Growth, structure and properties of ultra-thin copper films on a V(110) surface

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Abstract

In this work we study the evolution and electronic properties of copper ultra-thin films grown at room temperature on a V(110) single crystal surface using angle-resolved ultraviolet photoemission spectroscopy (ARUPS), X-ray photoemission spectroscopy (XPS), Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). Up to 5 monolayers (5 ML) the films grow in an imperfect layer-by-layer mode; this being more pronounced at coverages above 2 ML. The LEED studies show that films up to 2 ML coverage grow pseudomorphically, forming thus a body-centered cubic (bcc) copper film. The 5 ML film shows no clear LEED pattern, although the appearance of quantum well states (QWS) at 1.1 and 1.9 eV binding energy in the ARUPS spectrum suggests that the film as a whole is rather well ordered. Dispersion of the Cu 3d bands of the 5 ML film follows the calculated dispersion of the bcc copper along the ΓN high symmetry axis. The 2 ML film also shows a QWS (at 1.8 eV) of very high intensity. Annealing affects significantly only the films of coverages higher than 2 ML: clusters are formed on the 2 ML thick copper overlayer. These findings contribute also to a better understanding of the results obtained by thermal treatment of ultra-thin vanadium films grown on a Cu(100) surface, in which case a segregated copper film is formed on top of the bcc-vanadium film. The work function of the clean and ordered V(110) surface is found to be 4.65 ± 0.08 eV.

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1. Introduction

Ultra-thin metallic films are the focus of interest of many research groups, primarily due to their novel properties [1] when compared with their bulky counterparts. It is therefore important to examine as many systems as possible in order to accumulate knowledge that may eventually lead to design of new materials for applications in so-called nano-technologies. Vanadium and copper have both been investigated in the roles of ultra-thin films and substrates in a number of metallic systems, but only in a few both were present [2–7]. In particular, there is no information about the Cu/V(110) system in the literature and it is certainly of interest to add new data to the interesting and important field of noble-metal-layer/transition-metal-substrate interactions.

In our recent study [2] of the growth of vanadium ultra-thin films on a Cu(100) surface we showed that, upon an annealing of a several layers thick vanadium film at 700 K, an ordered layer of segregated copper was formed. The low-energy electron diffraction (LEED) pattern of the film was the same as the one of the under-laying vanadium layer, i.e. 4 domains of a (110)-oriented...
body-centred cubic (bcc) copper film were formed. The corresponding ultraviolet photoemission (UP) spectra, taken by using 21.2 eV excitation energy and in normal emission (n.e.), were characterized by a bulk-like Cu 3d band emission and an additional emission peak at 1.8 eV binding energy (see Fig. 5 in Ref. [2]). Such a peak may not be found in the n.e. spectra of the copper (100), (110) and (111) surfaces. The origin of this peak, as well as the thickness of the segregated copper film, could not be determined in that study.

The Cu/V(110) system is a simpler version of the above-discussed Cu/V/Cu(100) case (which consists of the 4-domain bcc vanadium substrate and 4-domain segregated copper on top of it) and therefore enables one to study the initial stages of copper film growth and the nature of the 1.8 eV peak in detail. In this work, we study the evolution and electronic properties of copper ultra-thin films grown on a V(110) single crystal surface with the aim of assessing: (a) their structural and electronic properties in the coverage range up to several monolayers; and (b) the origin of the peak at 1.8 eV.

In order to achieve this goal we used the following experimental methods: angle resolved ultraviolet photoemission spectroscopy (ARUPS), X-ray photoemission spectroscopy (XPS), Auger electron spectroscopy (AES) and low-energy electron diffraction.

2. Experimental

The experiments were performed in an ultrahigh vacuum apparatus equipped with a hemispherical analyzer with an angular resolution of ±3°, a helium discharge lamp, an Mg/Al anode, an electron gun, low energy electron diffraction facility and a quadrupole mass spectrometer. Copper was evaporated from a resistively heated tungsten basket. Pressure was always below 1 × 10⁻⁸ Pa except during evaporation, in which case it never exceeded 2 × 10⁻⁶ Pa.

A vanadium monocrystal of 2 mm thickness and 8 mm diameter was mechanically polished, inserted into the ultrahigh vacuum chamber and after a series of cleaning cycles a clean, well-ordered V(110) surface was obtained. The cleaning procedure is described elsewhere [8]. This surface has a work function of 4.65 ± 0.08 eV as measured from the width of the corresponding UP spectrum ¹. For the sake of comparison, we mention that the less densely packed surface, V(100) ², has a work function value of 4.1 eV. The V(110) surface, when probed by LEED, gave rise to a sharp pattern characteristic of the primitive, rectangular, 1 × 1 structure. No additional features may be observed in the pattern as expected for the clean and non-reconstructed, well-ordered V(110) surface [9].

3. Results and discussion

Fig. 1 shows the peak-to-peak (ptp) intensities of copper Auger emission at 61 eV and vanadium at 470 eV (the V signal is multiplied by 100 in the figure) as a function of deposition time. During the deposition the sample was kept at RT. The spectra were recorded keeping the pass energy constant at a value of 50 eV. Fig. 1 shows an almost linear decrease of the vanadium signal during the deposition while the copper signal shows a linear increase of intensity with two clear breaks at approximately 6 and 11 min of deposition. This suggests completion of the first and second Cu layer, respectively. However, in order to assign correctly such a behavior of the copper signal one should make a proper coverage calibration. This may be done by using the data for vanadium signal attenuation of the well-characterized system, Ag/V(100), where 2 ML of silver are very well defined [10,11]: after completion of two, well-ordered Ag layers, the V(470 eV) signal decreases to 60% of the initial value. The same attenuation is achieved in the experiment shown in Fig. 1 after deposition of ~12 min, which is indicated by an arrow in Fig. 1. Therefore, we may safely assume that the first linear increase of the

¹ A UPS spectrum of the clean V(110) surface is shown in Fig. 4 of Ref. [2].
² In Ref. [8] a value of 4.3 eV is reported. In the meantime, we repeatedly measure a value of 4.1 eV on a crystal in much better shape than the first one.
Cu(61 eV) signal (completed after 6 min deposition) corresponds to the formation of the first copper layer. After the completion of the first layer the Cu curve changes slope, but persists to increase linearly. Disorder, which manifests itself as a deviation from linearity, sets on only after approximately half of the second layer is filled. A disordered growth persists also at higher coverages, but remains in its essence layer-by-layer growth mode, as may be seen from the data in Fig 1: the Cu(61 eV) peak slowly increases while the V(470 eV) signal monotonously decreases and the Cu/V ratio value (not show in the figure) doubles when compared with the 2 ML film value.

Fig. 2 displays a set of UP spectra taken after stepwise deposition of copper on a V(110) surface kept at room temperature. There are two prominent characteristics in these spectra. The first one is the development of the Cu 3d bands as the coverage increases from a very low one to the 5 ML thick film. Up to 1 ML coverage the Cu 3d bands have an atomic-like lineshape with the center of gravity at 3.1 eV. At coverages from 1 to 2 ML an additional peak develops at 2.5 eV. Yet, the width and the lineshape of the 2 ML Cu 3d band spectrum is markedly different from the spectra of thicker films.

There is a large surface free energy difference between Cu (1.85 J/m²) [12] and V (2.9 J/m²) [12]mately half of the second layer is filled. A disor-

dered growth persists also at higher coverages, but that suggests the layer-by-layer growth mode as a favorable one, at least for the first copper layer deposited on a V(110) surface. In such cases, very often the initial growth is pseudomorphic and the deposited layer attains a non-equilibrium structure that is characterized by its volume and strain energies. These may eventually cause a breakdown of the pseudomorphic growth and formation of a new layer structure [13,14]. For the case of copper films it is important to notice that both the bcc and hcp copper structures are only slightly less stable than the equilibrium fcc structure [15-17].

Therefore, in the case of copper layers grown on a V(110) surface, the initial pseudomorphic
(bcc layer) growth may, with increasing coverage, gradually transform into a hcp and eventually, at higher coverages, into the fcc structure. Recently, Wormeester et al. [18,19] proposed a criterion, based on the ratio of the atomic radii of fcc deposits on the (100) face of bcc substrates, that enables one to predict whether the film has an hcp orientation or both hcp and bcc orientations co-exist. According to this criterion (the Cu-V ratio = 0.977) both orientations may be present in a copper film grown on a V(110) surface. Such a case has been found for the Cu films produced on a W(100) system [19]. It should also be noted that due to a rather small Cu-V atomic radii mismatch the role of the strain energy [20] is negligible, and in its initial phase the Cu film growth is mainly governed by the free surface energies difference and the copper-vanadium interface energy.

In several systems consisting of a transition metal overlayer (Ni, Co) atop a transition metal (110) surface (Mo, W), a clear transition from the pseudomorphic to the closed-packed overlayer surface at room temperature as a function of the sample coverage exceeded the initial (pseudomorphic) monolayer [21–24]. The transition was accompanied by a change of the 1×1 to the 8×2 LEED pattern.

The LEED patterns of the films studied in this work showed no dramatic changes as the copper coverage increased from 0 to 5 ML. the 1×1 pattern found for the clean and ordered V(110) surface was also found for Cu films up to 5 ML coverage, though with increasing coverage the pattern gradually lost its sharpness and eventually (around 5 ML) disappeared in a very diffuse background. These LEED findings suggest a gradual transformation [18] from the bcc structure (at several first monolayers) to a disordered top layer rather than the pseudomorphic-to-closed-packed restructuring [13,14].

The ARUP spectra in Fig. 2 present an additional argument for the absence of any dramatic structural changes during the Cu film growth at RT: in the coverage range 2–5 ML the Cu 3d band spectrum continuously develops from a 2D-like to a 3D-like band spectrum.

A comparison of the ARUPS measurements of the at RT deposited 5 ML thick Cu film shown in Fig. 3 with the calculated 3d-band structure of the bcc copper [25] also support the idea about the bcc nature of the film. The ΓΣN high symmetry direction of the bulk Brillouine zone (BBZ) of the overlayer bcc copper is perpendicular to the (110)-bcc Cu plane and as such is probed in the n.e. photoemission experiment. Assuming a free electron final band, we have calculated the initial k-p to be 1.3(2 p/a) which suggests that the dominant contribution to the intensity of the n.e. spectrum in Fig. 3 comes from a point close to the ground. These LEED findings suggest a gradual transformation [18] from the bcc structure (at the center of the BBZ (Γ point). The calculated 3d-band structure of the bcc copper [25] suggests that the double peak structure of the n.e. spectrum, between 2 and 4 eV below the Fermi level, can be associated with the emission from the Γ25 and Γ35 points which are 1 eV apart. However, in order to make an absolute energy comparison with the measured spectrum a shift of calculated bands by 0.3 eV away from the Fermi level is necessary. Within the approximation of the free electron final band, the rotation of the sample around the (100) axis, as we do in our experiment, moves the point in the BBZ, probed by 21.2 eV photons, from Γ
to N, closely along the Σ high symmetry line. A clear dispersion of the high energy shoulder to higher binding energy and apparent absence of any shift of the peak at 2.8 eV, with polar angle (Fig. 1) is compatible with the dispersion of the Σ band away from the Fermi level and the flat nature of the Σ band as k changes from Γ to N. The broadening of the peak at higher polar angles can be associated with the dispersion of the Σ band.

It should be noted however that, as the very diffuse LEED pattern of this film suggests, the structure of the top layers is not well ordered and a drawing of a firm conclusion about its structure on a layer-by-layer basis is not possible.

However, the bcc copper structure was determined [26] for Cu layers in niobium/copper multilayer systems where all copper films thinner than 11 Å were found to grow pseudomorphically on Nb. Interestingly, copper when grown on a Mo(110) surface follows the layer by layer growth mode only for the first two layers [27].

The second significant feature in the spectra in Fig. 2 is the appearance of additional intensities in the region between the Fermi level and the Cu d-band where in the case of very thick films one should observe only an sp band derived peak, if at a given photon energy the direct transition are possible, and possibly also a surface state. The sp band derived peak position is independent of the layer thickness (at a fixed photon energy), whereas the intensities in Fig. 2 have different positions at different film thicknesses. These additional intensities are marked in the spectra in Fig. 2 under the assumption that they are sp-derived quantum well (QW) states. It is well known [28] that QW states may appear in those cases where the layers are ordered and a substrate band, e.g. an sp band, has a gap that overlaps with e.g. sp valence electron energy range of the adsorbate. Indeed, vanadium has a sp band gap along the ΓN high symmetry (110) axis which ranges from approximately the Fermi level to 3.5 eV below it [29]. In order to predict the positions of possible copper sp-derived QW states within the sp band gap of the V(110) substrate at different film thicknesses we solved the Schrödinger equation for an electron placed into one-dimensional quantum well with the V(110) sp-band gap (interface side – a step function) and the image potential (vacuum side) as the well walls. The procedure has been tested using the case of the Ag ultra-thin films on the V(100) where a number of very intense QW states have been experimentally identified [31] and the predicted positions were very satisfactory. In the case of the Cu/V(110) system, these calculations predicted no QW state for 1 ML thick Cu film, and a QW state at 1.8, 0.7, 0.1, 1.9, 1.3 and 0.8 eV below the Fermi level for the film thickness of 2, 3, 4, 5, 6 and 7 ML, respectively. The nomenclature used [31, 32] is based on the number of monolayers N within a particular film and a number of nodes m of the corresponding electron wave function, whereas QW states having same v = N − m value get same label, e.g. a, b, c,… for v = 0, 1, 2,…, respectively, while the subscript accompanying a label equals m + 1. In such a way, the QW states are classified [31–33] according to their wavelength and number of nodes of the corresponding wavefunction.

Apart from the b2 state (2 ML film) all other QW states indicated in Fig. 2 are either of very small intensity or non-discriminable. There are several possible reasons to account for such a behaviour: 1. QW states are very sensitive to the ordering of the films. In general, perfectly ordered films enable formation of intense QW states [33]. In our case, at RT and above 1 ML copper films grow in an imperfect layer by layer mode: the layers are not fully ordered and several layers grow at the same time. This is clearly seen in Fig. 2 at higher coverage UP spectra: the 5 ML film has a peak at 1.1 eV which corresponds to the c4 state of the 6 ML film. Obviously, at a nominal coverage of 5 ML, there are patches of 6 ML thickness. Similarly, the b2 state (characteristic for the 4 ML film) appears more intense at a nominal coverage of 3 ML than at 4 ML. The c4 state which is characteristic for the 5 ML Cu film and should peak at 1.9 eV may not be seen in the corresponding ARUP spectrum. However, it is present and may be observed at different sample polar angles.

We used the so-called Numerov algorithm as described in Ref. [30].
(Fig. 3) where its intensity appears to be higher than in the n.e. spectrum in Fig. 2.

2. It has been found [31,33–35] that the photo-emission cross-section of a QW state depends strongly on the excitation photon energy, thickness of the film and interaction of the film with the substrate. It may happen that at 21.2 eV, the energy of the HeI radiation, hits a significant cross-section for the $b_2$ state only as was found in the case of Ag films deposited on V(100) surface [33].

The influence of the ordering of a film on the QWS intensity is illustrated for the case of 2 ML copper film. The ARUP spectrum of the well-ordered 2 ML film is shown in Fig. 4, full line. The dashed spectrum was taken after RT deposition of approximately 3 ML equivalent amount of copper and the full-line spectrum after a flash of this film up to 860 K. The former spectrum shows essentially the 3D Cu 3d valence band (induced by the multilayer, i.e. imperfect, growth front) between 2 and 4 eV binding energy. The flash at 860 K induced a drastic change of the spectrum: the $b_2$ QW state at 1.8 eV emerged while the intensity of the 3d band decreased significantly and simultaneously shifts by 0.1 eV towards the Fermi level. At the same time, also the intensity of the 3d vanadium band at the Fermi level increased. A comparison with the 2 ML spectrum of the at RT deposited film in Fig. 2 shows that ordering of the film induces significantly higher intensity of the QW state.

The LEED pattern of the 2 ML copper film grown at RT was very diffuse. However, after a flash to temperatures above 650 K the LEED pattern was very sharp and exhibited the same features as the pattern of the clean V(110) surface. The LEED pattern of the well-ordered 2 ML Cu film is shown as the inset in Fig. 4.

Obviously, the at RT deposited 3 ML thick copper film after the thermal treatment reduced to two pseudomorphically perfectly ordered layers. The same behaviour was also found for thicker films. In all these cases the Cu films collapsed into the 2 ML film which served as a substrate for small Cu clusters whose total contribution to the ARUP spectrum intensity was very small.

Based on the data shown above, we may conclude that the 2 ML copper film deposited on the V(110) surface at RT and annealed above 650 K has the same atomic order as the substrate surface and in addition to the Cu 3d valence band the $b_2$ state at 1.8 eV is the dominant characteristic of the film.

In addition, the $b_2$ QW state associated with 2 ML copper film on a different V surface (100) this time, was found [31] at 0.9 eV b.e. In the case of V(100), the sp band gap covers the range of 2 eV below and above the Fermi level. The deeper gap in the V(110) case and the different structure of the Cu film, i.e. the different width of the well, are the main causes for the large difference in energy of the two QW states.

The $b_2$ state disperses significantly as the polar angle is varied, as one would expect for a nearly free electron state [31]. This is shown in Fig. 5. It is worthwhile mentioning here that at some points
The X-ray photoelectron spectroscopy (XPS) of the films studied in this work showed, as in the case of Cu/V(100) [3], that deposition of copper does not induce any Cu 2p or V 2p core level shifts irrespective of adsorption temperature and coverage. For the sake of reference we mention here that the annealed 2 ML film has a Cu(2p)/V(2p) peak area (corrected for the corresponding sensitivity factors) ratio value of 1.43 at a photoelectron emission angle of 45°.

4. Conclusions

We have studied growth and properties of ultrathin Cu films grown at RT on a V(110) surface and shown that the 2 ML film, when annealed, has a perfectly ordered bcc-like structure [of the V(110) surface] and is characterized by intense photoemission from a QW state at 1.8 eV binding energy. This finding explains the origin of the state at 1.8 eV, which was previously observed in the UP spectra of Cu films segregated on the vanadium in the fcc Cu BBZ one can observe a so-called Tamm state. At RT the films grow in an imperfect layer-by-layer mode, the imperfection being more pronounced at coverages above 2 ML. The LEED studies show that films up to 2 ML coverage grow pseudomorphically forming thus a bcc-copper film. The 5 ML film shows no clear LEED pattern although the appearance of quantum well states (QWS) at 1.1 and 1.9 eV binding energy in the corresponding UP spectrum suggests that the film as a whole is rather well ordered. The dispersion of the Cu 3d bands of the 5 ML film follows the calculated dispersion of the bcc copper along the ΓN high symmetry axis.

The work function of the clean and ordered V(110) surface is reported to be 4.65 ± 0.08 eV.

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