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Preparation and characterization of well-ordered MoO_x films on $Cu_3Au(1\ 0\ 0)$–oxygen substrate (CAOS)

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Abstract

The goal of this work is to prepare well-ordered molybdenum oxide films using oxygen implanted $Cu_3Au(1\ 0\ 0)$ substrate (CAOS, Cu_3Au–Oxygen Substrate) and identify the structure of the different oxide phases. Those films were grown on an UHV chamber (2×10^{-10} mbar background pressure) and prepared by electron beam deposition. The structure of the films was studied using low energy electron diffraction (LEED), scanning tunnelling microscopy (STM), and X-ray photoelectron spectroscopy (XPS). The ultra thin molybdenum film shows the formation of an oxide layer with hexagonal symmetry plus a square lattice. The hexagonal mesh units are rotated by 90° (or 30°) with respect to one another. Based on XPS data, the Mo cations are in an oxidation state that ranges from 4+ to 6+. STM results show the presence of hexagonal islands formed over a square symmetry phase.

Keywords: Molybdenum oxide; Cu_3Au; CAOS

1. Introduction

Molybdenum oxide is a widely used catalyst in the chemical industry. For example, supported molybdenum oxide catalysts exhibits unique activity, selectivity and stability for many different catalytic reactions such as the oxidation of methanol [1], izomerization and hydrogenation of olefins and the hydro treatment of oil-derived feedstocks (hydrodesulphurization (HDS) ([2] and references therein). In addition, MoOx species can play an important role for optimizing the C_2–C_3 olefin selectivity by CO hydrogenation [3]. However, the selective production of targeted hydrocarbon(s) by CO hydrogenation requires a molecular level understanding of the surface chemistry of the catalysts. In the last decade, innumerable researchers have directed its efforts towards developing heterogeneous model catalysts in order to understand, through an atomic view, how it behaves regarding adsorption probe molecules and what is the relationship between structure and reactivity [4]. For this purpose, the surface science approach has been essential and several studies among different transition metal oxides have been published. However, despite of those innumerous studies very little is known about some oxide surfaces such as molybdenum and niobium oxides [5–7]. Problems of surface instability have made it difficult to study oxides of Mo, being MoO_3 (0 1 0) the most stable single crystal surface [7]. Several attempts have been done towards the preparation of a well Mo ordered oxide surface and an understanding of molybdenum oxide structure and stoichiometry, but it is still a key issue. Moreover, with the help of powerful techniques such as low energy electron diffraction (LEED), scanning tunneling microscopy (STM), and photoelectron spectroscopy (XPS), among others, the light of knowledge starts to appear. Recently, we have reported that well-ordered transition metal oxide films (V, Nb and Mo) on a metallic substrate can be prepared by applying oxygen

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implanted Cu_3Au(1 0 0) substrate (CAOS, Cu_3Au–Oxygen Substrate) [5].

Here in this work we prepare different well-ordered Mo oxide films by applying CAOS method and investigate the morphology and structure of these films.

2. Experimental

The experiments were performed in two UHV chambers denoted as "STM" and "XPS" (base pressure below 3×10^{-10} mbar). Both chambers were equipped with an AES/LEED (Specs), and standard facilities for surface cleaning. "STM" chamber was equipped also with quartz crystal microbalance. The LEED patterns of the samples were used to judge the quality of the films for combining the results, obtained in different chambers.

The Cu_3Au(1 0 0) single crystal (7 mm width, 10 mm length and 2 mm thickness) was used as substrate. During the preparation, the temperature was controlled using a K-type thermocouple attached directly to the sample support. The sample heating was achieved by electron bombardment. A SPECS sample heating controller (SH100) allowed to change the acceleration voltage from 0 to 1000 V (dc) with a maximum emission current of 100 mA.

The surface was cleaned by cycles of Ar sputtering (1.0 keV Ar^+) followed by annealing 800 K for 5 min until no detectable impurities were found by AES.

The clean Cu_3Au(1 0 0) surface was sputtered at 300 K with oxygen, using the ion sputter gun (1 keV, 2×10^{-5} mbar of O_2, 30 min). Subsequently, the sample was annealed in vacuum at 650 K for 5 min to smooth the surface after sputtering. AES spectra from this surface showed O (510 eV)/Cu (918 eV) ratio of about 0.2. Molybdenum was vapor deposited onto the substrate kept at 300 K from a Mo wire using a commercial evaporator (OMICRON). Molybdenum was deposited in a single step in the amounts of 1.5 ML coverage. After Mo deposition, the samples were oxidized in 10^{-7} mbar O_2 at 800 K for 30 min by backfilling the chamber and after that, the surface was annealed in vacuum at 800 K.

Surface composition was analyzed using a SPECS electron spectrometer equipped with a hemispherical analyzer PHOIBOS and AES, UPS, ISS. All the results presented here corresponded to the use of the Al Kα X-ray radiation. A pass energy (E_{pass}) of 50 eV was used to obtain the wide scan spectra, while 15 or 25 eV, depending on the signal intensity, were used for high-resolution (HR) spectra of Mo 3d. The FWHM in the HR spectra was about 1.0–1.5 eV (E_{pass}: 15–25 eV). Each spectra was calibrated by using the Au $4f_{7/2}$ signal with a FWHM of (1.08 ± 0.01) eV and peak position of (84.66 ± 0.04) eV. Usually an Au 4f HR XPS spectrum was obtained together with the Mo ones. We used 83.9 eV as calibration value for Au $4f_{7/2}$ [8]. The Mo 3d envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian–Lorenzian peak shapes obtained from the CasaXPS software package.

The STM images were obtained at room temperature with Pt–Ir tips at tunnelling biases of −1.3 V and current of 1 nA.

3. Results and discussion

3.1. LEED

Cu_3Au crystals have an L12-structure with a lattice constant 3.75 Å and a shortest metal–metal distance of 2.65 Å. The surface structure of Cu_3Au(1 0 0) is well documented in the literature [9,10]. Normal to the (1 0 0) surface, the Cu_3Au crystal consists of alternating pure Cu (1 0 0) and 1:1 [Au:Cu] layers in which two diagonal Cu atoms in the unit cell are substituted by gold. The LEED pattern of the clean Cu_3Au(1 0 0) surface [11] thus exhibits diffraction spots similar to Cu (1 0 0) with the additional spots of a c (2×2) structure due to the presence of gold. The spots of this LEED pattern correspond to the distances of 3.75 Å and 2.65 Å along the {0 0 1} and {1 1 0} directions of the Cu_3Au(1 0 0) surface. Utilizing these known distances and their corresponding directions allows us to calculate distances within the Molybdenum oxide film and its orientation with respect to the Cu_3Au(1 0 0) surface. Oxygen sputtering and annealing at 650 K produced no discernable changes in the LEED pattern as expected [6], thus leading to the same c (2×2) LEED pattern as the clean, non-treated surface.

Deposition of Mo onto the O-implanted substrate and subsequent oxidation at 800 K results in LEED patterns as shown in Fig. 1. Taking the Mo oxide LEED pattern in the same conditions as obtained with the substrate, we can find the contribution of substrate spots on the oxide film surface. Fig. 1 shows LEED pattern obtained for a MoO_x surface prepared after 12 min of Mo deposition and the photo was taken at the same conditions (zoom and lens exposition time) as the substrate was taken. A similar LEED pattern was obtained at "STM" chamber where the evaporation rate was calibrated to achieve a metal coverage around 1.5 ML. The features in the LEED pattern presented in Fig. 1 are composed by five 12-spot

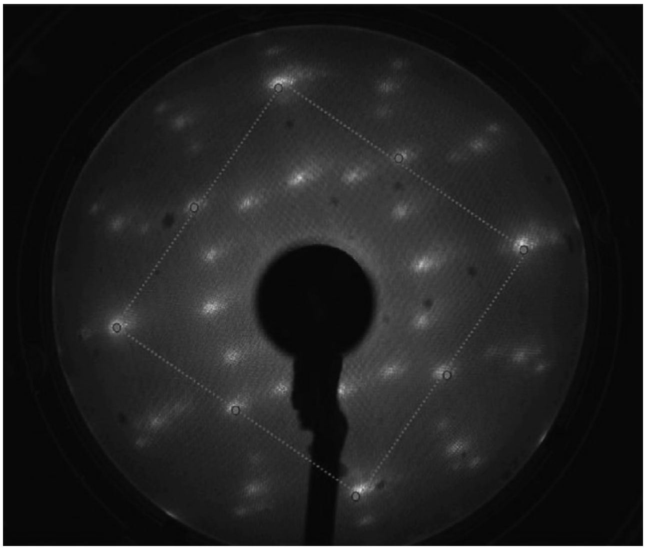

Fig. 1. The LEED pattern ($E = 70$ eV) of Mo oxide film formed on Cu_3Au(1 0 0)–O by oxidation of a 1.5 ML Mo layer at 800 K in 10^{-7} mbar of O_2. The surface unit cells of the substrate (square) are shown.

rings clearly indicating the formation of different oxides layer with hexagonal symmetry. The presence of 12-spot rings can be readily attributed to two domains arising from two hexagonal mesh units rotated by 90° (or 30°) with respect to one another. The five rings are distinguished from one another as one ''inner'' (1) and ''outer'' rings denoted as 2, 3, 4 and 5, as marked in Fig. 2.

For each domain of rings 2 and 4, two of the six hexagonal spots of the ring (2) coincide with the (1 × 1) spots of the $Cu_3Au(1\,0\,0)$ substrate, indicating a good epitaxial relationship between the oxide film and the substrate. The hexagonal rings can be assigned to the O (or Mo) sub-lattice, which in real space can be expressed in matrix notation by

$$\begin{pmatrix} A' \\ B' \end{pmatrix} = \begin{pmatrix} 1 & \dfrac{-1}{\sqrt{3}} \\ 0 & \dfrac{2}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}$$

on the $Cu_3Au(1\,0\,0)$ surface. The vectors (A, B) indicate the unit vectors of the $Cu_3Au(1\,0\,0)$ substrate while the primed vectors are the unit vectors of the oxide sub-lattice. Using the known metal–metal distance on the $Cu_3Au(1\,0\,0)$ surface, we have calculated that the spots in ring (3), (4) and (5) correspond to a distance of 3.49 Å, 3.06 Å, and 2.78 Å, respectively, which is quite reasonable for O–O distance in oxide thin films. The inner ring (1) is in a $(\sqrt{3} \times \sqrt{3})$ R30° registry with respect to the ring (2), with a characteristic distance of ~6.12 Å. Ring (2) is formed by the second order spots of ring (1).

In addition, the LEED pattern exhibits many diffraction spots, running along the diagonal spots (c (2 × 2) structure) of the substrate. The intensity of these spots is weak. This structure has a p (4 × 4) square lattice. Fig. 3 shows the LEED pattern of the same surface at a higher electron energy (93 eV), where the square lattice can be better seen (solid dark blue circle). The dashed red circle shows the five spots, related to hexagonal lattices 2, 3, 4 and 5 (see Fig. 2).

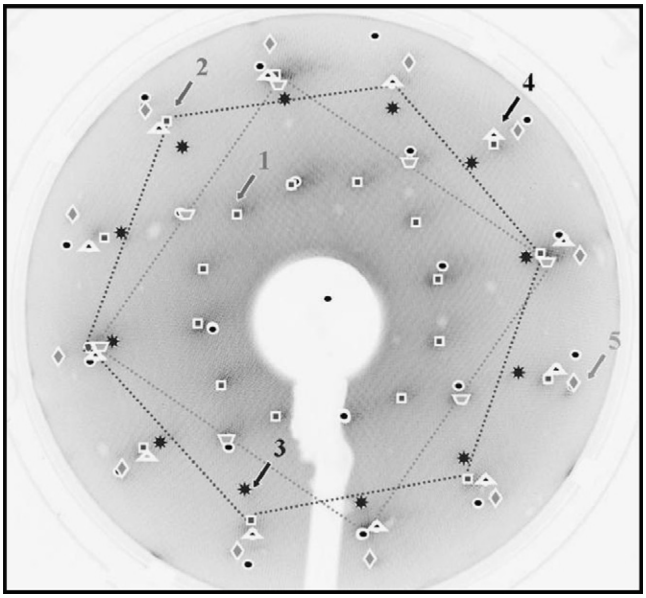

Fig. 2. The LEED pattern ($E = 70$ eV) of Mo oxide film formed on $Cu_3Au(1\,0\,0)$–O by oxidation of a 1.5 ML Mo layer at 800 K in 10^{-7} mbar of O_2. The 12 spots rings (1–5) are observed due to the presence of two hexagonal domains. The spots of one single domain are marked as the hexagonal symmetry (2). The unit cells of the substrate (square) are also shown. Legend: spots of the ring 1 and ring 2: filled square; ring 3: black star; ring 4: triangle; ring 5: rhombus; substrate spots: trapezoid.

In summary, the LEED results show that the film contains at least five hexagonal layers and one square layer, where two of the hexagonal layers form a coincidence structure with respect to underlying metal substrate, and another layer(s) resulting in a $(\sqrt{3} \times \sqrt{3})$ R30° structure with respect to one of the hexagonal layers.

3.2. XPS

Fig. 4 shows high-resolution spectra of Mo 3d signal together with the fitting of the envelope just after the metal deposition. The result clearly indicates that even before the oxidation exposure, some partial oxidation of metallic Mo occurs (amorphous precursor MoO_x layer). After the oxidation procedure (Fig. 5) more Mo oxide species are formed, as expected. Mo^{5+} is the predominant specie. The oxide surface obtained just after the oxidation (LEED pattern not shown) is not well ordered and in order to improve the film quality (to get more ordered and well-defined spots) an annealing in vacuum treatment was performed. The Mo high-resolution spectra is shown in Fig. 6. From the results it is clear that morphology changes occurred during the annealing procedure. In fact, it is well known that molybdenum oxides can easily be reduced. The easy of reduction no doubt occurs due to many reduced oxides of Mo that are stable in the bulk; for example, between MoO_3 and MoO_2 stable Magnéli phases of $Mo_{18}O_{52}$, $Mo_{17}O_{47}$,

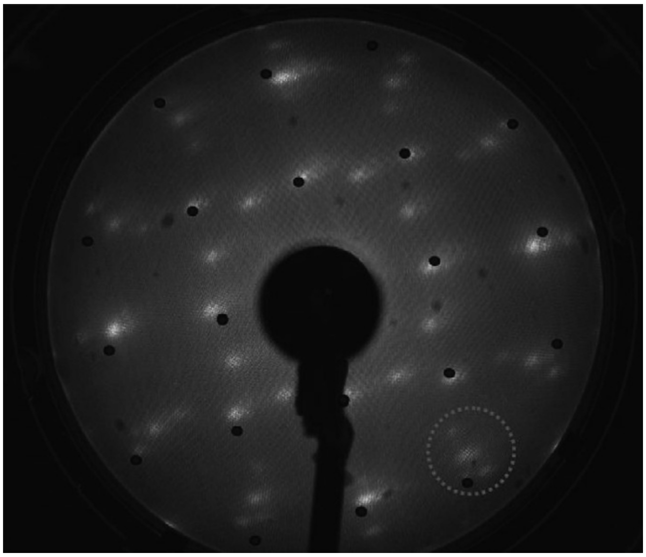

Fig. 3. The LEED pattern ($E = 93$ eV) of Mo oxide film formed on $Cu_3Au(1\,0\,0)$–O by oxidation of a 1.5 ML Mo layer at 800 K in 10^{-7} mbar of O_2. The square lattice can be better seen (solid dark blue circle). The dashed red circle shows the 5 spots, related to hexagonal lattices 2, 3, 4 and 5 (see Fig. 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

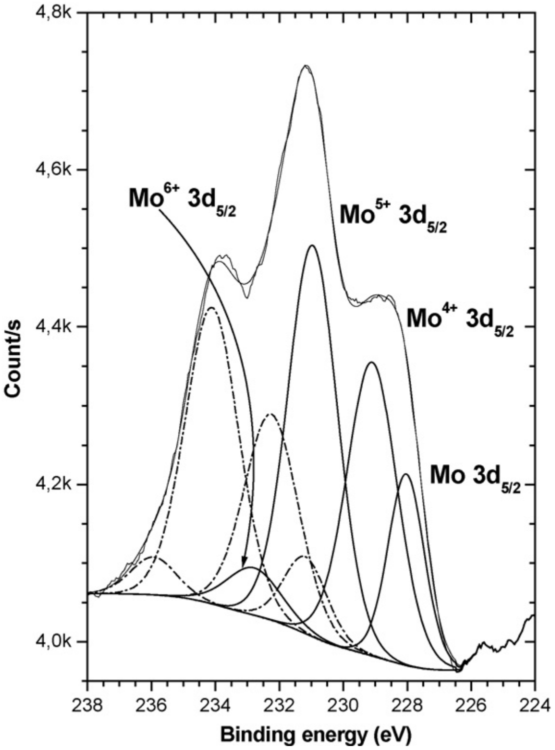

Fig. 4. High-resolution XPS spectra of the Mo 3d peak before oxidation (Mo "as deposited"). Dash-dot lines indicate $3d_{3/2}$ Mo species.

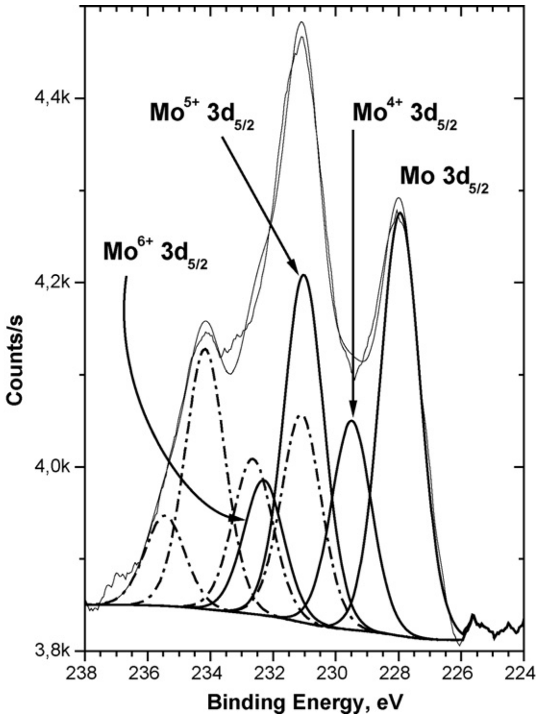

Fig. 6. High-resolution XPS spectra of the Mo 3d peak after oxidation at 800 K (1×10^{-7} mbar O_2) for 30 min, followed by annealing in vacuum at 800 K/for 30 min.

Mo_9O_{26}, Mo_8O_{23}, Mo_7O_{20}, Mo_6O_{17}, Mo_5O_{14} and Mo_4O_{11} all exist ([7] and references therein). However, despite of the reduction, the surface becomes stable after annealing above 800 K (Fig. 6). The elemental composition of Mo species calculated from the data shown in the high-resolution spectra of Figs. 4–6 is summarized in Table 1. The results obviously show that the oxidation processes decreased the metallic Mo concentration and that different molybdenum oxides are formed. The stoichiometry ranges from Mo^{4+} to Mo^{6+} and Mo^{5+} is still the main oxidation state.

Fig. 7(a) shows a large-scale STM image of the molybdenum oxide film, with similar LEED pattern presented in Fig. 2. The image shows the presence of two-dimensional islands. Fig. 7(b) displays the islands in atomic resolution presenting protrusions forming a hexagonal lattice over a full square lattice. The square lattice is underneath the hexagon islands, but it can be better seen for lower metal coverage, as shown in detail in Fig. 7(c). The hexagonal lattice has a 5.7 Å periodicity. Taking into account that the atom positions were determined by LEED only approximately, we can say that the periodicity encountered by STM (5.7 Å) is in close agreement with the distance of 6.1 Å assigned to ring (1) in the LEED pattern of Fig. 2.

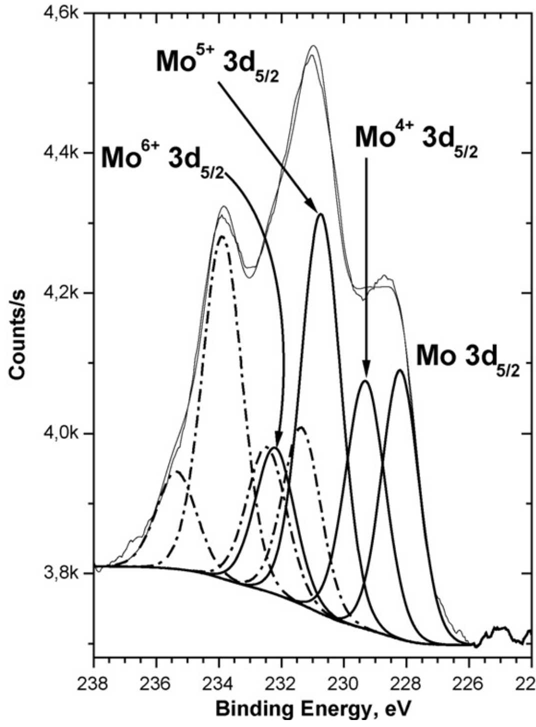

Fig. 5. High-resolution XPS spectra of the Mo 3d peak after oxidation at 800 K (1×10^{-7} mbar O_2).

Table 1
Elemental composition of Mo species calculated from the high-resolution spectra after (A) Mo deposition; (B) oxidation (1×10^{-7} mbar) at 800 K and (C) after oxidation, followed by annealing in vacuum at 800 K

Sample	Mo^0	Mo^{4+}	Mo^{5+}	Mo^{6+}
A	23.8	16.8	10.3	–
B	11.8	11.6	18.7	6.8
C	19.7	9.7	16.1	6.3

Only the contribution of Mo $3d_{5/2}$ species is informed.

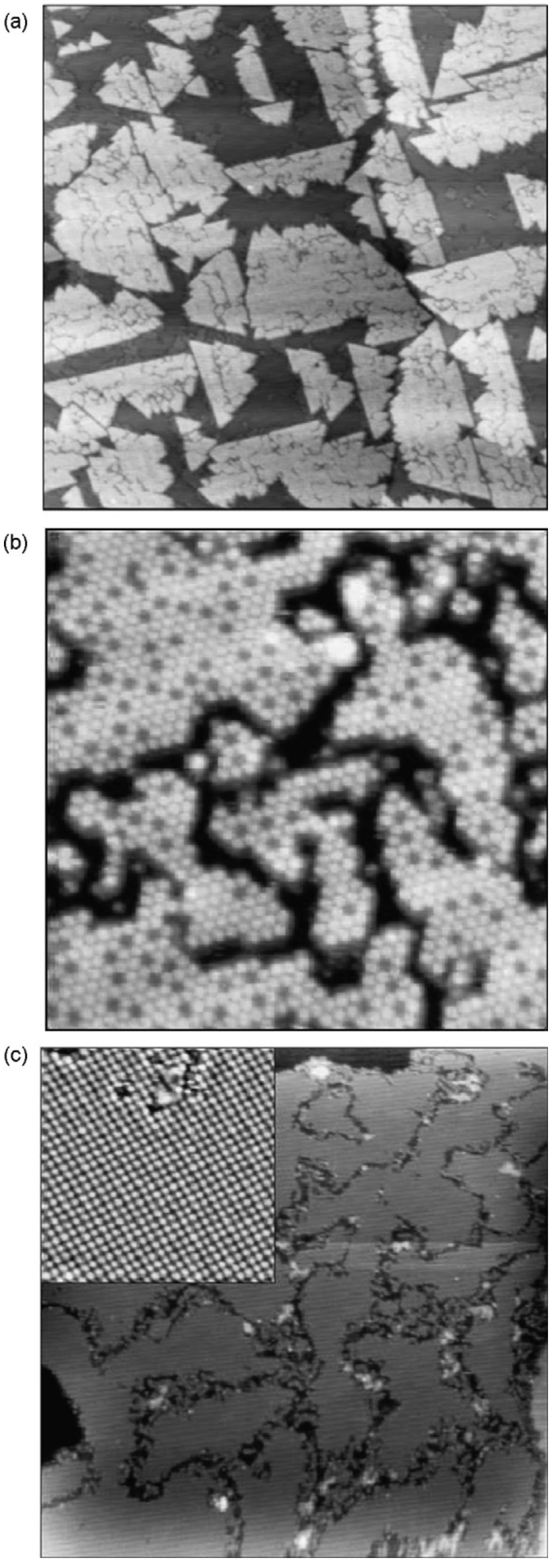

Fig. 7. STM images of the molybdenum oxide film grown on $Cu_3Au(1\,0\,0)$; image size and tunneling parameters are (a) 200 nm × 200 nm, (b) 25 nm × 25 nm; (c) 150 nm × 150 nm, $V_s = 1.3$ V, $I = 1.0$ nA.

4. Conclusions

A well-ordered molybdenum oxide film at about 1.5 ML was prepared using the CAOS oxide preparation technique (*i.e.* oxide growth on a $Cu_3Au(1\,0\,0)$–O substrate. The obtained surface is a film composed by different Mo oxides, whose stoichiometry ranges from 4+ to 6+, as revealed by XPS technique. STM and LEED results are in agreement showing the formation of hexagonal islands plus a square layer. The film quality after the oxidation step was improved by the annealing thermal treatment. Although the annealing treatment promotes the surface reduction, the surface is stable above 800 K and Mo^{5+} and Mo^{4+} oxide states predominate after oxidation and annealing treatment.

The results are quite promising showing that an ordered molybdenum oxide film can be prepared through the CAOS technique, but the oxide stoichiometry control is still a challenge and further studies are being developed in order to obtain a detailed structure determination.

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