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Lithium-molybdate nanostructures grown on the Mo(001) surface

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ABSTRACT

Ordered Li–Mo mixed-oxide films of different compositions have been grown on a Mo(001) surface and analysed by means of scanning tunnelling microscopy, low-energy-electron-diffraction and cathodoluminescence spectroscopy. Starting from a disordered Li_xO ad-layer grown at room temperature, a *scheelite*-type Li_2MoO_4 phase develops on the Mo surface after annealing to 700 K. The building blocks of this structure are regular nanorods of approximately 30 nm length, which exhibit strong light emission in the green spectral range upon electron injection. Further annealing induces a restructuring of the film that evolves into various mixed-oxide phases of decreasing Li content. The Li fully desorbs from the surface above 1000 K, leaving behind a nano-crystalline Mo-oxide. Our approach demonstrates that ternary Li–Mo oxides of high structural quality can be grown as thin films, making them accessible to conventional surface science techniques without charging problems.

1. Introduction

Ternary and multi-component oxide systems play an important role in heterogeneous catalysis, as they exhibit unique chemical and physical properties that cannot be found in binary oxides [1,2]. The versatility of mixed oxides arises from the interplay of the different cations that fulfil complementary tasks in the compound, such as improving the temperature stability, providing suitable adsorption and reaction sites on the surface and acting as charge donors or acceptors [3]. Moreover, the structure and composition of mixed oxides can be varied over wide ranges, opening efficient pathways to adopt the properties of such materials to the needs of a given application. Molybdates represent a particularly interesting class of materials, as they form the basis for highly reactive and selective catalysts especially for the oxidation of hydrocarbons [4,5]. They also find applications as electrode materials in lithium batteries [6], as light-emitting phosphors [7], and corrosion inhibitors [8]. Molybdates in different frameworks turned out to be thermo-dynamically stable and can therefore be used as catalysts in high temperature reactions without deactivation over years [9]. The main factor controlling the performance of molybdates and Mo-oxides in catalysis was shown to be the charge state of the surface species that should be as high as possible to stimulate oxidation processes [4,10]. The role of surface defects, on the other hand, has hardly been investigated in such materials so far [11,12].

One of the technologically most relevant molybdate is Li_2MoO_4 that has been exploited as catalyst for the methane oxidation and finds applications in lithium batteries [6,13]. Li-molybdates were prepared with a variety of methods, including wet-chemical, sol–gel as well as combustion techniques [14–16]. Transmission-electron microscopy, X-ray diffraction and luminescence spectroscopy are the classical tools to analyse the Li–Mo compounds, while surface science techniques are rarely applied due to the insulating nature of the material (4.2 eV band gap) [17,18]. In this work, we demonstrate that well ordered and morphologically defined Li-molybdates nanostructures can be produced by depositing Li onto Mo(001) followed by different annealing steps in oxygen. Due to their limited thickness, the films are insensitive against charging and can be probed with all common surface science techniques. The ternary Li–Mo oxide grows in the form of uniform nanorods, as seen in scanning-tunnelling-microscopy (STM) images. Information on structural and electronic properties was derived from low-energy-electron-diffraction (LEED) and cathodoluminescence spectroscopy. Owing to their nano-crystalline nature, we expect the Li–Mo–O films to display unique physical and chemical properties that cannot be found in the respective bulk materials.

2. Experiment

The measurements were performed in an ultrahigh vacuum chamber (2×10^{-10} mbar) equipped with a liquid-nitrogen (LN_2) cooled STM and standard tools for sample preparation and analysis. The STM setup was designed specifically to detect photons emitted from the tip-sample junction [19]. For this purpose, a Beetle-type head was placed inside a parabolic mirror with the tip being in the focal point. The mirror collects light from a large solid angle of the tunnel junction. A second mirror outside the vacuum focuses the light onto the entrance slit of a grating spectrograph (150 lines/mm) coupled to a LN_2- cooled charge-coupled-device. The optical setup allows us to detect very low photon fluxes in a wavelength range of 200–1200 nm. All STM images presented

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here were obtained at LN_2 temperature in the constant current mode using Ag tips. The bias voltage is given with respect to the sample.

The Mo(001) substrate was prepared by cycles of Ar^+ sputtering and annealing to 2000 K, as monitored with an infrared pyrometer. The first cycles were performed in O_2 ambience in order to remove carbon from the surface. The as-prepared sample displayed a sharp (1×1) square pattern in LEED and wide, atomically-flat terraces in STM. Li was deposited from a commercial SAES dispenser onto the Mo substrate at 350–400 K. The coverage was calibrated via deposition onto MgO thin films, where Li grows into monolayer islands the surface fraction of which is readily determined with STM [20].

3. Results

An STM topographic image of Mo(001) after 2 ML Li exposure is shown in Fig. 1a. The surface is covered with nm-sized protrusions that exhibit neither an internal structure nor a long-range order. Also the suppression of the (1×1) LEED pattern suggests a disordered Li distribution on the Mo surface. The Li adsorption on metals has been studied in detail before, and a complex $c(7\sqrt{2}\times\sqrt{2})R45°$ super-structure was found for the Mo(001) surface [21–23]. The absence of any ordered Li phase in our case might be explained with inappropriate dosing conditions or the presence of residual oxygen/water in our chamber. Depositing the same amount of Li in 5×10^{-7} mbar O_2 leads to a coarsening of the surface and the formation of ad-particles with 3–4 nm diameter and 0.6 nm apparent height (Fig. 1b). Given the high reactivity of Li, we expect those particles to be made of Li_xO. Also this phase is amorphous as no LEED pattern is detected. The morphology of the ad-layer changes completely upon annealing to 700 K in UHV, when a characteristic stripe pattern comprising parallel nanorods of ~2 nm width, ~1 nm height and up to 30 nm length develops on the surface (Fig. 1c,d) [24]. Already single rods seem to be thermodynamically stable, as isolated units with similar geometric parameters are found at much lower Li loads (Fig. 1c, inset). The stripes align with the two Mo⟨100⟩ directions and thus develop two orthogonal domains. We suggest that the observed surface reorganization is the result of Li–Mo intermixing at the elevated temperature.

The crystalline nature of the nanorods is deduced from a sharp, yet complex LEED pattern, as shown in Fig. 2. The LEED reflexes can be divided into two groups. Spots of the first group form a simple square pattern and move towards the centre of the LEED screen with increasing electron energy (dashed circles). They are readily identified as the Mo(001) spots and can be used as internal reference in the diffraction pattern. The second group shows an atypical behaviour, as the spots already appear at very low energies (below 35 eV) and propagate outward with increasing electron energy (Fig. 2, arrows). This behaviour is incompatible with electron diffraction at atomic planes parallel to the sample surface, as the increase of the scattering vector with energy in this case pushes the diffraction spots towards the centre of the LEED screen where they collapse into the (0,0) spot. The occurrence of outward propagating spots thus indicates the presence of facets that are tilted against the macroscopic sample surface [25]. The tilt direction is given by the crystallographic direction along which the spots move in reciprocal space, which are the Mo⟨100⟩ directions in our case. The tilt angle can only be approximated here because the (0,0) spots of the individual facets are already outside the screen. A

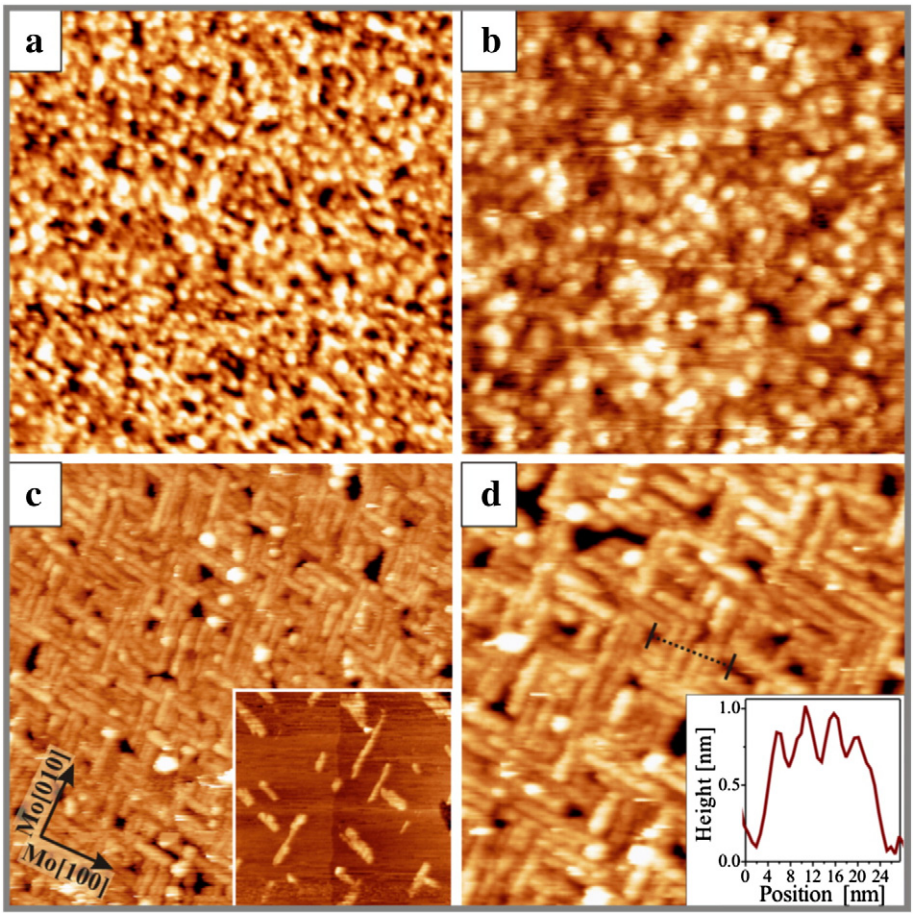

Fig. 1. STM topographic images of the Mo(001) surface after depositing (a) 2 ML metallic Li and (b) 2 ML Li in 5×10^{-7} mbar O_2 (3.5 V, 200×200 nm^2). (c,d) Same surface as in (b) but after annealing to 700 K in UHV (4.5 V, 200×200 nm^2 and 100×100 nm^2). The inset in (c) shows the nucleation regime of the Li-molybdate nanorods (1.5 V, 100×100 nm^2). The inset in (d) displays a height profile across the four nanorods marked in the main image.