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Atomic structure of $Cu_2O(1\,1\,1)$

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ABSTRACT

Low-energy electron diffraction and scanning tunneling microscopy have been used to probe the surface atomic structure of $Cu_2O(1\,1\,1)$ after various sample preparations. Annealing in oxygen gives a stoichiometric (1×1) oxygen terminated surface and further annealing in ultra-high vacuum results in a clear $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction and surface faceting. Tunneling from filled states in the reconstructed surface reveals a hexagonal pattern of large protrusions, which show an internal structure. The reconstruction is believed to be due to one-third of a monolayer of ordered oxygen vacancies. At areas on the surface where the large features are missing, another smaller type of protrusions is visible, which is associated with the ideal (1×1) surface. The relative position of the two types of features gives two possible models of the $(1\,1\,1)$ surface. In the first model, the (1×1) surface is the ideal bulk terminated surface and coordinatively unsaturated oxygen ions are missing in the reconstructed surface. The second model agrees with the first model with the exception that coordinatively unsaturated copper ions in the outmost copper layer are missing in both the (1×1) and the reconstructed surface. The latter model is supported by previous surface free energy calculations. Since the undercoordinated copper ions have been suggested to be the catalytic active sites of $Cu_2O(1\,1\,1)$, the presence or absence of these cations could be of great importance for the fundamental understanding of the surface reactivity of Cu_2O and of copper-based catalysts.

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconductor with a 2.17 eV band gap measured with optical absorption [1,2]. Since the 1950s, it has aroused interest due to its rich excitonic spectrum and long-lived excitons [3–5]. Cu_2O is also one of the most abundant initial corrosion products of copper [6] and has been identified as a thermodynamically stable phase of copper-based catalysts at relevant catalytic conditions [7]. Furthermore, Cu^+ ions are known to be an active component in the ZnO/Cu catalyst [8], which is used in various chemical processes such as methanol synthesis [8] and the water gas shift reaction [9,10]. Potential future applications for this oxide are found in solar energy conversion [11] and photocatalytic splitting of water [12]. In addition, an increased knowledge on the electronic properties of cuprous oxide will help understanding the properties of closely related but more complex compounds, e.g., high temperature superconducting cuprate materials and transparent conducting oxides (TCOs) such as $CuAlO_2$ [13] and $SrCu_2O_2$ [14].

The crystal structure of Cu_2O, as well as of Ag_2O, Pb_2O, $Zn(CN)_2$ and $Cd(CN)_2$ [15] is called the cuprite structure and it can be described in at least two ways. First, the oxygen ions form a BCC lattice, where every oxygen ion is surrounded by a tetrahedron of copper ions. Secondly, the structure can be illustrated by two independent and intercalated cristobalitelike sublattices. Two distinguishing and unusual characteristics of this oxide are the linear O–Cu–O bond and the negative thermal expansion [16].

The majority of the studies made so far on single crystalline Cu_2O surfaces are theoretical and involve adsorbates such as H_2O [17,18], H_2S [18], NO [19–21], CO [19,22–24], N_2O [25] and benzatriazole [26]. For the clean surfaces, density functional theory (DFT) calculations have been performed to investigate the surface relaxation of $Cu_2O(1\,0\,0)$ [21]. Furthermore, theoretical studies have been made on the electronic properties [7,24], atomic structure [7], free energy [7] and relaxation of $Cu_2O(1\,1\,1)$ [20,26]. The experimental studies found are all made in the early nineties by Schulz and Cox [27–31]. They have studied the geometric and electronic structure of $Cu_2O(1\,0\,0)$ and $Cu_2O(1\,1\,1)$ by means of photoemission and low-energy electron diffraction (LEED) [27]. In the mentioned work, a weak $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern was obtained from the $(1\,1\,1)$ surface upon ion bombardment and annealing to 280 °C. Annealing at higher temperatures (680–730 °C) gave a LEED pattern with (1×1) periodicity. In a thermal desorption spectroscopy (TDS) and photoemission study [28], a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern was acquired from the $(1\,1\,1)$ surface after repeated exposures to propene followed by a slow increase of the sample temperature up to 180°. Small amounts of CO were observed as a trace reaction

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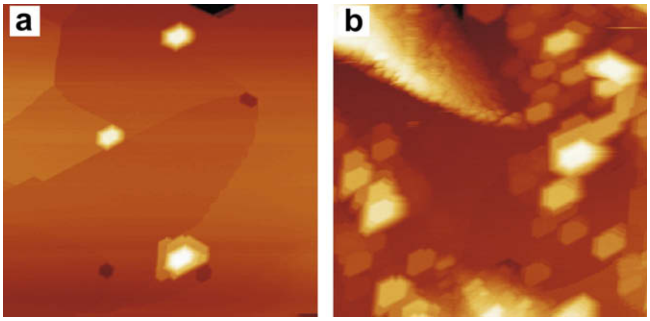

Fig. 1. (a) 1 μm × 1 μm STM image (+2.6 V, 0.4 nA) of a sample subjected to five sputter and anneal cycles. (b) 1 × 1 μm STM image (+2.5 V, 0.4 nA) of a sample subjected to 12 sputter and anneal cycles.

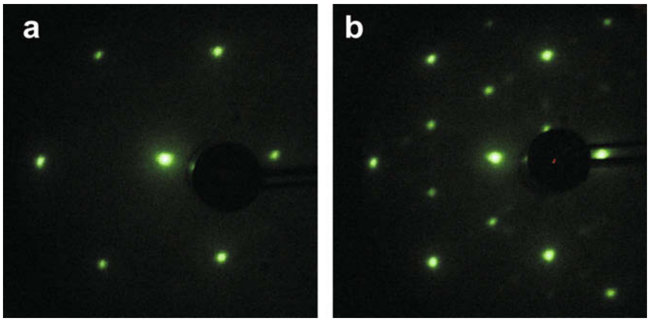

Fig. 2. LEED patterns recorded at 26 eV. (a) (1 × 1) pattern obtained after annealing in O_2. (b) $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern obtained after an additional anneal in UHV.

product, which indicated that a slow surface reduction developed upon propene exposure followed by heating. The authors suggested that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern arises from removal of a third of the surface oxygen ions.

To the best of our knowledge, there are no scanning tunneling microscopy (STM) studies on single crystalline Cu_2O surfaces reported in the literature. It has nevertheless been found that a Cu_2O(1 1 1)-like structure forms on Cu(1 1 1) upon oxygen adsorption and several STM studies [32–35] have been made on this subject. These images reveal a hexagonal pattern of holes [32,33,35] or protrusions [34] with a periodicity of around 6 Å. The authors suggested that the protrusions could represent single copper atoms [34]. When considering the stoichiometric ideal (1 1 1) surface, the only identical copper atoms, which are separated with as much as 6 Å are the coordinatively unsaturated copper ions in the outermost copper layer (Cu_{CUS}). However, these copper atoms where not included in the atomic models of the overlayer oxide on Cu(1 1 1) [34]. In addition, in a quite recent study [7], DFT calculations showed that a (1×1) Cu_2O(1 1 1) surface, where the Cu_{CUS} ions are missing has a lower surface free energy than the ideal bulk terminated surface. This was shown to hold in a large range of oxygen chemical potentials, including ultra-high vacuum (UHV) conditions.

In the present study, the surface atomic structure of Cu_2O(1 1 1) is studied with LEED and STM. The influence of the sample preparation on the surface atomic structure is investigated. Argon ion bombardment and annealing in O_2 gives a (1 × 1) LEED pattern. Further annealing in vacuum results in a sharp $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern and well-resolved STM images, which indicate that one-third of the outmost oxygen ions are missing. The images reveal a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodic surface with various defects and small (1 × 1) regions. Two possible models of the surface are presented where one model involves missing Cu_{CUS} ions in the outermost surface copper layer, in accordance with the DFT study mentioned [7].

2. Experimental details

The experiments were performed in a UHV system, which consists of an STM chamber that houses an Omicron VT–STM and a preparation chamber that is equipped with LEED apparatus, a sputter gun and annealing equipment. The sample was mounted on a tantalum plate, which was heated through electron bombardment. The annealing temperature was measured with a pyrometer, which was focused on the sample plate, since the sample appears to be nearly transparent to infrared radiation. The STM measurements were performed in constant current mode and at room temperature. A mechanically cut Pt–Ir tip was used as an STM probe. The base pressure in both chambers was below 1×10^{-10} mbar.

The Cu_2O(1 1 1) crystal was purchased from Surface Preparation Laboratory and is a natural crystal containing <1% Ca detected with X-ray photoelectron spectroscopy (XPS) in an earlier study [36]. The sample was first cleaned through 19 cycles of Ar^+ ion bombardment (700–900 V, 0.55–0.85 μA) for 20–90 min followed by annealing at 600–730 °C for 10–30 min. After this treatment, the sample was exposed to various sample cleaning procedures including an anneal at 550 °C for 13.5 h and cycles of sputtering (0.8–1 kV, 0.65–0.85 μA) for 15–30 min and annealing at 550–700 °C for 5 min–3 h, sometimes involving a low pressure oxygen environment ($1–2 \times 10^{-6}$ mbar). Except for the initial 5–15 sputter and anneal cycles, the only treatment that gave satisfactory STM images was cycles of sputtering (900–1000 V, 0.8–0.85 μA), annealing in O_2 (2×10^{-6} mbar) at 650–700 °C for 30 min and a subsequent anneal in UHV at 550 °C for 0.5–2 h.

3. Results

3.1. Impact of sample preparation on surface structure

The influence of the sample preparation procedure on the Cu_2O(1 1 1) surface atomic structure has been investigated with LEED and STM. Ion bombardment results in a weak (1 × 1) LEED pattern. Several cycles of ion bombardment and annealing in UHV at 600–730 °C for 10–30 min give rise to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern with weak additional spots moving in the symmetry directions when altering the electron energy and STM images showing a $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity. This sample preparation gives a surface that appears flat with large terraces and a few hexagonally shaped islands and pits as shown in Fig. 1a. The observed step heights are 2.5, 5.0 and 7.5 Å, i.e., multiples of 2.5 Å. The pit depth varies between 20 and 60 Å and the hexagonal islands are as high as 100–140 Å. As the number of ion bombardment and annealing cycles grow, the number of islands increases substantially, as shown in Fig. 1b and cloudlike features as the one in the upper left corner of the same figure become more abundant. After more than 15 cleaning cycles, STM reveals a rough surface with small terraces.

The highly corrugated surface can be partly recovered by adding an oxygen anneal to the cleaning cycle and by performing the anneal in UHV at lower temperature (550 °C) and for a longer time period (0.5–2 h). Even though the sample surface is flattened by this treatment, the terraces are still smaller and the unordered regions of the surface are larger when comparing to the sample surface at an early point of the preparation procedure when the sample has been subjected to only a few sputter-anneal cycles. Ion bombardment and annealing in O_2 (2×10^{-6} mbar) at 650–