RZ 3008 (# 93054) 03/30/98
Engineering & Technology 6 pages

Research Report

Single Crystals with Clean, Atomically Flat, Low-Index 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

IBM Research Division
Almaden · Austin · Beijing · Haifa · T.J. Watson · Tokyo · Zurich

Single Crystals with Clean, Atomically Flat, Low-Index 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 method to prepare small single crystals with clean, atomically flat, low-index facets from thin rods or wires of conductive matter under ultrahigh vacuum conditions will be reported. A detailed description of the apparatus and its handling is given. In situ atomic resolution of iodine-passivated Au(111) and Ni(111) facets, using scanning probe microscopes, is presented.

INTRODUCTION

Scanning probe microscopy (SPM), which includes electrochemical scanning tunnel microscopy (ECSTM) and electrochemical atomic force microscopy (ECAFM), has been a breakthrough for direct in situ atomic observation of adsorption/desorption processes. Moreover, certain slow dynamic processes are also observable. Environmental cleanliness and quality of substrates are crucial for SPM measurements. Especially in the case of AFM, atomically flat terraces of 100×100 nm^2 and more are highly desirable because of the tip apex size and its long-range interactions with the surface. Usually the low-index facets on a single-crystal bead (SCB), made of noble-metal wires, show large, atomically flat terraces [1]. Preparing SCBs in air using a hydrogen–oxygen flame is a well-known technique [2,3]. In this report we describe an advanced method that also allows the preparation of SCBs from conductive matter other than noble metals.

EXPERIMENT

Sample setup

SCBs are melted from small rods or wires of ultrapure material in an ultrahigh vacuum (UHV) apparatus (Fig. 1). The chamber (9) is attached to an UHV system, which has been described elsewhere [4]. The raw material (1) is fixed onto a sample holder plate (2). The diameter of the raw material is between 0.3 and 1 mm. Usually it is easier to obtain single crystals from small-diameter wires or rods. But the maximum size of the crystal is also limited by the diameter of the raw material. Diameters of more than 1 mm often lead to polycrystalism. The sample holder plate is attached to a magnetic linear translator (3) for

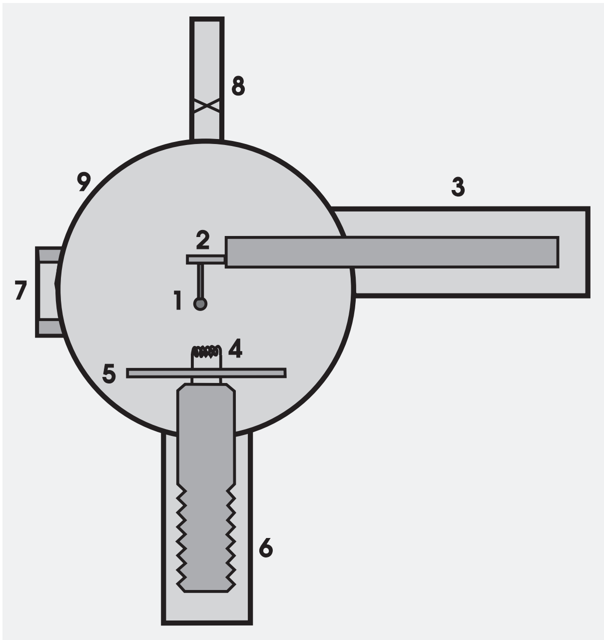

FIG. 1. Sketch of the UHV single-crystal bead melting apparatus. (1) Sample, (2) sample holder plate, (3) magnetic linear translator, (4) filament, (5) ion collector, (6) vertical translator, (7) view-port, (8) leak value, and (9) chamber.

transferring the sample into the electrochemical preparation chamber or into the analysis chamber.

Sample pretreatment

The pretreatment of the raw material always follows the same procedure.

Step one is the sample transfer into the UHV. After the vacuum chamber is pumped down, the sample is moved over the electron gun and carefully heated (to about 800 K) to degas the newly introduced sample and its holder plate. When the vacuum reaches approximately 10^{-9} torr, the degasing procedure is finished, and the electron gun switched off.

Step two is a chemical treatment in an etchant. For this purpose the sample is transferred to the electrochemical preparation chamber [4]. After the chamber is flooded with ultrapure argon, the sample is immersed into the solution. The solution itself is degased by argon bubbling. Theoretically, this process could take place under potential control, but this has not yet been tested. The etchant for gold is aqua regia [5], whereas for nickel, silver, and copper it is nitric acid [6]. After the sample is washed with degased ultrapure water [7], step one is repeated.

Step three is a heavy argon ion bombardment of the sample in order to remove the top atom layers. This takes about 10 min.

Step four is a flash annealing of the sample by the electron gun. If the vacuum deteriorates during this step (higher than 10^{-9} torr), steps three and four must be repeated.

In step five the sample is transferred to the analysis chamber and its surface cleanness is analyzed by Auger electron spectroscopy (AES). If this step shows any impurities on the sample surface, steps three to five must be repeated until the AES spectrum is correct.

In step six the sample is transferred back and positioned over the electron gun. The pretreatment is now finished.

Melting setup

Basically the sample (1) will be melted by electron bombardment from the filament (4), see Fig. 1. Some features of the electron gun will be explained. The electron gun consists of four elements: The filament (4), the ion collector (5), the vertical translator (6) and the power controller (not shown in Fig. 1). The sample and the entire chamber are on return potential (ground). The filament is powered by a low-voltage DC power supply, which delivers up to about 10 W on 10 V [8]. The DC high voltage between sample and filament can be adjusted to deliver up to 100 W at a voltage of between 300 and 1000 V [8]. The distance between sample and filament is also adjustable. Usually it is between 20 mm and only a few millimeters. Because of the expected outgasing of the sample, the outspreading atoms of the filament and the small sample–filament distance, an ion collector is installed behind the filament, as shown in Fig. 1. The DC potential of the ion collector is also adjustable between 300 and 1000 V. This potential is relative to the filament potential. As the potential of the filament is always between the sample and the ion collector, the electrons will hit the sample and the ions will be directed to the ion collector. The ion collector potential is usually adjusted together with the UHV gauge controller and is expected to change during the experiment.

Melting process

The first step is to adjust the sample–filament distance. For a material with a low melting point (1200 K and lower) it may be between 15 and 20 mm. For a material with a high melting point, the distance may be 10 mm or less.

Next, the ion collector has to be activated and its potential set to the minimum (300 V).

Then the filament has to be heated. About 5 to 6 W are an ideal starting point. Now the sample filament potential is increased until the end of the sample starts to melt. If the UHV gauge controller shows outgasing, then the ion collector potential has to be increased until the vacuum pressure stabilizes.

Now the melting zone can be moved up and down by the vertical translator. A small melted drop will form at the lower end of the raw material (see Fig. 2). When the filament is lowered, the ball will crystallize spontaneously. The existence of the low-index facets can be checked immediately through the viewport (7).

To melt clean SCBs from materials other than noble metals it is important to maintain a vacuum in the 10^{-9} torr range throughout the experiment. Otherwise it is possible to get a nice SCB but its surface will be dirty, meaning that its facets will not be atomically flat or there will be no facets to observe.

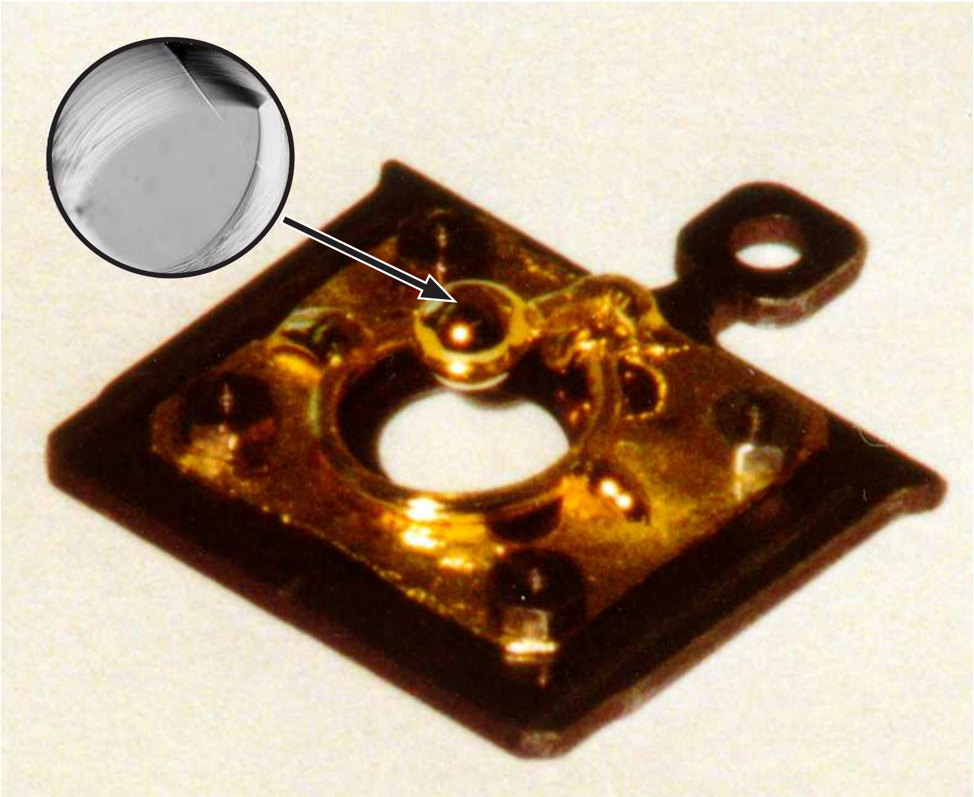

FIG. 2. Example of a gold single-crystal bead mounted on a sample holder plate for ultrahigh vacuum operation. The little ball is the single crystal. One facet with [111] orientation is perfectly adjusted parallel to the sample holder plate. The hole in the sample holder plate behind the crystal is used to heat or remelt the crystal from the backside by means of an electron gun.

Post treatment

In some cases an additional argon ion sputtering of the SCB may be needed. For example in the case of nickel, the natural sulfur impurities will aggregate at the surface during the melting phase. After sputtering, a flash annealing cycle by the electron gun may produce large, atomically flat areas on the facets.

An additional AES analysis of the surface turned out to be useful.

The last step is to passivate the SCB surface. This is especially important for a non-noble-metal SCB. For this purpose a gas-phase evaporation of iodine produced very reliable results [9,10]. The conditions are 5×10^{-6} torr iodine [11] pressure for 3 min at room temperature. A second method is to dip the SCB for about 3 min into a solution containing 1 mmol/kg of KI. After this treatment, it is useful to move the sample back to UHV for outgasing.

RESULTS

The method described was successfully applied to Au, Pt, Ag, and Ni. Gold was the test material in all cases because it is the best known system in which to melt SCBs. In the case of copper, clean, atomically flat, low-index facets have never been observed, to our knowledge. Figure 3 shows the facets of a perfectly grown Ag SCB. The top facet (1) is related to the [111]-oriented plane of the crystal structure. Each of the three facets in [100] orientation (2) and in [110] orientation (3) is clearly visible. Some higher-index facets (4) around the [110]-oriented facet are also observable. A microscopic view of an I-passivated Ni(111) facet is shown in Fig. 4. Several huge steps between the [111]-oriented terraces are visible. The wavy structures in the upper area of the image are a sign of the irregular growth of the crystal. This effect originates from the vertical translator of the crystal melting apparatus, which must be operated manually.

Figure 5 shows a nanoscopic ECAFM [12] view of an I-passivated Au(111) facet [13]. The electrolyte contained 100 mmol/kg of $HClO_4$ [14] and 0.1 mmol/kg of KI [15] dissolved in ultrapure water [7]. The counter electrode was a Pt foil and the reference electrode a Ag/AgI wire. The electrochemical potential was fixed at 1.35 V versus reversible hydrogen evolution (RHE) throughout the experiment. The ECAFM was operated in the constant-force mode and the force was set in the range of 10^{-10} N. The cantilever was bought from Olympus [16]. The scan size was limited to 800 nm because this is the limit of the piezo scanner used. The image shown is a typical example, similar to ones that can also be obtained for other metals such as Ni. In the case of I-passivated Au(111) facets, 1×1 μm^2 and larger atomic step-free areas are observable.

Figure 6 shows an I-passivated Ni(111) surface [17] in 50 mmol/kg of HF [18] at an electrochemical potential of 250 mV versus RHE. The image was acquired with an ECSTM in constant-height mode with a tip-bias potential of 18 mV and a resulting current ranging between 0 and 30 nA, represented as gray shades. There is a distortion due to the mechanical drift of the ECSTM. But the I adlayer shown is in a perfect $\sqrt{3}\times\sqrt{3}$, R-30° order relative to the underlying Ni(111) substrate.

As shown by these first experiments, the method works well. Successful application to other metals or materials such doped semiconductors or alloys should be possible and might reveal interesting results.

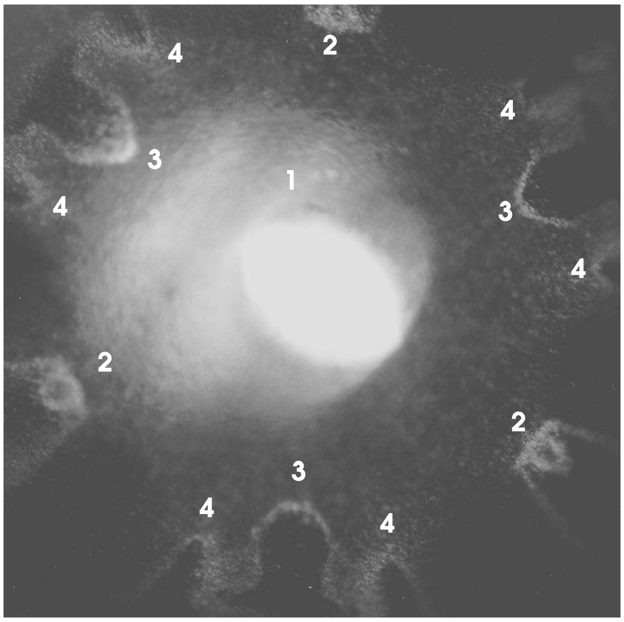

FIG. 3. Ag single-crystal bead. The diameter of the crystal is about 3 mm.

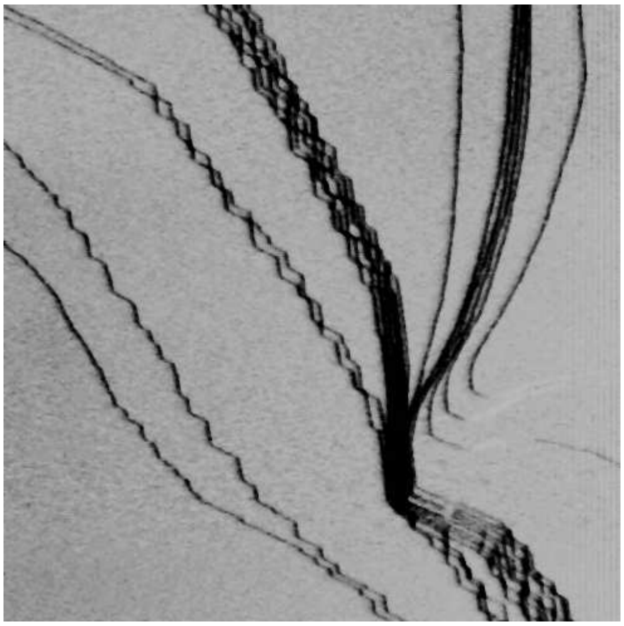

FIG. 5. ECAFM view of an I-passivated Au(111) facet. The dimensions are 800$\times$800 nm^2.

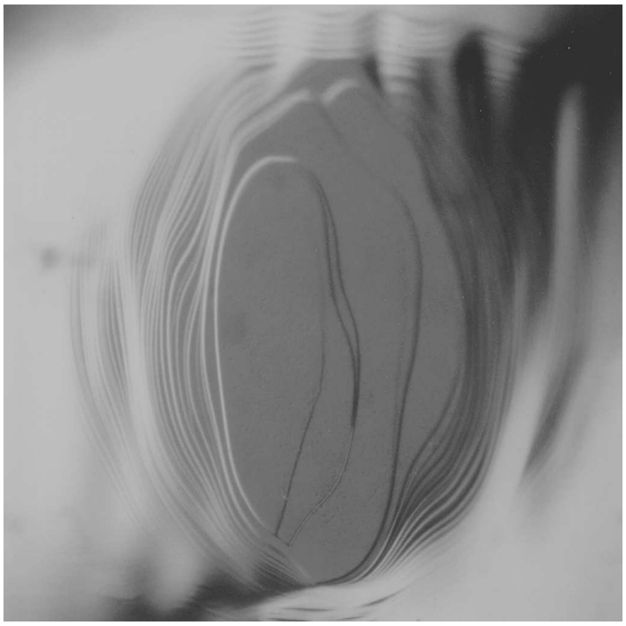

FIG. 4. Ni(111) facet of a single-crystal bead. The dimensions of the facet are about 0.3$\times$0.5 mm^2.

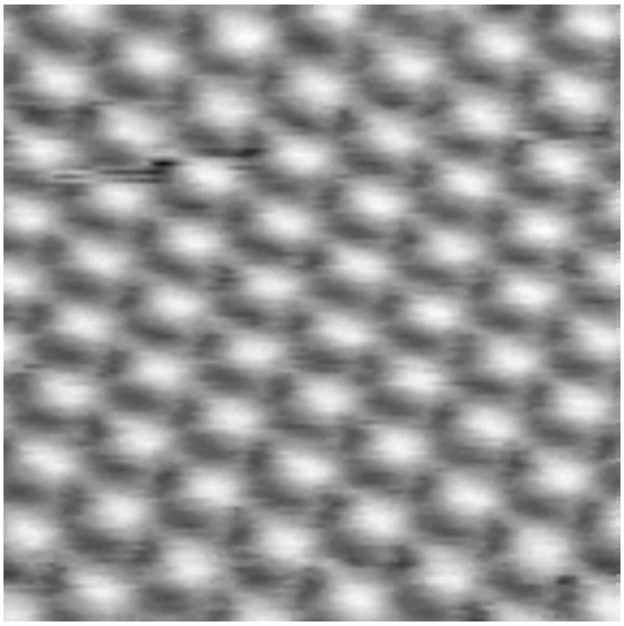

FIG. 6. ECSTM atomic-resolution view of an I-passivated Ni(111) facet. The dimensions are about 2.5 nm in width and 3 nm in height.

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] K. Itaya *et al.*, J. Vac. Sci. Technol. A8, 515 (1990).
[2] J. Clavilier *et al.*, Electroanal. Chem. 107, 205 (1980).
[3] H. Honbo *et al.*, Anal. Chem. 62, 2424 (1990).
[4] T. Yamada *et al.*, J. Phys. Chem. 99, 8817 (1995).
[5] Aqua regia, HCl:HNO_3 = 3:1, HCL, hydrochloric acid, Cica Merck HNO_3 [6].
[6] HNO_3, nitric acid, Cica Merck.
[7] Millipore Milli-Q, ($R > 18$ MΩcm).
[8] All power supplies are adjustable with primary voltage control by phase-controlled thyristors.
[9] A. Wieckowski *et al.*, Inorg. Chem. 23, 565 (1984).
[10] F. Lu *et al*, J. Electroanal. Chem. 22, 305 (1987).
[11] I, iodine, Aldrich, ultrapure crystal, slightly heated in vacuum to produce I_2 gas and connected via a leak valve to the UHV system.
[12] The STM and contact-mode AFM used were a Nanoscope III of Digital Instruments, Santa Barbara, CA, USA.
[13] P. Müller and K. Itaya, IBM Research Report, Electrochemical Atomic Force Microscopy on Single-Crystal Bead Facets. RZ 3005 (March 30, 1998).
[14] $HClO_4$, perchloric acid, Cica Merck, ultrapure grade.
[15] KI, potassium iodide, Kanto Chemicals, ACS grade.
[16] Olympus cantilevers with sharped pyramid tip, a length of 200 μm and a spring constant of about 0.022 N/m. Tip and lever materials are silicon nitride. The cantilever is coated on the backside with a Cr/Au reflecting layer and mounted on a Pyrex chip.
[17] P. Müller and K. Itaya, IBM Research Report, First Observation of I on Ni(111) in HF Solution. RZ 3006 (March 30, 1998).
[18] HF, hydrofluoric acid, Cica Merck, ultrapure grade.