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LETTER TO THE EDITOR

Aluminium oxide ultrathin-film growth on the Mo(110) surface: a work-function study

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Abstract
Submonolayer-to-multilayer films deposited onto the surface of Mo(110) crystal by thermal evaporation of bulk aluminium oxide in ultrahigh vacuum have been studied by Auger electron spectroscopy, low-energy electron diffraction and work-function measurements (the Anderson method). The Auger spectra of the films at all coverages studied are composed of the lines characteristic for the bulk oxide; no evidence of a metallic Al signal is found. The layer-by-layer growth mode occurs up to two monolayers. Increase of the reflectivity of the low-energy electrons (1 to 4 eV) as the film grows indicates that the film has a reduced density of states, which probably resembles the band gap of the bulk alumina. The films deposited on a substrate held at room temperature are amorphous, whereas deposition at 1300 K results in a hexagonal superstructure.

Recently, surface science studies of the growth of thin oxide films on metal surfaces have been attracting much attention due to the importance for applications of such films, as well as oxide/metal interfaces, in various technological areas such as nanoelectronic device building, materials processing and heterogeneous catalysis [1–5]. In this regard, aluminium oxide is one of the most extensively studied oxides. Over the last decade, considerable progress has been achieved in the understanding of the morphology and electronic and structural properties of Al_2O_3 grown on different metal substrates [4–7] and metallic alloys [1, 8, 9]. Interaction at the oxide/metal interface has a considerable impact on the properties of the growing oxide film [1, 4, 5]. One of the most widely used procedures of growth of aluminium oxide on refractory metal surfaces is the deposition of metallic aluminium in an oxygen ambient at a substrate held at room or higher temperature with or without subsequent annealing in oxygen [4–6]. This procedure allows one to obtain films which have structural and electronic properties closely

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resembling those of bulk oxide crystal. The disadvantage of using of this procedure is that the oxide film is being adsorbed not on a pure metal surface, but on a substrate being oxidized by the ambient oxygen. This considerably changes the thermodynamics at the interface border, thus affecting the properties of the film, especially at submonolayer coverage [5]. For instance, the occurrence of a Frank–van der Merwe, Volmer–Weber or Stranski–Krastanov growth mode, according to thermodynamic considerations, will depend on whether the surface free energy of the substrate (G_s) is greater than (or equal to) the sum of the surface energies of the adsorbed film (G_f) and the film/substrate interface (G_{fs}) [10]. For refractory metals, such as W(110), Mo(110), Re(1000), Ru(1000), the value of G_s (ranging from 2200 to 2700 erg cm^{-2}) is much higher than that of Al_2O_3 (690 erg cm^{-2}) and for oxide/substrate interfaces (about 60 erg cm^{-2}) [11], so the full two-dimensional layer of oxide would be thermodynamically stable. However, when the refractory metal is oxidized, its surface energy is considerably changed (for instance the surface free energy of Re_2O_7 is only 33 erg cm^{-2} [11]). This may lead to a growth mode different to what is expected from thermodynamic considerations with account taken of G_s for pure metal substrates.

It would have been possible to predict the growth mode even in the case of the oxidized substrate, taking into account the corresponding values of the surface energies. However, in most cases the type of the oxide formed on the surface of the metal substrate is not clearly known, which makes it difficult to estimate the values of G_s. One of the ways to circumvent such difficulties is to deposit the aluminium oxide on the metal substrate directly from a source containing bulk aluminium oxide.

The aim of this study is to show that such deposition is possible and that it results in the growth of oxide films with features resembling those of bulk oxide, even at submonolayer coverage. The Mo(110) surface was chosen as a substrate for aluminium oxide deposition because its lattice constant (2.73 Å) matches closely with the in-plane O^{2-} lattice constant (2.77 Å) of single-crystal Al_2O_3 [12]. Investigations were carried out in an UHV chamber (base pressure 2×10^{-10} Torr) with the aid of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and work-function measurements (the Anderson method). For the AES a single-pass cylindrical mirror analyser with a coaxial gun (Riber, LAS-3000) was used with a primary electron energy of 3 keV and a beam current of 0.1 μA. All Auger spectra were recorded in the differential $\mathrm{d}N/\mathrm{d}E$ mode. LEED patterns were observed using a four-grid rear-view hemispherical optics device. The primary electron energy was in the range of 60 to 120 eV. For the work-function measurements a special low-energy electron gun operating at energies lower than 10 eV was used. In most of the reported studies on measuring the work function by the Anderson method, only the voltage required to compensate the change of the contact potential difference (CPD) between the cathode of the electron gun and the sample, as the film grows, is monitored. This compensating voltage gives the change of the work function. In the present study, however, the CPD curves were measured completely from the onset to the saturation region. This turned out to be useful because during the deposition of aluminium oxide the shapes of these curves were changing (see below), thus providing additional information on the film properties. Aluminium oxide films were deposited by thermal evaporation of bulk sapphire crystal. The latter, of approximate size $0.5\times0.5\times0.5$ mm^3 was placed inside a basket made of 0.2 mm diameter W/Re wire heated by a direct current. The basket was shielded with a cylindrically shaped Ta screen with an exit nozzle. The Ta screen, the W/Re filament and the piece of sapphire were carefully outgassed in a preliminary UHV chamber at high temperature. During the deposition the sample was placed at a distance of about 1 cm from the source exit nozzle. The flux produced by this source was stable and reproducible. The growth rate of the film estimated by analysing the Auger uptake curves was about 0.025 ML min^{-1}. It was not possible to exclude the possibility that during the

evaporation of the sapphire there would be loss of oxygen by the source. However, analysing the residual gases using a quadrupole mass spectrometer with an entrance slit put close to the source during the sapphire evaporation, we did not detect any major increase of O_2 mass signal. This is consistent with the Auger results showing only the peaks characteristic for bulk aluminium oxide crystal at all coverages studied. It may turn out that breaking the bonds between Al_xO_y and Al_xO_y species during Al_2O_3 evaporation is a more favourable process than breaking the bonds between Al^{3+} and O^{2-} ions. The stable gas phases over alumina are Al_2O and AlO, and the aluminium oxide film growth on the surface probably occurs via recombination of these species. Nevertheless, one cannot exclude the possibility that oxygen may be released to a certain extent during the sapphire evaporation, although no evidence of this was found in this study. Another possibility is the reaction of aluminium oxide in contact with hot W/Re wire. Due to this reaction, W–Al and Re–Al alloys as well as W and Re binary oxides or W–Re–Al ternary oxides may be formed, thus resulting in the deposition of W and Re species onto the surface along with the aluminium oxide. Special care was taken to check whether such species appear on the surface. Using AES at its highest sensitivity level revealed nothing resembling the Auger signals of Re and W.

Aluminium oxide was stepwise deposited (each deposition for 2 min) until about two monolayers had been deposited onto Mo(110) held at a two different temperatures: (1) room temperature (RT); (2) 1300 K. Deposition at RT resulted in a decrease of the intensity of the LEED spots of Mo(110) with no extra spots appearing, and a background intensity increase. This indicates that the adsorbed film has no long-range structural order. However, when an oxide was deposited on a substrate held at 1300 K, a very complicated LEED pattern appeared beginning from the coverage of 0.2 ML. As the coverage increases the LEED pattern changes and the intensity of some extra spots increases whereas the other spots fade. At a coverage of about 1.1 ML the LEED pattern consists of spots located at the positions of Mo(110) diffraction spots, but these spots are not as sharp and intense as those of Mo(110). Moreover, the background intensity is higher than in the case of the clean Mo(110). With the increase of the oxide coverage this background intensity decreases and the diffraction spots become sharper. Therefore one can consider that at a substrate temperature of 1300 K the mobility of the oxide species is high enough that they can form an ordered structure on the surface. The symmetry of the LEED pattern at higher than 1 ML coverage suggests that the film has a hexagonal order.

AES investigation of the film reveals that there is no sign of a metallic Al^0 LVV Auger peak at a kinetic energy of 68 eV at all coverages and at both substrate temperatures studied. The only aluminium peaks which are seen are the interatomic $Al^{3+}(L)$–$O^{2-}(VV)$ transitions at the Auger energies of 55, 46, 39 and 27 eV characteristic for aluminium oxide. These peaks can be detected beginning from the coverage of 0.05 ML. As the coverage grows, the intensity of these peaks increases with no detectable shift of their energy position and change of the line shape. Growth of these peaks with coverage is accompanied by increase of the oxygen O(KLL) Auger signal intensity at a kinetic energy of 503 eV. No difference in behaviour of the Auger spectra for the two different substrate temperatures was observed. These Auger results suggest that there is no dissociation of Al_xO_y species on the surface into Al and O atoms, within the sensitivity limit of the spectrometer. To find out the possible growth mode of the oxide film on the Mo(110) surface, we used a well known procedure of plotting the Auger uptake curves [13]. Peak-to-peak height was chosen as the Auger intensity, instead of calculating the peak area with background subtraction. The former is considered to be a good approximation when the peak shape does not change during the film growth [14]. Special care was taken in measuring this type of curve, because in some cases, plotting the fits (linear or nonlinear) to the experimental points is rather ambiguous. Figure 1(a) represents the Auger uptake curves of

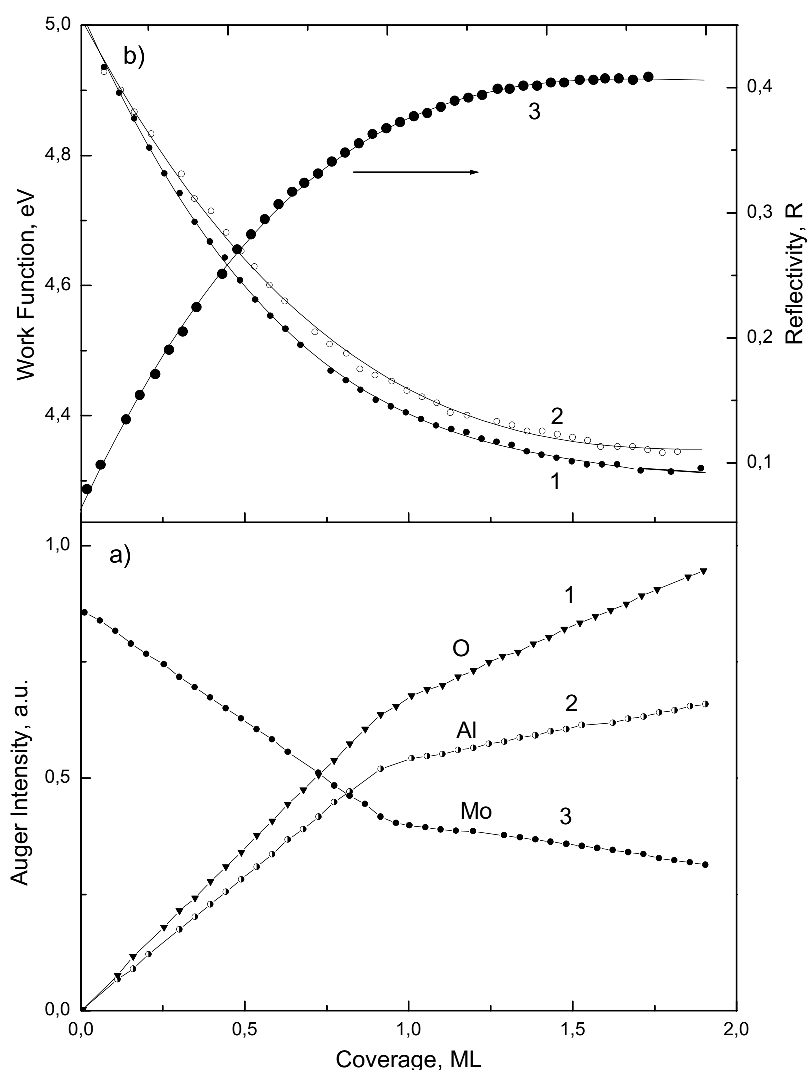

Figure 1. (a) Mo(MNV) (1), Al^{3+}(LVV) (2) and O(KLL) (3) Auger intensities versus aluminium oxide coverage on Mo(110) at RT. (b) The work function ((1), (2)) and the reflectivity, *R* (3), versus aluminium oxide coverage on a Mo(110) surface held during oxide deposition at RT ((1), (3)) and 1300 K (2).

O(KVV), Al^{3+}(LVV) and Mo(MNV) signals for aluminium oxide being deposited at RT. An observed linear change of the plots accompanied by a break indicates that the layer-by-layer growth mode occurs, at least up to 2 ML. It is assumed that the coverage at which a break occurs is equal to 1 ML. Similar behaviour was observed during the deposition of an oxide on a substrate held at 1300 K, indicating that formation of a full 2D monolayer of alumina on Mo(110) is the thermodynamically favoured process, although kinetic constraints prevent long-range ordering of the film at RT.

There are many reported data on adsorption of many metal atoms and some compounds on refractory metal surfaces, including Mo(110) [15]. The work function has been extensively measured for such systems and much useful information was extracted from these

measurements [15]. As far as we are aware, there are no reported data on work-function measurements of the adsorption of aluminium oxide on Mo(110) surfaces. Therefore, we made an attempt to perform such a measurement in this study. For this purpose an Anderson method was used, as mentioned above. This method is based on measuring the current–voltage (C–V) curves—that is, the current (i) flowing through the sample as the bias voltage between the cathode of an electron gun and the sample sweeps over the contact potential difference range. Change of the sample work function leads to a parallel shift of the C–V curves, and the value of this shift is proportional to the work-function change. As is mentioned above, the C–V curves were measured completely over the accessible range of bias voltages (-5 to 5 V). It was found that during the aluminium oxide deposition the C–V curves not only shift, but also change their shape in the way shown in figure 2. Curve 1 corresponds to the clean Mo(110). For convenience the C–V curve can be considered as being composed of two parts: the 'onset-cut-off' part (ab) and the 'saturation' part (bc). The parallel shift of the 'ab' part gives the work-function change $\Delta\phi$, whereas the 'bc' part gives the maximum possible current flowing through the sample. Curves 2 and 3 correspond to 0.8 and 1.9 ML of aluminium oxide, respectively. It is seen that aluminium oxide deposition, apart from the change of the work function (the parallel shift of the 'ab' part), leads to a considerable decrease of the current through the sample at bias voltages corresponding to saturation (the 'bc' part). In other words, the reflectivity of the primary electrons is higher for the surface covered by the oxide than for the clean Mo(110) surface. A similar change of the shape of the C–V curve starts from the very beginning of the oxide deposition. The value of the reflectivity, which determines the change of the C–V curve shape, and which is defined in this case as $R = A/B$ (figure 2), as well as the work function, plotted versus the aluminium oxide coverage, are shown in figure 1(b). The work function of the clean Mo(110) surface was assumed to be 5.0 eV [16]. It is worth mentioning that before studying the adsorption of the aluminium oxide, we performed work-function measurements of the adsorption of many metallic adsorbates (namely, all of the first-row transition metals (Sc to Cu), rare-earth metals (La to Eu), Al, Ba and also B), and in none of these cases did we observed such a change of the C–V curve: in all the cases at all adsorbate coverages studied, the saturation level (the 'bc' part) remained at about the same level. Quite recently, a change of the shape of the C–V curves similar to that shown in figure 2 was also observed during the growth of LiF film, a highly insulating material (band gap: 14 eV), on the Si(111) surface [17]. Therefore we tend to attribute the decrease of the current through

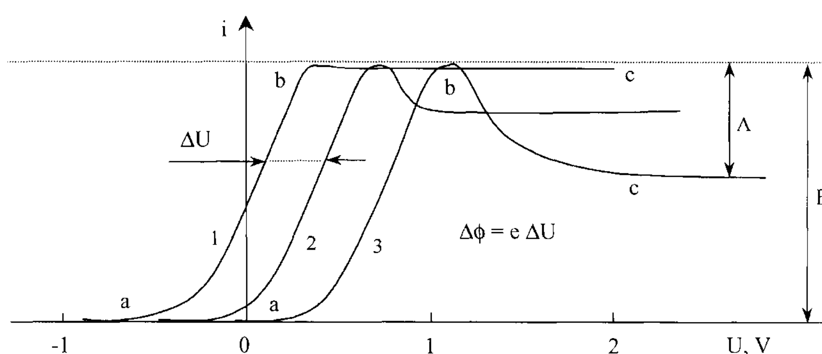

Figure 2. C–V curves of Mo(110) (1) and the alumina/Mo(110) system at alumina coverages of 0.8 (2) and 1.9 ML (3). Aluminium oxide deposition leads to a change of the shape of the curves originating from the increase of the reflectivity (R) of the primary low-energy electrons as the oxide grows on the surface.

the oxide/metal sample as due to the insulating properties of the film. In other words, one may assume that a reduced density of electronic states featuring certain properties of the oxide band gap is already apparent in the amorphous adsorbed layer formed at RT. Probably the same also holds for the system obtained by deposition of alumina on a substrate held at 1300 K, because in this case too the C–V curve shape undergoes the same change as at RT. At 1300 K the work function qualitatively changes in a similar way to at RT, except that the absolute values of ϕ are systematically higher by about 0.05 eV (figure 1(b), curve 2). That the work function exhibits the same trend at both temperatures can be explained by the fact that the value of ϕ is more sensitive to the short-range order than to the long-range order [15]. Thus, the amorphous and the ordered films may have similar characters of the short-range order. Annealing leads to a long-range ordering, which is usually accompanied by some increase of the work function [15]. The hexagonal LEED pattern formed at 1300 K at a coverage higher than 1 ML, with the spots located at positions close to those of the primary spots of Mo(110), suggests that this pattern is formed by the oxygen anions rather than Al ions, because the lattice constant of Mo(110) is close to the in-plane O^{2-} lattice constant of single-crystal alumina [12]. In this sense it may turn out that the film resembles the structure of the bulk alumina. However, it is unlikely that at a coverage lower than 2 ML the film assumes the structure of any known alumina crystals, α-, γ-, γ'-, κ- or θ-Al_2O_3. A two-monolayer film may be roughly considered as consisting of a hexagonal array of oxygen ions with the aluminium ions occupying tetrahedral and/or octahedral vacancies in the middle of the film and corresponding threefold hollow sites at the film/vacuum interface. This is consistent with the decrease of the work function (figure 1(b), curves 1, 2); that is, the anion layer is located closer to the substrate surface, whereas the cation layer is shifted towards the vacuum. Subsequent increase of the film coverage may lead to the formation of the structure of the corresponding bulk alumina crystals at a certain film thickness. However, the fact that at a coverage of about 2 ML the work function, as well as the value of R, has already stabilized (figure 1(b), curves 1–3) suggests that the properties of the film are generally established and may not dramatically change as the coverage grows further. This conclusion is corroborated by the reported observation that two-monolayer aluminium oxide films are self-limited in thickness when produced by NiAl alloy oxidation [1, 8], and the recent theoretical calculations suggesting that two-layer aluminium oxide films on Mo(110), Ru(1000) and Al(111) may feature most of the electronic and structural properties of the bulk aluminium oxide crystal [7].

Concluding, the present results show that thermal evaporation of bulk alumina can be used for deposition of thin aluminium oxide films on the Mo(110) surface. Two-dimensional one-layer-thick films deposited in this way already show some features that resemble those of the bulk aluminium oxide.

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