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# Reconstruction on Au(001) vicinal surfaces in UHV and in sulfuric acid solution

Marina Moiseeva [a], Ernesto Pichardo-Pedrero [b], Guillermo Beltramo [b], Harald Ibach [a], Margret Giesen [b,*]

[a] Institut für Bio- und Nanosysteme, IBN 3, Forschungszentrum Jülich, D 52425 Jülich, Germany
[b] Institut für Bio- und Nanosysteme, IBN 4, Forschungszentrum Jülich, D 52425 Jülich, Germany

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ABSTRACT

Using scanning tunneling microscopy we have studied the reconstruction on Au(11$n$) surfaces in ultra-high vacuum and in electrolyte. Similar to the well-known $(5\times 20)$ quasi-"hex" reconstruction on Au(001), the reconstruction consists of parallel reconstruction lines along the steps indicative of a higher atom density in the first Au layer. In contrast to nominally flat Au(001) where the reconstruction period is 1.44 nm, we find considerably larger reconstruction periods (1.8–1.96 nm) on incidentally flatter regions of nominal Au(119), Au$(1\,1\,11)$, and Au$(1\,1\,17)$ surfaces. The enlarged reconstruction period is attributed to the stress field on stepped surfaces. In agreement with previous studies we find a reconstruction free zone at the step edges.

## 1. Introduction

Since its first observation in early low-energy electron diffraction (LEED) studies [1,2], and later in one of the first scanning tunneling microscopy (STM) investigations [3], the $(5\times 20)$ "quasi-hex" reconstruction of the clean Au(001) surface has attracted quite some interest. The atomic structure of the uppermost, incommensurate reconstructed layer is well understood today for surfaces in vacuum [4–6] as well as in electrolyte environment [7–9]: the topmost layer consists approximately of a hexagonal close packed layer with a higher atom density by about 25% which is incommensurate with the substrate because of a slight rotation by about 0.81° [5] with respect to the [110]-direction. The mismatch between the hexagonal overlayer and the substrate leads to a buckling of about 0.3 Å that is easily seen in STM studies.

The reconstruction has a significant effect on the distance between steps on vicinal surfaces. LEED studies by Boulliard and Sotto showed that the surface reconstruction stabilizes some surface orientations, which were denoted as "magical" vicinals [10]. Bartolini et al. performed extensive surface energy calculations and confirmed that stepped Au surfaces with (115) and $(1\,1\,11)$ orientation are very stable in vacuum [11] whereas other nearby vicinal orientations separate into (115) and $(1\,1\,11)$ phases. Phase separation of the (117) and the (119) surface into the (115) and the (001) surface was experimentally confirmed by Sotto and Boulliard [12]. In an electrolyte, a similar phase separation is observed. For Au(11$n$), $n = 9, 17$, in 10 mM $H_2SO_4$, e.g., we find stable vicinal orientations corresponding to (115) and approximately $(1\,1\,35)$ planes. This phase separation seems to belong to a new universality class. Details of this investigation are, however, beyond the scope of this paper and will be published elsewhere [13].

While the effect of the reconstruction on the stability of vicinal surfaces is well documented, the reverse effect of the steps on the reconstruction unit cell was rarely mentioned. First evidence for a possible influence of steps on the buckling periodicity was reported by Yamazaki et al. [14]. Watson et al. found enlarged reconstruction periods in the stepped sections of a 1.7° miscut Au(100) surface that showed phase separation into (100) facets and "magic" ~2° vicinals [15]. In a theoretical work, Bartolini et al. postulated the existence of a reconstruction-free region ("*dead zone*") of about 2.5 atoms length (=0.72 nm) at the foot of the steps [11]. A similar observation was made by Binnig et al. in early STM data on reconstructed Au(001). These authors mentioned that a region of about 1.5 atoms from the step foot is not reconstructed [3]. More recently, Bombis and Ibach showed that the reconstruction stripes are always strictly parallel to step edges and that furthermore the stripes of one atom-layer-high islands are 180° out-of-phase with the stripes on the terraces below [16], in perfect agreement with the prediction of Bartolini et al.

While the existence of a reconstruction free zone is understood insofar as it is reproduced by theory, the enlarged reconstruction period on stepped surfaces as mentioned by Watson et al. is not. The expansion is particular puzzling in view of the fact that the reconstruction period next to steps on a nominally flat Au(100) surface remains practically unchanged. In order to study this issue further we have investigated the surface morphology on the

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* Corresponding author. Fax: +49 2461 613907.
*E-mail address:* m.giesen@fz-juelich.de (M. Giesen).
*URL:* http://www.fz-juelich.de/isg/index.php?index=225 (M. Giesen).

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incidentally flatter areas of nominal Au(119), Au(1111), and Au(1117) surfaces in ultra-high vacuum (UHV) and in electrolyte using scanning tunneling microscopy. We find that the repeat distance of the reconstruction induced buckling changes from 1.44 nm [17,18] on flat Au(001) to 1.8–1.9 nm on stepped surfaces. Furthermore we studied the terrace width distribution and find that the distance between adjacent steps are multiples $k$ of the buckling periodicity. As a consequence, the terrace width $L$ in units of atom diameters is described in terms of a multiple $k$ of a corrugation period $l_p$ and a constant term $l_d$, $L = l_p k + l_d$ ("magical" rule).

The paper is organized as follows: Section 2 describes the experimental procedures and is followed by the presentation of the experimental results in Section 3. The data is discussed in Section 4. The paper ends with a summary in Section 5.

## 2. Experimental

### 2.1. Electrochemical STM measurements

The measurements were performed using the electrochemical version of the Topometrix TMX 2010 Discoverer STM Our instrument was modified to enable temperature variable STM recording with high thermal drift stability and is described in detail elsewhere [19,20]. In the studies reported here, however, all experimental results were obtained at 294 K. The tip and the sample potential are independently controlled via a bipotentiostat.

Our studies were performed on Au(119) and (1117) single crystal electrodes which are inclined with respect to the (001) plane along the atomically dense ⟨110⟩-direction by $\theta = 8.9°$ and 4.8°, respectively. Ideally, the surfaces would consist of parallel, monatomic high steps along $\langle 1\bar{1}0\rangle$ separated by (001)-terraces with an average width of $L = 4.5a_\perp$ and $L = 8.5a_\perp$ corresponding to 1.30 nm and 2.45 nm, respectively (with $L = 0.288a_\perp$ nm the distance between adjacent atomic rows along ⟨110⟩ in the bulk.) The Au(11$n$) electrodes were cut by spark erosion from a single crystal rod, oriented by diffractometry and polished to the desired orientation within 0.1°, which is the accuracy of high-quality single crystals. The accuracy is naturally limited by the mosaic structure of the crystal.

Prior to experiment, the electrodes were heated in a hydrogen atmosphere and then flame annealed for about 5 min to about 900 °C. The temperature was visually controlled by the color of the annealed crystal.

After thoroughly rinsing the cell with Milli-Q water, the crystals were mounted in the electrochemical STM cell which was connected to the bipotentiostat. The crystal surfaces were then brought in contact with the electrolyte under potential control. As an electrolyte, we used suprapure $H_2SO_4$ (Merck) as well as Milli-Q water from a Millipore Elix 3 and A10 Gradient system (18.2 MΩ cm$^{-1}$; organic contents <3 ppb). The STM measurements were performed in 10 mM $H_2SO_4$.

The tunneling tips used in the experiments were etched from polycrystalline tungsten wires and coated with polyethylene to avoid Faraday currents at the foremost part of the tip [21]. We used a tunneling current of 2 nA. The typical time per image was about 80 s and the STM images were recorded with a 400 × 400 pixel resolution in the constant current mode. High-purity, flame-annealed Pt wires (Goodfellow, 99.999%) served as counter and quasi-reference electrodes. In the following, the electrode potentials of the metal sample are, however, given with respect to the saturated calomel electrode (SCE). As a caveat we emphasize that the electrode potentials denoted here are the nominal values given by the bipotentiostat. After each experiment we checked the potential by measuring a cyclic voltammogram in the STM cell. Still we cannot exclude that the potential values as denoted here might deviate from the real potential by about 50 mV due to possible shifts in the potential during experiment. Depending on the chosen electrode potential, good experimental conditions lasted up to 2 h. Then, generally, contamination of the electrolyte in the open STM cell became visible and the measurements were terminated.

### 2.2. UHV STM measurements

The STM measurements in UHV were performed using an Omicron variable temperature STM (VT-STM). As sample we used a bead-type Au crystal of (1111)-orientation prepared according to [22]. Similar to the electrodes as used in electrochemical studies, the bead crystals were then flame-annealed for about 5 min to about 900 °C and transferred via a load-lock system into the UHV chamber with a base pressure of $10^{-10}$ mbar within a couple of minutes without any further treatment in UHV. Auger spectra revealed small amounts of potassium contamination which diffuses from the crystal bulk to the surface during flame annealing. The potassium could be removed by sputtering and annealing cycles in vacuum. However, in order to preserve the structure of the flame annealed crystal the crystals were not further treated in UHV[1].

Au(1111) is inclined with respect to (001) by 7.3° along ⟨110⟩ and the nominal mean terrace width is $L = 5.5a_\perp$ corresponding to 1.58 nm. However, similar to the electrochemical measurements, the local terrace widths in the inspected areas were larger than the nominal width. In the case of the UHV studies, the local surface orientation was inclined to (001) by 1.2°.

## 3. Results

### 3.1. STM images and line profile analyses of Au(119) and Au(1117) in 10 mM $H_2SO_4$ and of Au(1111) in UHV

The electrode surfaces Au(119) and (1117) as prepared according to Section 2.1 show a phase separation into (115) oriented areas leaving the rest of the surface almost free of steps [13]. An example is given in Fig. 1 which shows (a) an STM image of the Au(119) electrode after flame annealing and immersion into 10 mM $H_2SO_4$ at 294 K and $\phi = -150$ mV SCE. Fig. 1b displays as an example, a height profile analysis as obtained from an STM image comparable to the one shown in Fig. 1a. The steeper regions correspond to a (115) orientation, the flatter to (1133). The studies described here were performed in those flat areas with small inclination angles to (001).

Fig. 2 shows room temperature STM images of (a) a nominal Au(1117) electrode in 10 mM $H_2SO_4$ and $\phi = -150$ mV SCE and (b) a nominal Au(1111) crystal in UHV. In both cases, the Au(11$n$) surfaces display monatomic high, parallel steps. The steps separate terraces of (001) orientation which are reconstructed. The reconstruction is similar to the "quasi-hex" reconstruction known from flat Au(001). However the reconstruction lines are aligned exactly along the step edges with no sign of the 0.81° inclination that is observed on Au(001). Furthermore, the periodicity of the reconstruction lines significantly differs from the value 1.44 nm as found for flat Au(001) [17,18]. Fig. 2c and (d) show representative line profiles for the Au(1117) surface in 10 mM $H_2SO_4$ and the Au(1111) surface in UHV, respectively. The profiles were taken from the STM images in Fig. 2a and b (without subtraction of a plane). The positions of the profiles are marked by black lines in (a) and (b). We find stripe periodicities of $d = 1.8 \pm 0.1$ nm and

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[1] In electrolyte, the potassium is instantly removed from the surface when the electrode surface is in contact with the liquid at low potentials (here $\phi = 150$ mV SCE).