Nanotribology at single crystal electrodes: Influence of ionic adsorbates on friction forces studied with AFM

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A B S T R A C T

We present friction force measurements on Au(1 1 1) single crystal electrode surfaces performed under electrochemical conditions using an atomic force microscope (AFM). At monoatomic steps friction is increased in both scan directions. In 0.05 M sulfuric acid an increase of friction is observed with the increase of adsorbed sulfate. Friction force increases non-linearly with load. Cu UPD also increases friction in presence of sulfate. However, in presence of 4×10^{-4} M chloride friction is much smaller for all deposited Cu coverages – ranging from a submonolayer up to bulk copper compared to the solution without chloride. After dissolution of bulk copper clusters deposited on Au(1 1 1) we observed an area with higher friction forces due to the formation of an alloy between gold and copper.

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1. Introduction

The atomic force microscope (AFM) [1] has proven to be a useful tool for measuring interactions between surfaces: tip–surface interactions [2–5], elasticity of biological materials [6,7], magnetic interaction [8] and metallic adhesion between a metal tip and a metal surface [9,10]. The AFM is also capable of measuring friction forces and is then usually described as a friction force microscope (FFM) [11–15]. Thus, also friction on thin organic films has been measured [16,17]. The analysis of friction forces play a key role, e.g. in controlling wear in mechanical apparatuses. Despite recent experimental and theoretical progress in tribology, the understanding of the fundamentals of friction and the underlying tribological processes is still limited [15,18–20].

Binggeli et al. [21] measured frictional forces between a FFM tip and a highly orientated pyrolytic graphite (HOPG) surface in an electrolytic solution as a function of potential. They found an electrochemical dependence of the frictional force at step edges. Weilandt et al. [22] investigated friction effects at steps (HOPG) in electrolytic environment (100 mM NaClO$_4$) with and without potential control. They observed a reversible change of friction forces at steps after applying a potential to the sample. Whether this behavior is due to chemical reactions at the graphite or because of adsorbates at steps could not be decided. Schnyder et al. [23] stud-

ied the electrochemical intercalation of perchlorate ions in HOPG. Because of a specific adsorption of perchlorate ions at the steps the intercalation causes a friction change at the steps. No change of friction could be observed at the basal plane.

Following our interest in nanoscopic imaging of electrochemical adsorbates and modification of single crystal electrode surfaces by tip surface interactions [24–27], we also started to investigate the influence of foreign metals on single crystal electrodes under electrochemical conditions on friction forces. In our recent communication [28] we reported for the first time on the effect of an foreign metal deposited on a single crystal electrode on friction. As compared to similar experiments in the gas phase or in ultra high vacuum (UHV), the presence of an adsorbate on an electrode surface can be easily triggered by the applied electrode potential and changes of coverage can be easily achieved by varying the electrode potential. We had found that friction increases when the Cu coverage is increased from 0 to 2/3 and further to full coverage. Astonishingly, the observed friction force was not proportional to the load, as expected from classical friction laws, instead, the friction coefficient increased above certain values of the load.

The objective of the present work is to explore the influence of sulfate anion adlayers at the Au(1 1 1) metal-electrolyte interface on friction forces. We also investigated how trace amounts of chloride – which induce the transformation of the $(\sqrt{3} \times \sqrt{3})R30°$ Cu UPD adlayer to a (5×5) structure – result in a change of friction forces.

Friction force measurements under electrochemical conditions offer some advantages in comparison to measurements performed

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under UHV conditions. By varying the potential of the working electrode, the electrode surface can quickly and reversibly be modified with adsorbed anions or a (sub)monolayer or multilayer of a foreign metal. Effects caused by possible changes of the tip structure can easily be recognized as artefacts, leading to a high reliability of the AFM measurements.

2. Experimental

The measurements were performed with a commercially available AFM scanner (Molecular Imaging) and a Nanoscope III E controller (Digital Instruments, Santa Barbara, CA) fitted with a liquid cell. The nominal spring constants of the commercial Si cantilevers used (Vecco MP31100) were 0.9 N/m. Cantilever motions were measured by the laser deflection method with a four quadrant photodiode detector to measure both the normal and the torsional forces. The torsional force exerted on the cantilever is a measure of the friction forces between the tip and the surface. The spring constant for this type of cantilever varies between 0.6 and 1.2 N/m (manufacturer specifications). External load is calculated as the product of the z-displacement of the cantilever and the nominal cantilever force constant ($k = 0.9$ N/m). Since the exact torsional force constant of the cantilever is unknown, the value of the friction force will be given in volts (output signal of the photodetector). Please note: in grayscale friction force images, brighter colors correspond to a higher friction force. In the section through the friction force data more positive values of the voltage correspond to a higher friction force. For one series of experiments PtIr covered tips from Applied NanoStructures (Pt Coated Conduction TappingModeTM Probes Model ANSCM-PT, force constant: 3 N/m) were used. Scanning was always in a direction perpendicular to the long axis of the

cantilever beam, in constant force mode as usual in friction force measurements. All measurements were done at room temperature.

During friction force measurements the lateral signal is recorded while the tip travels along a length of the surface in opposing directions from left to right (trace) and from right to left (retrace), respectively. Most friction force images were obtained by subtracting images acquired with opposing scan directions, thus eliminating topographic effects on friction data. The Au(1 1 1) single crystal (obtained from Metal Crystals & Oxides), was oriented within an accuracy of 0.5°. The preparation of the single crystal was performed by flame annealing. The cooling was performed in a H-cell over Milli-Q water (Millipore) in a 5 N argon atmosphere. Preparation quality and cleanliness were checked in a conventional H-cell with 0.05 M H_2SO_4 by cyclic voltammetry. The electrolyte, consisting of 0.05 M H_2SO_4 and 4×10^{-4} M $CuSO_4$, was prepared from sulfuric acid (Merck, p.a.), copper sulfate pentahydrate (Fluka, p.a.), and Milli-Q water. A gold wire was used as the counter electrode. As a reference electrode, a Cu wire was immersed in the same solution, separated from the AFM cell by a glass frit. All potentials are quoted with respect to the Cu/Cu^{2+} redox couple of the copper solution. For experiments in Cu free sulfuric acid, a Pt pseudo reference electrode was used; potentials were converted to the RHE scale assuming a potential of the Pt wire of 950 mV.

3. Results and discussion

The topography of the gold electrode in sulfuric acid is shown in Fig. 1A. Monoatomic steps are well resolved (cf. the section analysis in Fig. 1B), step bunching is also evident. This part of the surface was chosen here because of the peninsula - shaped terraces. Fig. 1C and D show the friction force in the same area. In both cases, friction
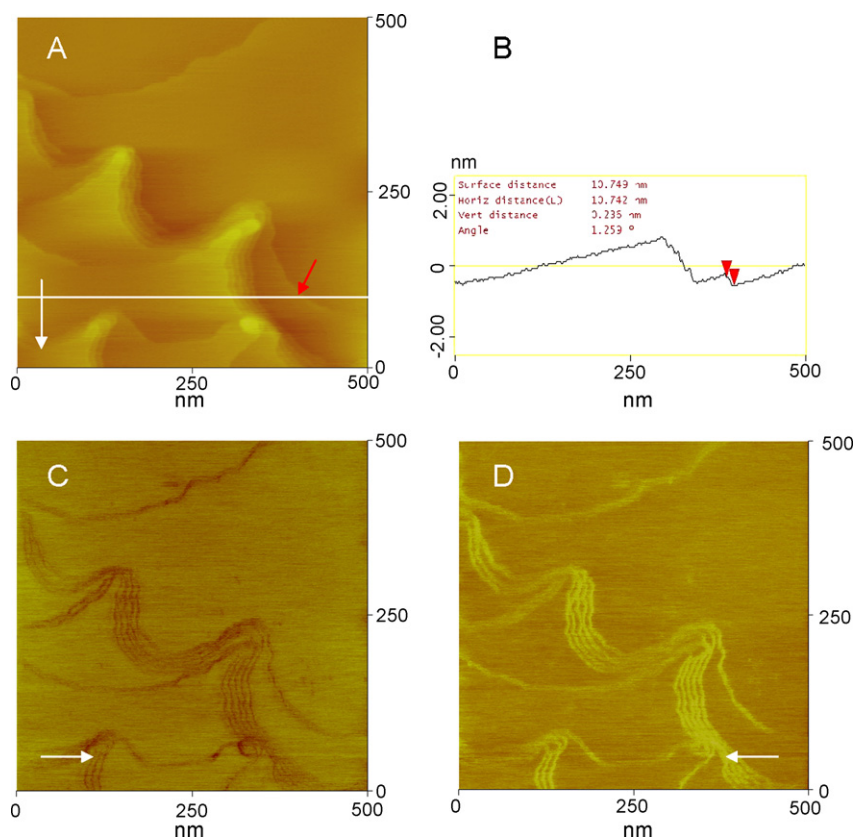
Fig. 1. Au(1 1 1) at 0.30 V. (A) Topography, (B) section through the topography image, (C) friction image (trace, left to right), (D) (retrace, right to left). (Normal force: ~10 nN, scan rate: 2.2 μm s^{-1}, electrolyte: 0.05 M H_2SO_4, E = 0.30 V Cantilever: NP-20, kN = 0.58 N m^{-1}. Different from other images, no difference between the trace and retrace image was calculated here.)