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High resolution electrochemical STM: New structural results for underpotentially deposited Cu on Au(1 1 1) in acid sulfate solution

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Abstract

Adsorption of sulfate assists Cu monolayer underpotential deposition (upd) on Au(1 1 1) in a unique way, rendering two distinct structural stages: (i) formation of a low-density Cu phase at coverage of 2/3 ML known as the $(\sqrt{3}\times\sqrt{3})R30^\circ$ or honeycomb phase; (ii) formation of a complete monolayer, i.e., Cu-(1 × 1) phase pseudomorphic with respect to underlying Au(1 1 1) substrate. In this paper we present new structural in situ scanning tunneling microscopy (STM) results for this system. We show and discuss the STM imaging of the copper honeycomb superstructure probed underneath the co-adsorbed $(\sqrt{3}\times\sqrt{3})R30^\circ$ sulfate adlayer in the low-density phase. High resolution imaging during the phase transition from the low to high density copper phase unambiguously shows the existence of an ordered sulfate structure p(2 × 2) on the pseudomorphic Cu-(1 × 1) layer. The new structure is seen during the co-existence of two copper phases as well as upon completion of the Cu-(1 × 1) monolayer. While supported by earlier chronocoulometric measurements in the same system, the new structural results raise questions that need to be addressed in a future work.

Keywords: In situ scanning tunneling microscopy; Underpotential deposition; Copper, Au(1 1 1); Sulfate; Anion adsorption

1. Introduction

The fascination with the Cu underpotential deposition (upd) system on Au(1 1 1) in sulfate is far from over. During the last two decades this has undoubtedly been the most studied system and is considered as an archetype for metal upd. It has been characterized by almost all analytical techniques used in modern electrochemical surface science [1]. The summary of both ex situ and in situ analytical and structural studies on Cu/Au(1 1 1) can be found in a recent review by Herrero et al. [1]. Almost all newly developed or adapted in situ structure-sensitive techniques in electrochemistry were introduced by or employed in studies of this system [2–9]. The wealth of results related to the behavior and structural characteristics renders the Cu upd layer on Au(1 1 1) in sulfate solution an excellent candidate for theoretical modeling. The unique phase transition aspects of this system warranted its choice as a prototype for which the first statistical mechanics lattice-gas model for upd systems was developed by Blum and Hickaby [10–12]. This theoretical work was extended later using Monte Carlo (MC) simulations, Rikvold et al. [13,14]. Dynamic MC simulations [15] were also employed to reproduce the experimentally obtained current transients shedding more light on the kinetic aspects of surface phase transitions taking place in that system [16].

Among the variety of upd systems, Cu on Au(1 1 1) in sulfate solution is unique with well-defined structural stages of monolayer formation governed by the co-adsorption of sulfate ions. These stages are clearly represented by cyclic voltammetry features (Fig. 1a) and interpreted by numerous experimental and theoretical studies: (i) the copper deposition starts by formation of a random lattice gas

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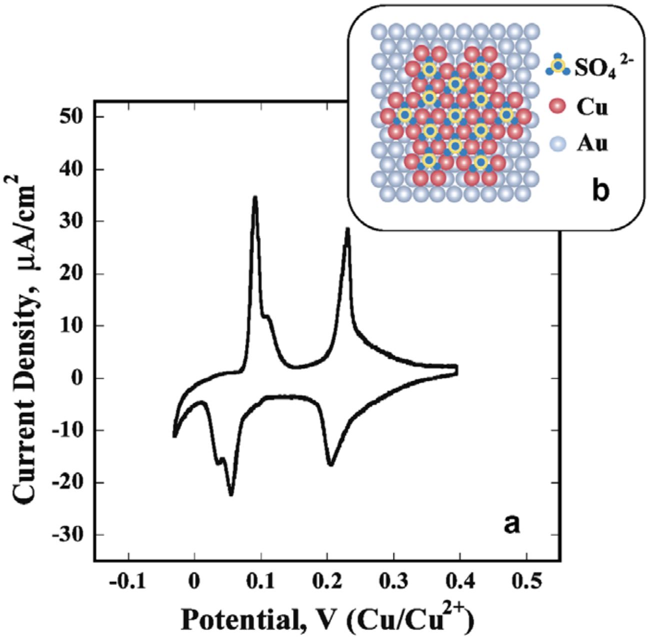

Fig. 1. (a) Cyclic voltammetry of Cu upd on Au(1 1 1) in 1×10^{-3} M $Cu(ClO_4)_2 + 1 \times 10^{-3}$ M $HClO_4 + 3 \times 10^{-2}$ M Na_2SO_4 with 5 mV/s. Inset (b) structural model of upd Cu low-density phase proposed by in situ X-ray reflectance spectroscopy [17].

structure of copper and co-adsorbed sulfate represented by a broad feature in the voltammetry; (ii) the first peak marks a first order transition to an ordered phase at 2/3 ML Cu coverage. This phase is a honeycomb copper superstructure stabilized by sulfate organized on top [17] in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ arrangement as shown schematically in Fig. 1b. This honeycomb structure exists over the entire potential range between the two voltammetric peaks; (iii) the final stage of deposition, marked by the second deposition peak, corresponds to the formation of a full density monolayer that is pseudomorphic with respect to underlying Au(1 1 1) substrate, i.e., a phase transition to Cu-(1×1) phase. The splitting of the second voltammetric peak shown in Fig. 1a represents the energetically separated nucleation of a Cu-(1×1) layer on a morphologically uniform Au(1 1 1) surface, consisting of well-defined surface steps and terraces, respectively, [18]. However, owing to the complexity of transitions behind this unique voltammetric picture, the distinct structural examination at characteristic potentials has never been straightforward. As a result, a fair share of controversy still accompanies discussions on that matter [2,5,17,19]. For instance, whereas the low-density honeycomb structure has been exhaustively described and characterized, until recently [5] there were no reports of direct STM imaging of the Cu atoms anticipated by the X-ray work of Toney et al. [17]. Also, it is not yet clear if the pseudomorphic Cu monolayer on Au(1 1 1) is covered by an ordered layer of sulfate ions as in the case of a bulk Cu(1 1 1) surface [20] or only a physically adsorbed and disordered sulfate adlayer. The co-adsorption of sulfate during this second stage of deposition has been considered by theoretical calculations [10–14], suggested by electrochemical measurements [13,21,22] and structural experiments [1,23–25]. Prior to this report, there have not been any scanning probe observations of the atomic structure of the sulfate layer on the completed (1×1) upd Cu ML [9,26,27].

In this paper we report on new structural results obtained by in situ STM in the upd system Cu/Au(1 1 1). Direct imaging and probing of Cu structure underneath the sulfate adlayer reveals unique and yet unexplored capabilities of the in situ STM technique, that could be developed in the future as a tool for not only atomic structure characterization but for the chemical characterization on an atomic scale [28]. Focusing our interest mainly on the phase transition between the two deposition stages, $(\sqrt{3} \times \sqrt{3})R30^\circ \rightarrow$ Cu-(1×1), our high resolution in situ STM work clearly demonstrates the existence of an ordered sulfate structure registered during the formation and after the completion of the pseudomorphic Cu-(1×1) layer.

2. Experimental methods

Our electrochemical and STM experiments were performed using Au(1 1 1) single crystals (Monocrystals Co.) of 10 mm diameter and 2 mm thickness as working electrodes. The preparation of Au(1 1 1) crystals included mechanical and electrochemical polishing followed by flame annealing. The mechanical polishing to 0.05 μm was done using water-based, de-agglomerated alumina suspensions (Buehler). The surface was electrochemically polished at 60 °C by anodization in a two-electrode cell with a platinum cathode. The polishing solution was 3:2:1 ethylene glycol, hydrochloric acid and glacial acetic acid. The crystal was anodized for 10–15 s at a dc current density of 2.5 A cm^{-2} several times until a bright and shiny surface was observed. After thorough rinsing with Barnsted Nanopure water (>18 MΩ cm), the Au(1 1 1) crystal was annealed to "red hot" in a hydrogen flame for 10 min and cooled rapidly in ultrahigh purity N_2 with less than 1 ppb oxygen, CO, CO_2, and moisture content. The surface terminated by a water droplet to prevent contamination, was mounted either on a holder for work in a "hanging meniscus" configuration [29] or into the STM cell.

In situ STM experiments were carried out with a molecular imaging (MI) Pico Scan 300S scanner, MI Pico Scan 2100 controller, and MI Pico Scan software in solution where the potential control was provided by MI 300S Pico bi-potentiostat. The custom made Teflon-liquid cell of 1 cm^3 volume used in this work exposes 0.3 cm^2 surface area of the sample to the solution. The STM tips were made by etching a 0.25 mm $Pt_{0.80}Ir_{0.20}$ wire in a 1:2 mixture of saturated $CaCl_2$ and water at 18–20 V (ac). As-prepared tips were thoroughly rinsed with Barnstead Nanopure (>18 MΩ cm) water and coated with Apiezon wax in order to minimize the background Faradaic current to values lower than 20 pA. In a part of our study we used W tips,