LEED and STM studies of the stability of the MoO$_2$(100) surface

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ABSTRACT

Atomic scale images and low energy electron diffraction pattern of a MoO$_2$(100) single crystal surface are presented, which show different structural modifications depending on surface preparation. A short in-situ heat treatment of the as-grown single crystal results in an atomically ordered surface whose diffraction pattern and STM images are consistent with those expected from the bulk structure. The symmetry of the STM images suggests an oxygen termination of the surface. A significantly longer heat treatment causes a thermodynamically stable (4×1) reconstruction which is interpreted to be due to a loss of oxygen chains. The (4×1) reconstruction vanishes after Ar-ion-sputtering and subsequent annealing. Additional long sputtering cycles result in a (2×1) reconstruction. The observed surface reconstructions can be transformed into each other by heating or sputtering cycles.

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1. Introduction

Molybdenum oxides are industrially important as selective oxidation catalysts for various reactions. Recent studies on the catalytic properties of MoO$_2$ focus on hydrocarbon reforming processes, for example the partial oxidation of liquid hydrocarbons [1–3]. For these processes the oxygen mobility in the vicinity of the catalyst surface plays a central role, due to the necessity of a transfer of surface oxygen atoms to hydrocarbon molecules and replenishing of oxygen from the bulk, first described by Mars and van Krevelen [4].

Due to its importance for catalytic applications the surface structure of MoO$_2$, in particular the location of the oxygen atoms, is an important open question which needs to be addressed. Most surface investigations on molybdenum oxide focus on the adsorption of oxygen and the oxide formation on stable low-index Mo surfaces. Especially the understanding of oxygen induced reconstructions of the Mo surfaces has been subject of various publications [5–11]. The Mo p(1×3) and the Mo p(2×3) reconstructions on the Mo(112) surface seem to be of particular interest, which are assumed to be precursors to the epitaxial growth of MoO$_2$(100) or MoO$_2$(010) [9–11]. The best way to shed light on the development of the oxygen order is an investigation of the single crystal surface structure on an atomic scale and its time and temperature dependent changes. However, to our knowledge, such investigations on either epitaxial grown film or MoO$_2$ single crystal surfaces have not been reported.

In the present study we investigate the atomic order of a single crystal MoO$_2$(100) surface. In particular the stability of this surface to different surface treatments, namely different heating and sputtering cycles, is analyzed. For the first time, scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have been used to produce atomic scale images and diffraction pattern, respectively, of a single crystal MoO$_2$(100) surface.

Our investigation shows that the treatment of the MoO$_2$(100) surface has crucial influence on its atomic order: a bulk-like surface structure, a (2×1), and a (4×1) reconstruction can be induced. The symmetry of the atomic order of the bulk-like surface points to an oxygen termination. The surface is dominated by stripe like structures, which are interpreted as oxygen chains characteristic of the bulk-like MoO$_2$(100) surface. The (4×1) reconstruction, caused by long heat treatment, can be explained by a loss of oxygen chains. Even under further intense heat treatment this (4×1) surface termination is stable, suggesting either an equilibrium state with a balance between oxygen loss and oxygen replenishing from the bulk or a stable surface which shows no oxygen loss.

2. The system MoO$_2$

MoO$_2$ crystallizes in a simple monoclinic lattice with space group $P2_1/c$ (C_{2h}^5). At room temperature the lattice parameters are $a = 5.6109$ Å, $b = 4.8562$ Å, $c = 5.6285$ Å and $\beta = 120.95°$[12]. A detailed description of the monoclinic crystal structure can be found in Ref. [13]. A comprehensive study on the electronic structure of MoO$_2$ was presented in our previous work, where a very good agreement between experimental and theoretical results has been found [14].

A top view of the MoO$_2$(100) surface is presented in Fig. 1. Only the atomic layers to a depth of **a**/3 are shown. All molybdenum atoms lie in one plane and are ordered in a centered rectangular 2D lattice. There are two crystallographic inequivalent sites for the oxygen atoms. Oxygen sites of the same type lie in the same plane and form

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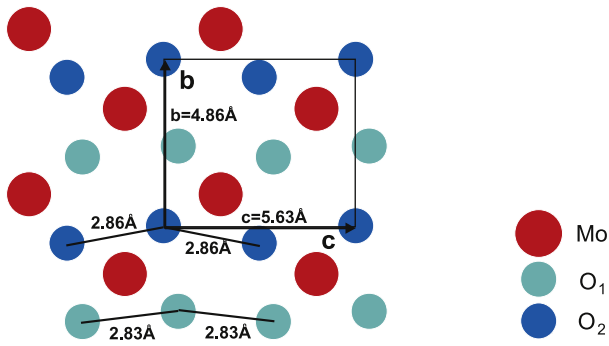*E-mail address:* judith.will@physik.uni-augsburg.de (J. Moosburger-Will).

Fig. 1. Top view of the MoO$_2$(100) surface.

zigzag chains along the **c**-direction. The surface elemental cell, marked in Fig. 1, is spanned by the vectors **b** and **c**. Fig. 2 shows a side view of the MoO$_2$ crystal along the **c**-direction. Pure molybdenum and oxygen layers alternate. A layer of molybdenum sites is followed by two layers of oxygen sites of the same type. The type of the oxygen sites changes after each molybdenum layer. The exact distances between the layers are given in Fig. 2.

Three inequivalent surface terminations are possible, i.e. the terminations (Mo/O/O) starting with a molybdenum layer, (O/O/Mo) or (O/Mo/O). The (O/O/Mo) and (Mo/O/O) terminations cause a polar surface, whereas the (O/Mo/O) termination is expected to have the smallest dipole moment. Polar surfaces tend to instabilities and distorted structures, resulting in changes of the electronic structure or the stoichiometry [15,16].

3. Experimental

MoO$_2$ single crystals were grown by chemical transport using TeCl$_4$ as transport agent [17]. Their crystals exhibit specular surfaces of a size up to 3×3 mm^2. The high quality and the surface orientation were determined by X-ray diffraction. Crystals were introduced into an Omicron ultra high vacuum (UHV) system with a base pressure <10^{-9} mbar. All the measurements presented were performed on the same single crystal surface. Different procedures of surface treatment were investigated. First, the as-grown surface was cleaned in situ by heating to 750 °C for 10 min (short heating: SH). Then the surface was exposed to an intense heat treatment up to 750 °C for 15 h (intense heating: IH). Finally the surface was Ar-sputtered in grazing incidence geometry followed by 10 min of annealing at 750 °C. The gentle sputter treatment was performed with an ion energy of 3 keV for 5 to 10 min (gentle sputtering: GS), the intense sputter treatment with an ion energy of 5 keV for more than 15 min (intense sputtering: IS).

STM measurements were performed using an Omicron variable temperature STM (VT SPM). All STM images were recorded in the constant current mode, using a W tip, a sample bias of 0.6 V or 1.0 V and a current between 0.1 nA and 0.2 nA. The topographic images show the height $z(x, y)$ of the tip over the sample after a plane and slope subtraction was performed. LEED patterns were recorded using an Omicron LEED system (SPECTALEED). All LEED patterns were taken
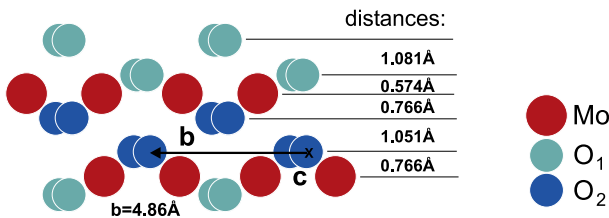

Fig. 2. Side view of the MoO$_2$(100) surface along the **c**-direction.

at an incident electron energy of 70 eV. All measurements were performed after in-situ surface treatment.

4. Results and discussion: scanning tunneling microscopy and low energy electron diffraction

4.1. Short heat treatment: bulk-like surface

The as-grown single crystal MoO$_2$(100) surface was cleaned of adsorbates by an in-situ heating at 750 °C for 10 min. Afterwards, the surface was characterized by LEED and STM measurements.

4.1.1. LEED

In Fig. 3 the LEED pattern of the shortly heated MoO$_2$(100) surface is shown. The clearly pronounced LEED spots are arranged in a rectangular structure, the corresponding reciprocal cell is marked in the figure.

Analysis of the LEED pattern results in the surface lattice parameters $b_{LEED} = 5.0$ Å ± 0.4 Å and $c_{LEED} = 5.9$ Å ± 0.4 Å. The symmetry and the lattice parameters determined from the LEED pattern correspond within the margins of error to the surface lattice structure of the MoO$_2$(100) surface expected from the bulk structure ($b = 4.86$ Å and $c = 5.63$ Å).

4.1.2. STM

Fig. 4 shows a STM image of the MoO$_2$(100) single crystal surface over a region of 75 Å×75 Å after short heating time. The maximal height variation is 1.93 Å. The image is characteristic for this type of surface treatment and similar images have been observed several times on different regions of the surface. Bright spots are arranged in an oblique surface lattice structure with spot distances 4.8 Å ± 0.4 Å and 3.2 Å ± 0.4 Å and angles of 81° ± 4° and 99° ± 4°. The surface is rich of defects.

The orientation of the oblique lattice vectors coincide within the margins of error very well with the lattice vectors determined by LEED. The deviation between the **b**-vector determined by STM and the **b**-vector determined by LEED amounts to 6°. The error in the value of the angle amounts to 10°. The lattice constant in **b**-direction as determined by STM of 4.8 Å ± 0.4 Å is in good agreement with the MoO$_2$ lattice constant of $b = 4.86$ Å (Mo–Mo or O–O-distance). The spot periodicity in **c**-direction is 3.2 Å ± 0.4 Å, which, within the margins of error, is in agreement with the MoO$_2$(100)oxygen to oxygen distance in **c**-direction of 2.86 Å. The minor deviation of the measured to the expected oxygen to oxygen distances and the slight
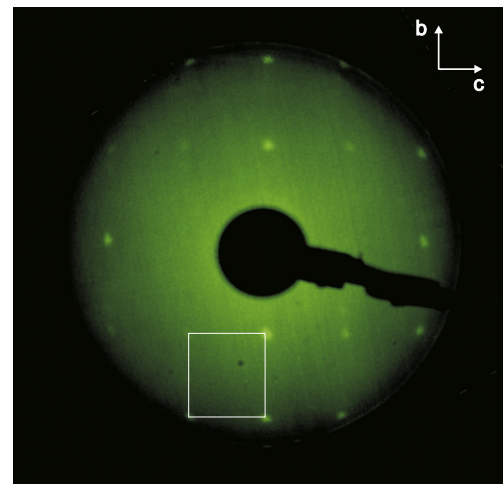

Fig. 3. LEED pattern of MoO$_2$(100) surface after short heat treatment. Incident electron energy: 70 eV.