribution to the spectrum at submonolayer coverage [0.24×10^{15} atoms/cm^2 in Fig. 2(a)]. Another evident point is the band narrowing in the islands with respect to bulk Mo seen experimentally [see Fig. 2(c)] and supported by the cluster calculations. We can thus say that the present results are strong support of the theoretical results on bcc cluster in Ref. 7.

In conclusion, we have pointed out a case in which the overgrowth of a d metal takes place via the formation of islands and that a photoemission investigation of this process is significant also for cluster physics. At present it is not possible to assess how general this experimental approach can be, but we have shown that for Mo onto Al at low temperature, the photoemission results are significant and support recent cluster calculations for $4d$ bcc refractory metals.

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