RZ 3005 (# 93051) 03/30/98
Chemistry / Physical Sciences 5 pages

Research Report

Electrochemical Atomic Force Microscopy on Single-Crystal Bead Facets

Peter Müller

(October 1994 - March 1996, Visiting Scientist)
ITAYA Electrochemiscopy Project ERATO/JST
Interface Structure Group
2-1-1 Yagiyama-Minami
Taihaku-ku
Sendai 982
Japan

(Permanent Address)
IBM Research Division
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

K. Itaya

Department of Engineering Science
Faculty of Engineering
Tohoku University
Aoba-ku
980 Sendai
Japan

Electrochemical Atomic Force Microscopy on Single-Crystal Bead Facets

Peter Müller

(October 1994 - March 1996, Visiting Scientist)
ITAYA Electrochemiscopy Project ERATO/JST, Interface Structure Group, 2-1-1 Yagiyama-Minami, Taihaku-ku, Sendai 982, Japan

(Permanent Address)
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

K. Itaya

Department of Engineering Science, Faculty of Engineering, Tohoku University, Aoba-ku, 980 Sendai, Japan

Abstract

A new method to work with an electrochemical atomic force microscope on atomically flat, single-crystal bead facets has been developed. Nondestructive atomic resolution of an iodine (I) adlayer on a Au(111) facet is presented. These experiments were carried out in ultrapure water and under potential control in a solution containing perchloric acid.

INTRODUCTION

Probing electrochemically controlled metal surfaces with an electrochemical atomic force microscope (ECAFM) is rarely reported in the literature [1]. The apparatus of the ECAFM is very similar to that of an electrochemical scanning tunneling microscope (ECSTM), but the physical parameters captured are different. The ECSTM acquires the electronic surface properties as a function of tip–sample distance, whereas the ECAFM acquires the sum of all forces between tip and sample versus distance. This sum of all forces is a critical parameter for an ECAFM. Typically this force is in the range of 10^{-11} to 10^{-6} N. For comparison, the interacting forces between two covalently-bonded atoms in an angstrom distance regime is about 10^{-9} N. The main forces between tip and sample surface in an ECAFM experiment carried out in an electrolytic solution are as follows.

Van der Waals forces (VdW) arise from instantaneous polarization of atoms or molecules (bodies) that interact with other bodies. In an ECAFM experiment the VdW forces can be either attractive or repulsive. They are highly influenced by the double layer and/or the diffuse region of potential drop. Therefore the VdW forces are relevant only in the range of several nanometers from the surface. In an ultrahigh vacuum (UHV) environment, the VdW forces for identical tip and sample materials are always attractive. But in an electrochemically controlled environment this rule is no longer valid due to the characteristics of the double layer and/or the diffuse region of potential drop.

Electrostatic forces originate from charged surfaces. In an electrolyte they are compensated by the double layer and/or a diffuse region of potential drop. In an electrochemical cell this force changes proportionately with the applied work electrode potential.

Capillary forces are relevant in an ambient air environment, where both tip and sample are covered with a thin layer of water. During the approach, these layers touch each other first, build a meniscus, and pull the tip strongly to the sample. When the tip and sample are immersed in an electrolyte, capillary forces no longer exist. But there are two double layers and/or regions of diffuse potential drop that also have interactions. These interactions can be attractive, very similar to capillary forces. But repulsive or alternating attractive and repulsive forces versus tip–sample distance are now possible. Which interaction type dominates depends on the material of the tip and sample, on the solution and its pH, and on the applied potentials. The capability to adjust all of these parameters is the strength of ECAFM.

Ionic repulsion forces are very short-range forces compared to the forces described above. They decay within tenths of an angstrom and originate from the Pauli exclusion principle. In the so-called "contact" mode, the ionic repulsion forces compensate for the sum of all attractive long-range forces that are still active.

Other forces, such as **magnetic forces**, **friction forces**, and **elastic** and **plastic deformation** shall not be mentioned here because they have to be minimized. They will be described below, or are without meaning in the current experiment.

EXPERIMENT

A commercial contact-mode ECAFM [2] was used in these experiments. The electrochemical cell was modified to reduce system drift and to achieve the capability to work on facets of single-crystal beads (SCB) [3]. Figure 1 is a sketch of the electrochemical cell used. (F) is an X-Y-Z translater piezo tube. On its top is a small permanent magnet to fix the sample holder plate (G). (H) is the sample fixing plate, which carries the SCB sample (I). (E) is a chemically inert O-ring [4] for sealing. It is simply pressed over the SCB. A real view of sample, holder

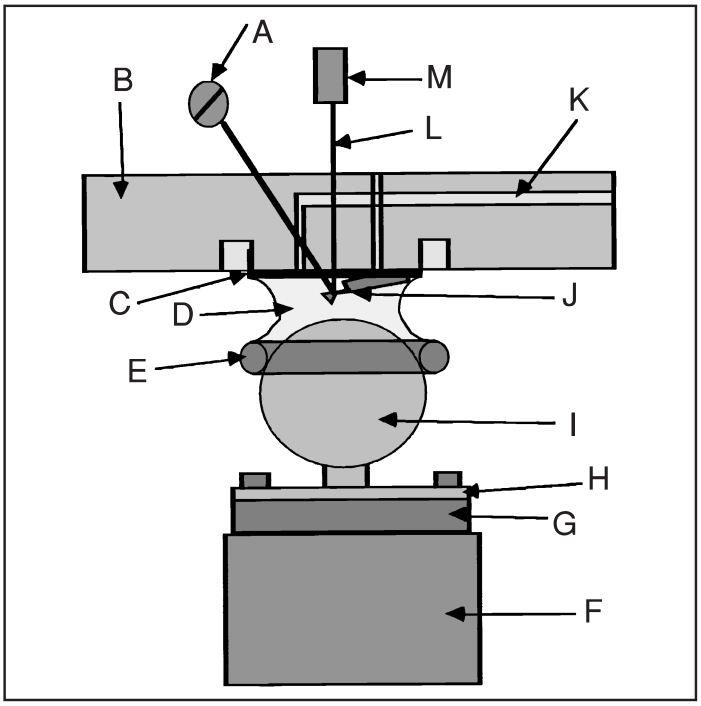

FIG. 1. Sketch of the experimental setup for electrochemical atomic force microscopy on a single-crystal bead.

plate, and O-ring is shown in figure 2. (B) is an optical gas plate [5], which carries the platinum counter electrode (C). A drop of electrolyte (D) is held by its own surface tension between the counter electrode (C) and the O-ring (E). (J) is the cantilever, adjusted over a atomically flat facet of the SCB. The inlet for electrolyte, H_2O-saturated Ar gas, and the reference electrode is marked by K. The optical deflection detection system is built of a red laser diode (M) and a dual photodiode (A). The laser beam (L) is reflected at the backside of the cantilever and directed to the detector, which measures the deviation caused by bending the cantilever. Not shown in figure 1 is an additional cover made from aluminum to protect the system from noise generated by the surrounding daylight and other sources. The entire system can be held under a slightly H_2O-saturated Ar gas overpressure. This prevents the small amount of electrolyte from drying out. The potential of tip and sample are independently adjustable.

The solutions were prepared from ultrapure water [6]. The electrolyte contained 100 mmol/kg of $HClO_4$ [7] and 0.1 mmol/kg of KI [8]. As reference electrode a Ag/AgI wire was used. The cantilevers [9] were rinsed prior to the experiment with the same solution used in the experiment itself.

After annealing the Au SCB in a pure hydrogen–oxygen flame, the sample was quenched in hydrogen-supersaturated ultrapure water and quickly immersed for 3 min in a solution containing 1 mmol/kg of KI. This procedure leads always to a monoatomic I adlayer on the Au(111) facets. The O-ring was assembled in solution. Afterwards the sample was removed from the solution with a protective drop of water or electrolyte over the facet and transferred to the ECAFM.

FIG. 2. Example of a single-crystal bead gold sample prepared for electrochemical atomic force microscopy. The bead diameter is about 3 mm. An atomically flat Au(111) facet is located horizontally at the top of the crystal. The white O-ring is simply pressed over the crystal. Under experimental conditions the meniscus of a solution drop always covers the top of the crystal to protect the working facet from ambient environment.

RESULTS

Figure 3 shows an 800×800 nm^2 area of an I-passivated Au(111) facet scanned in constant-height mode with an applied force of about 120 pN in ultrapure water. Only one atomic step can be observed. The dark hole near the image center was caused by the tip during the automatic approach procedure. In pure water such artificial defects are stable, whereas in a

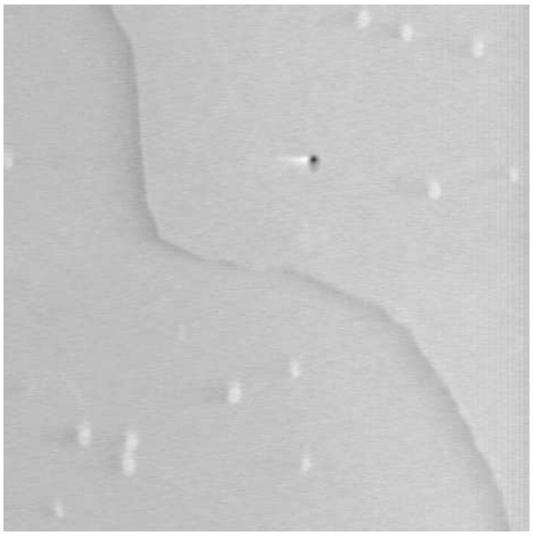

FIG. 3. An 800×800 nm^2 view of an I adlayer on a Au(111) facet in ultrapure water. Only one atomic step is observable.

solution containing perchloric acid they always disappear. The bright spots are not very well understood, but a possible explanation is the crystallization of I during sample preparation.

Figure 4 shows a force curve acquired from the sample described above. Even for the very low spring constant of the cantilever used [9], there is no jump to contact obtainable (approach). The low force and soft sliding into contact shown are signs of an ideal system. The retraction curve shows a slight trend toward a pulling away of the tip. This may be due to plastic deformation of the I adlayer and the first Au layers by the applied maximum force of about 1.2 nN. The effects are attributed to plastic deformations, because a hole could never be obtained, even by scanning the surface immediately after capturing the force curve. If a force curve is acquired near or on a step site, then the curve becomes very distorted and a damage at the step can usually be observed afterwards.

An atomically resolved I adlayer on an Au(111) facet captured in high mode is presented in Fig. 5. The applied force was 120 pN and the sample potential was 1.35 V versus reversible

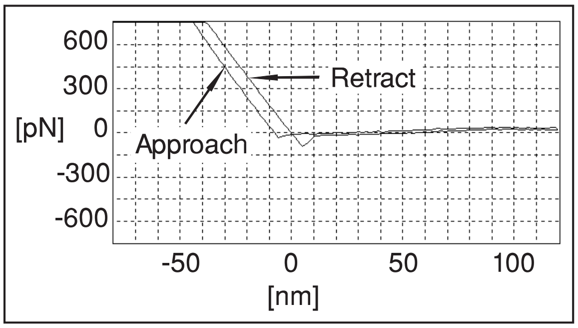

FIG. 4. Typical force curve of a silicon nitride cantilever on an I-passivated Au(111) facet. This curve was acquired with the sample presented in Fig. 3.

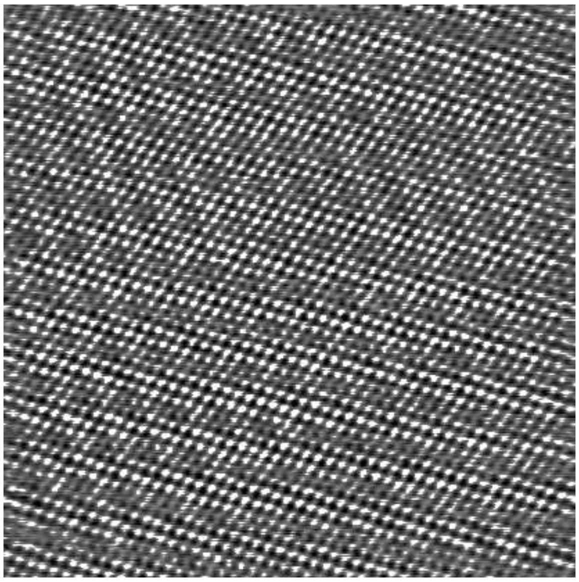

FIG. 5. ECAFM view of an I-passivated Au(111) facet in KI containing $HClO_4$ under potential control. The image size is 25×25 nm^2. The bright spots are I atoms. The long-range modulation originates from the different orientations and lattice constants of the I adlayer and its underlying Au(111) substrate.

hydrogen evolution (RHE). A Fourier analysis shows a corrugation of 0.1 nm for I atoms and a corrugation of 0.01 nm for the so-called rot-hex structure. Furthermore, the atomic nearest-neighbor distance in the I adlayer is 0.45 nm and the distance between the rot-hex sites is 1.95 nm. The I adlayer has a deviation of 2.5° to a perfect $\sqrt{3} \times \sqrt{3}$, R-30° orientation. This is the reason for the rot-hex interference structure and is in agreement with prior studies of the I-passivated Au(111) surface [10–12]. A plastic deformation caused by the tribological influence of the cantilever onto the I adlayer can also be observed. It leads to a slight distortion of the rot-hex structure in horizontal direction, which was the scanning direction.

The results presented show the enormous capabilities of the ECAFM to achieve very high resolution on samples that would deteriorate in a UHV environment.

ACKNOWLEDGMENTS

P. M. thanks all the members of the Itaya Electrochemiscopy Project involved and the IBM Zurich Research Laboratory, in particular Dr. H. Schindler for his help in writing this document.

The support given by ERATO/JST, Japan, and SATW, Switzerland, is gratefully acknowledged.

---

[1] C. Chen *et al.*, J. Am. Chem. Soc. 114, 451 (1992).

[2] The contact-mode ECAFM used was a Nanoscope III of Digital Instruments, Santa Barbara, CA, USA.

[3] P. Müller and K. Itaya, IBM Research Report, Single Crystals with Clean, Atomically Flat, Low-Index Facets, RZ 3008 (March 30, 1998).

[4] O-ring made from fluorocarbons, Chemraz.

[5] Optical glass, BK-7.

[6] Millipore Milli-Q, ($R > 18$ MΩcm).

[7] $HClO_4$, perchloric acid, Cica Merck, ultrapure grade.

[8] KI, potassium iodide, Kanto Chemicals, ACS grade.

[9] Cantilevers from Olympus, Japan, made of silicon nitride with a sharpened pyramidal tip, a length of 200 μm and a spring constant of 0.022 N/m. The backside is coated with gold to reflect the detection beam.

[10] B.M. Ocko *et al.*, J. Phys. Chem. 98, 897 (1994).

[11] N. Batina *et al.*, Langmuir 11, 4568 (1995).

[12] T. Yamada *et al.*, J. Phys. Chem. 99, 8817 (1995).