

The surface structure of flame-annealed Au(100) in aqueous solution: an STM study

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Abstract

The initial structure of flame-annealed Au(100) surfaces has been studied in air and in 0.1 M H₂SO₄ by scanning tunnelling microscopy (STM). It is shown that before, during and after contact with the electrolyte, at potentials sufficiently negative to prevent specific adsorption of anions, the flame-annealed Au(100) surface is reconstructed into exactly the same "hex" form as a surface which has been prepared by annealing in ultrahigh vacuum (UHV). However, the quality of the reconstructed surface depends sensitively on the sample preparation and on the experimental conditions of the flame-annealing procedure. The influence of the cooling procedure after flame annealing on the initial surface structure of the Au(100) electrode is demonstrated and briefly discussed in the light of results published previously.

1. Introduction

The preparation of clean and structurally well-defined single-crystal electrode surfaces has become a key issue in electrochemical surface science since single crystals were introduced to electrochemistry as an electrode material. The first serious approach to the preparation and characterization of single-crystal metal electrodes was adopted from surface physics and involved repetitive cycles of sputtering and annealing of the sample in an ultrahigh vacuum (UHV) chamber [1–4], where the crystallinity and cleanliness could be checked by electron diffraction and Auger spectroscopy, respectively. This rather elaborate and expensive route to well-defined surfaces significantly hampered access to single-crystal electrochemistry. The situation changed completely when Clavilier and coworkers [5,6] were able to demonstrate the use of a simple Bunsen burner for the preparation of clean well-defined low index surfaces for platinum electrodes. This so-called flame annealing was performed by heating the Pt crystal in a Bunsen flame for seconds

or minutes to approximately 1200–1400°C and then quenching it rapidly in ultrapure water. This method was later adopted for the preparation of single-crystal gold electrodes by Hamelin and Katayama [7], who claimed that rapid quenching was a prerequisite for obtaining clean surfaces, despite the detrimental heat shock to the crystal.

It is well known from UHV studies that the three low index surfaces of gold are reconstructed after annealing [8–10]. Further, it has been demonstrated over the last 7 years by a wide variety of in-situ and ex-situ techniques that (i) flame-annealed gold surfaces are also reconstructed [11] and (ii) the reconstructed surfaces are stable in an electrochemical environment, provided that certain precautions with respect to the applied potential and the electrolyte composition are met, regardless of whether the surface was prepared in UHV or in the Bunsen flame [12].

In the case of Au(100), reconstruction phenomena have a major impact on the electrochemical behaviour because the surface structures of reconstructed and unreconstructed Au(100) differ markedly: the reconstructed surface has a hexagonal close-packed structure and hence a significantly higher density of gold atoms than the unreconstructed surface with its square lattice arrangement. As a consequence, the presence of a reconstructed Au(100) surface is easily detectable in

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cyclic voltammograms or double-layer capacity measurements [11]. However, for many years our data on reconstructed Au(100) could not be reproduced by other groups and therefore the existence of reconstructed gold surfaces in an electrochemical cell was questioned [13,14]. Surface reconstruction for single-crystal gold electrodes has now been observed by various groups [15–18], confirming our earlier findings, but the origin of the failure to produce reconstructed surfaces by the flame-annealing method is still unknown although it is suspected to lie in the details of the crystal handling.

In this paper we present the results of an in-situ scanning tunnelling microscopy (STM) study which reveals that the surface structure of flame-annealed Au(100) depends sensitively on the preparation procedure, particularly on the rate of cooling after flame annealing, and also on the immersion potential and the initial electropolishing of the electrode surface. Furthermore, differences between the surface structures of initial (thermally induced) reconstruction and potential-induced reconstruction are clearly revealed by STM.

2. Experimental

The pocket-size scanning tunnelling microscope employed here for in-situ electrochemical investigations has been described in detail previously [19,20]. Tungsten tips electrochemically etched from a 0.25 mm diameter wire in 2 M NaOH and coated with Apiezon wax, leaving only the last 10 μm exposed, were used throughout this study. The potential of the tip, which acts as a fourth electrode in the electrochemical cell, was generally held in a region where charge transfer reactions were minimal, i.e. between -0.33 and 0.09 V/SCE. The faradaic current at the tip was typically less than 50 pA.

All scanning tunnelling micrographs were obtained in the constant-current mode, in which the tip height is adjusted via a feedback mechanism to maintain a constant tunnelling current. Values of the tunnelling current I_t were between 2.5 and 250 nA. Recording a complete scanning tunnelling micrograph took about 1 min. The images are represented either as three-dimensional line scans or as “top views”, in which different heights within the image are coloured in different shades of grey, with lighter shades corresponding to higher points.

The gold electrodes used in the STM study were single-crystal discs with (100) surface orientation, about 8 mm in diameter and about 2 mm thick. Because the gold crystal was fully immersed in the electrochemical cell of the scanning tunnelling microscope, cyclic

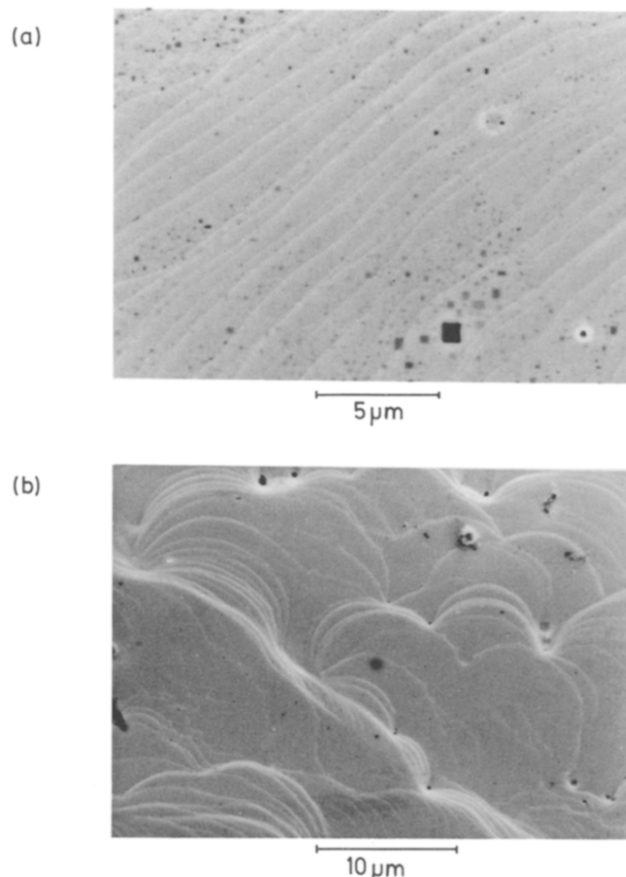


Fig. 1. Scanning electron micrographs of Au(100) surfaces: (a) flame-annealed electrode; (b) electrode subjected to electropolishing in a cyanide solution prior to flame annealing. These micrographs were obtained in the Department of Electron Microscopy, University of Ulm, with a Zeiss DSM-962 scanning electron microscope.

voltammograms for an electrochemical characterization of the (100) face had to be obtained in another cell in which the dipping method could be employed.

In this study the gold crystals had been additionally electropolished in cyanide solution after mechanical polishing and before flame annealing, whereas in earlier investigations the crystals were often subjected directly to (extensive) flame annealing after the mechanical polishing without any electropolishing. The former treatment was recently shown to yield very large atomically smooth terraces [21]. Mechanically polished flame-annealed gold crystals usually exhibit atomically flat terraces several tens of nanometres width, separated by monatomic high steps, whereas crystals which have been subjected to additional electropolishing in cyanide solution show much larger terraces, about $0.1\text{--}0.5$ μm wide, separated by bunches of steps up to 6 nm high. This is demonstrated in Fig. 1 which shows scanning electron micrographs of two different Au(100) surfaces. The upper image (Fig. 1(a))

corresponds to a surface which had not been electropolished in cyanide solution prior to flame annealing, while the surface shown in the lower image (Fig. 1(b)) was electropolished [22]. The latter treatment leads to large micrometre-size flat areas which makes such surfaces ideally suited for STM studies, whereas omitting the cyanide electropolishing results in surfaces with much smaller terraces and a higher density of defects, which show up in Fig. 1(a) as dark spots (the monatomic high steps cannot be seen in these micrographs).

Prior to each STM experiment the gold samples were flame-annealed in a Bunsen burner at red heat for a total of ca. 10 min, depending on crystal size or surface conditions, and then transferred into either the STM or the standard electrochemical cell. The gold electrodes were immersed in the electrolyte under potential control, typically at -0.2 V/SCE. After flame annealing and before the transfer, the samples were either cooled in air for ca. 8 min or for 4 s and then quenched in ultrapure water, or quenched directly in water.

The electrolyte was 0.1 M H_2SO_4 prepared from Milli-Q water and suprapure H_2SO_4 (Merck). The reference electrode was $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (sat.), but all potentials are quoted with respect to the saturated calomel electrode (SCE).

3. Results

3.1. Imaging in air

In order to assess the structure of a Au(100) surface directly after flame annealing, scanning tunnelling micrographs were taken in air immediately after the electrode had been cooled down to room temperature, which took about 8 min (Fig. 2). Parallel reconstruction rows were observed all over the electrode surface, which is typical for reconstructed Au(100) [21]. This observation agrees with the results obtained by Hamelin et al. [23] and confirms our previous finding that the Au(100) surface is reconstructed after flame annealing [11], in very much the same way as it is after treatment in UHV [24]. However, after a relatively short period of time (approximately 30 min) the images started to become rather blurred, probably because of adsorption of impurities from the laboratory environment.

We should mention here that the same result was obtained when the electrode was cooled in air for 4 s only after flame annealing and then quenched in water. This result supports recent findings by Robinson et al. [16] who used synchrotron X-ray diffraction to observe *ex situ* that a flame-annealed Au(100) surface, cooled in air for 10–15 s before quenching in water, possesses a hexagonal overlayer with domains whose size de-

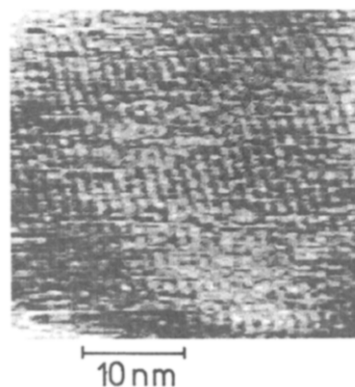


Fig. 2. Scanning tunnelling micrograph ($34\text{ nm} \times 34\text{ nm}$) of a flame-annealed Au(100) electrode taken in air directly after the annealing procedure showing a reconstructed surface. Tunnelling conditions: $I_t = 2.5\text{ nA}$; bias voltage $V_b = 0.65\text{ V}$.

pends upon the annealing time. However, our findings are at variance with recently published results of Hamelin et al. [23] who categorically claimed that a freshly flame-annealed Au(100) surface which was cooled in ultrapure water was inherently unreconstructed.

3.2. Imaging in situ

In order to learn more about the influence of the cooling procedure after flame annealing on the surface structure, particularly on surface reconstruction, the electrode surfaces were investigated *in situ* by STM.

In the first type of experiment the Au(100) crystal was heated in a Bunsen flame to red heat for about 8 min and then cooled in air over a period of 8 min before it was transferred to the electrochemical cell and immersed in 0.1 M H_2SO_4 under potential control at -0.2 V/SCE. As a result of this treatment, the (hex)-reconstruction has been retained in full, as can be seen in Figs. 3 and 4 by the so-called reconstruction rows which are separated by 1.45 nm and aligned along step edges and which cover even 100 nm wide terraces as single domains (Fig. 3). Scanning tunnelling micrographs of this type have been obtained at different places all over the electrode surface, even several hours after the experiment had begun. They demonstrate beyond any doubt that the initial reconstruction of the flame-annealed Au(100) surface is preserved during and after contact with the electrolyte solution, if the electrode potential is sufficiently negative, so that specific adsorption of anions is avoided. Figure 5(a) shows a close-up of the reconstructed surface, in which reveals intensity modulations along the reconstruction rows due to a slight rotation of the (hex)-structure with respect to the substrate. A rough estimate of the unit cell leads to a $c(26 \times 68)$ structure for the recon-

structed Au(100), in agreement with previous in-situ [21] and ex-situ [25] studies. Finally, the hexagonal arrangement of the individual gold surface atoms with an interatomic spacing of 0.29 nm as well as the one-dimensional intensity modulation with the 1.45 nm spacing due to the structural misfit between bulk and reconstructed surface are clearly seen in Fig. 5(b). Similar high resolution scanning tunnelling micrographs of reconstructed gold surfaces have been reported before [18,21].

In a second type of preparation experiment, the gold crystal was allowed to cool in air for a few seconds after flame annealing until the red heat had disappeared before it was quenched in ultrapure water. Such a treatment has been routinely applied in the past in our laboratory for the study of reconstruction phenomena and it was considered to be a compromise between minimizing the heat shock and minimizing surface contamination by laboratory air [12]. After quenching, the crystal was transferred to the electrochemical cell with a droplet of water adhering to its surface to protect it from air. The surface structure of such a Au(100) electrode is shown in Fig. 6(a), which was obtained a few minutes after immersion. Large areas of the surface are reconstructed in single domains, as seen by the presence of the reconstruction

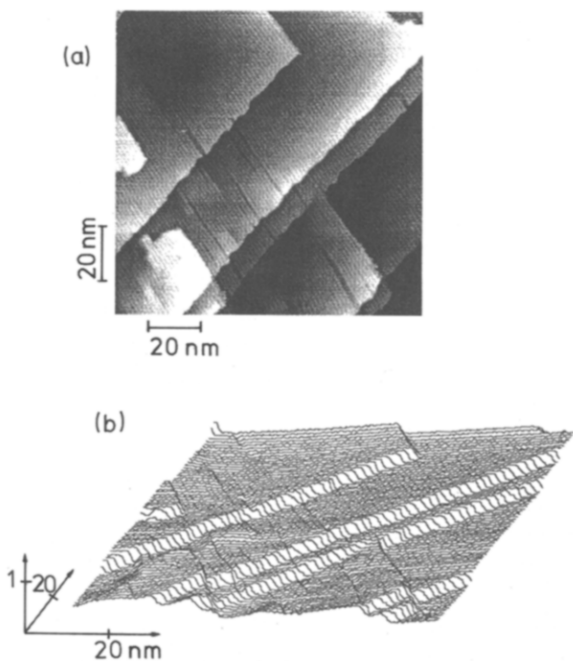


Fig. 3. Typical scanning tunnelling micrograph (115 nm \times 110 nm) of a reconstructed Au(100) surface obtained in situ directly after the electrode had been flame annealed, cooled in air for 8 min and immersed into 0.1 M H₂SO₄ at -0.18 V/SCE: (a) top view; (b) three-dimensional line scan plot. $I_t = 40$ nA; $E_{tip} = -0.29$ V/SCE.

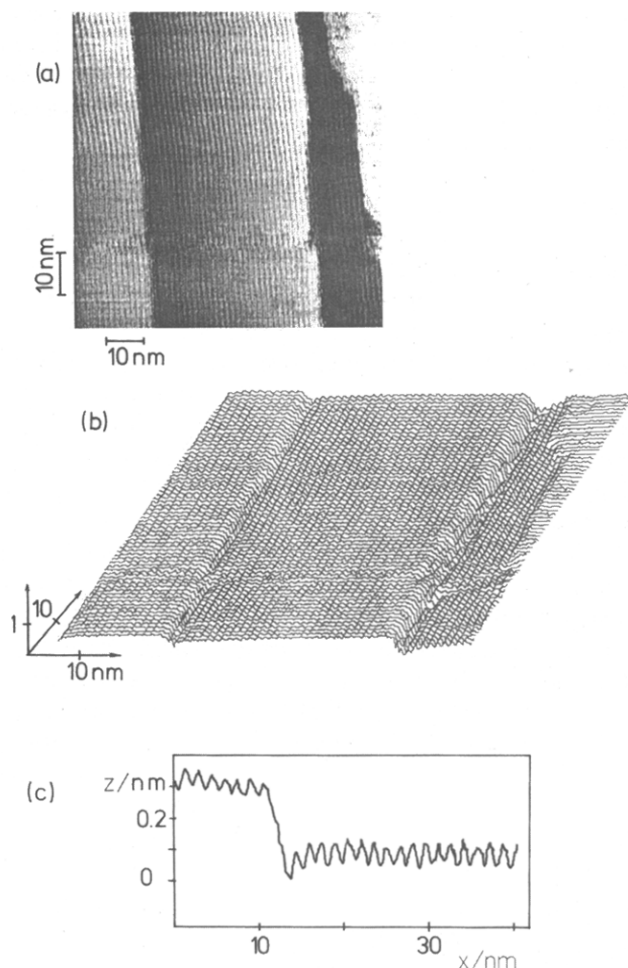


Fig. 4. Scanning tunnelling micrograph (81 nm \times 73 nm) of reconstructed Au(100) in 0.1 M H₂SO₄ showing three monatomic steps and reconstruction rows aligned along the straight portions of the steps: (a) top view; (b) three-dimensional line scan plot; (c) section across the reconstruction rows which have a separation of 1.45 nm and a corrugation amplitude of 0.05–0.06 nm. Sample preparation as described in Fig. 3; immersion and recording at -0.2 V/SCE; $I_t = 12$ nA; $E_{tip} = -0.32$ V/SCE.

rows (on average, 70%–80% of the total surface area was reconstructed), but there are also dark areas seen to the right of the image which are about 0.05 nm lower than the reconstructed areas and show several monatomic high gold islands, indicating that reconstruction had been lifted during the surface preparation and handling. This means that even the second type of crystal preparation yields surfaces which contain large areas of the initial reconstruction and therefore are well suited to the study of reconstruction phenomena.

In order to demonstrate that the appearance of monatomic high islands on a Au(100) surface is indicative of the (hex) \rightarrow (1 \times 1) transition, i.e. the lifting of

the (hex)-reconstruction, the surface shown in Fig. 6(a) was subjected to a potential cycle in the positive direction up to +0.25 V/SCE, where specific adsorption of sulphate ions is known to remove reconstruction. The change in topography is obvious (Fig. 6(b)) as the 25% extra atoms of the densely packed (hex) structure are expelled onto the surface during the (hex) \rightarrow (1 \times 1) transition, where they coalesce into small islands [21]. The size of the islands, roughly 1–2 nm in diameter in Fig. 6(b) increases with time owing to surface diffusion (Ostwald ripening) until they reach several tens of nanometres. It may be noteworthy that the islands in Fig. 6(a), which were obviously generated during quenching of the (still hot) crystal, are relatively large compared with those generated by the anion-induced lifting of the reconstruction at room temperature. This may be explained by the higher temperature at which the Ostwald ripening took place during quenching.

In a third type of experiment, the gold crystal was quenched in ultrapure water immediately after flame annealing, a treatment frequently advocated for reducing as much as possible the danger of surface contamination by laboratory air. The result of a structure study is shown in Figs. 7(a) and 7(b), which clearly demon-

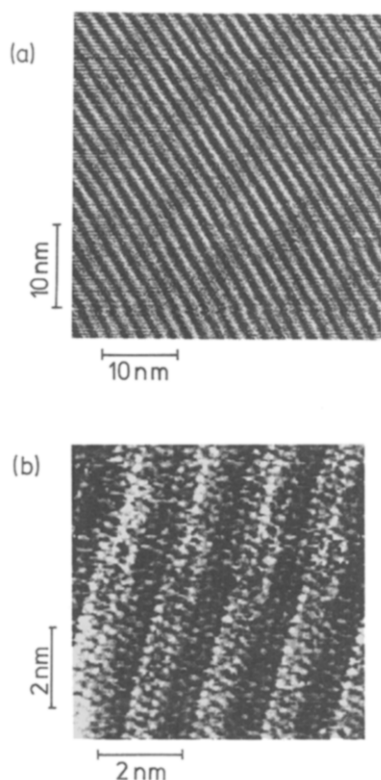


Fig. 5. In-situ scanning tunnelling micrographs of reconstructed Au(100) showing (a) the reconstruction rows and (b) the individual surface atoms of the (hex) structure. Sample preparation and immersion as in Fig. 4; $I_t = 108$ nA; $E_{tip} = -0.33$ V/SCE.

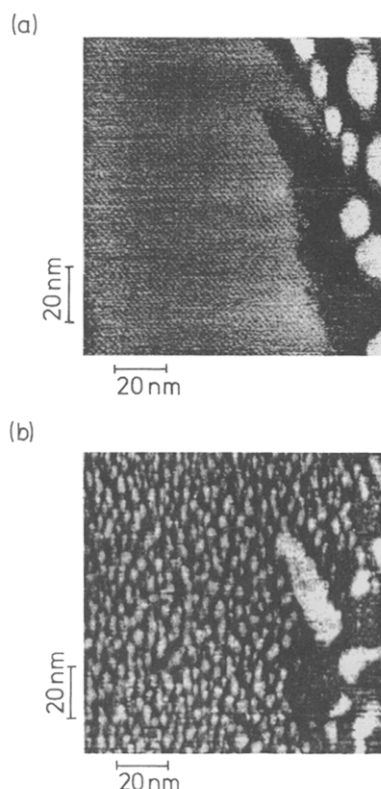


Fig. 6. (a) Scanning tunnelling micrograph (120 nm \times 120 nm) of a flame-annealed Au(100) electrode in 0.1 M H₂SO₄ which was cooled in air for 4 s after flame annealing and then quenched in water before immersion into the electrolyte at -0.15 V/SCE; (b) scanning tunnelling micrograph of approximately the same area, but recorded at 0.25 V/SCE where reconstruction is lifted. The formation of monatomic high islands, which is typical of the (hex) \rightarrow (1 \times 1) transition, is clearly seen. $I_t = 60$ nA; $E_{tip} = -0.03$ V/SCE.

strate that fast quenching leaves the surface in a highly disordered and, as far as one can judge from the blurred micrographs, rather unreconstructed state. Subsequent application of a positive potential scan up to +0.27 V/SCE did not produce extra gold islands, supporting the view that the rapidly quenched surface did not contain a significant amount of the initial reconstruction (Figs. 7(c) and 7(d)).

4. Discussion

The results of our STM study of flame-annealed Au(100) electrodes show unequivocally that (i) the surface structure depends markedly on the cooling procedure and (ii) the initial reconstruction obtained by flame annealing is indeed preserved even during and after contact with the electrolyte if certain precautions regarding crystal temperature and electrode potential at the time of contact with the solution are met. The scanning tunnelling micrographs of Figs. 3 and 4 prove point (ii) beyond any doubt, which contradicts the

results of Hamelin et al. [23] who stated that contact with water inherently removes reconstruction. Our results also demonstrate that fast quenching of the crystal is detrimental to reconstructed surfaces. Such a procedure is known to introduce twinning in the bulk [16] as well as elastic and plastic deformation of the gold surface [26] which will probably act as nucleation centres for the (hex) \rightarrow (1 \times 1) structural transition. As has been shown before, lifting of the reconstruction starts almost exclusively at surface defects [21], and it is reasonable to assume that thermal stress generated at the contact of a hot sample with the liquid phase supplies these active sites for the removal of the (hex) form. Obviously, it was fast quenching of the crystal which prevented other groups from detecting the surface reconstruction of Au(100) which inherently exists after flame annealing. This procedure was falsely considered as a necessary requirement for obtaining clean surfaces. Scanning tunnelling micrographs as well as double-layer capacity measurements have revealed that, at least for gold, the danger of surface contamination through laboratory air during cooling has been grossly overestimated and that equally clean surfaces are obtained by letting the crystal cool in air until the red heat has disappeared before quenching it in water. In contrast, fast quenching produces rough structurally

ill-defined surfaces and eventually destroys the bulk crystal.

As well as the initial reconstruction of a Au(100) surface which is obtained by flame annealing and which yields very large reconstructed domains (Figs. 3 and 4), we also have to consider the so-called potential-induced reconstruction [12,27] obtained at room temperature by applying a negative surface charge to the electrode. In the latter case the surface has been shown to consist of many small (hex) domains oriented at 90° with respect to each other (e.g. Fig. 8 of ref. 21). This leads to a criss-cross pattern of reconstruction rows which is very different from the single-domain character of reconstructed surfaces prepared at elevated temperatures (initial reconstruction). Inspection of in-situ scanning tunnelling micrographs for Au(100) published by Gao and coworkers [28,29] reveals that their surfaces show the potential-induced reconstruction only, i.e. the (hex) structure initially present was obviously destroyed during further handling after flame annealing. This again emphasizes the importance of proper cooling of the sample after flame annealing which should not be too fast.

Why is it important to distinguish between the initial (thermally induced) and the potential-induced reconstruction of Au(100)? We have shown in previous stud-

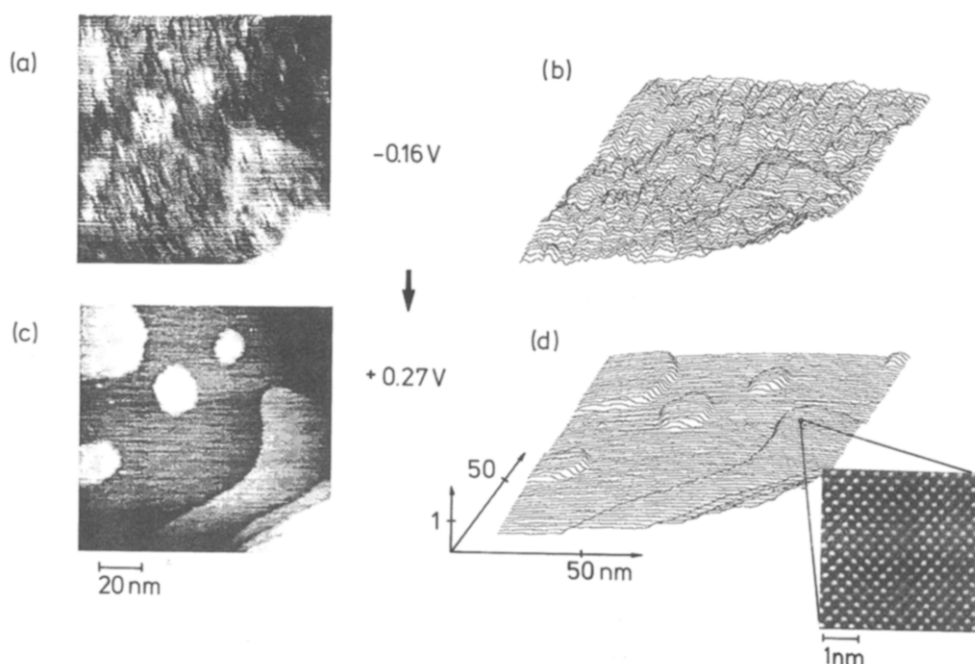


Fig. 7. Scanning tunnelling micrographs (118 nm \times 114 nm) of a Au(100) electrode in 0.1 M H₂SO₄, which was rapidly quenched in water after flame annealing before immersion at -0.16 V/SCE: (a) top view and (b) three-dimensional line scan plot revealing a highly disordered surface at -0.16 V; (c), (d) micrographs recorded after the electrode potential was increased to 0.27 V. $I_t = 45$ nA; $E_{tip} = 0.09$ V/SCE. The close-up in Fig. 7(d), which shows the atomic structure of the unreconstructed Au(100) surface, was taken with a tunnelling current I_t of 250 nA.

ies that under appropriate experimental conditions, such as sufficiently negative electrode potentials and long waiting times, large fractions, if not almost all, of the electrode area can be transformed back into the (hex) structure [12,27,30]. Nevertheless, recent STM studies [21,29] have demonstrated marked differences between the two types of (hex) structure as far as domain size and consequently transition kinetics are concerned. As already mentioned, the initial reconstruction covers the surface in large domains, with the latter usually being limited by step edges (Figs. 3 and 4), whereas surfaces with a (hex) structure due to potential-induced reconstruction often show a large number of monatomic high islands (generated by the preceding (hex) \rightarrow (1 \times 1) transition for the initially reconstructed surface), small (hex) domains rotated by 90° with respect to each other (criss-cross pattern) and reconstruction rows which occasionally run around or across the islands. Previous STM studies have shown that the kinetics for the two structural transitions, (hex) \rightarrow (1 \times 1) as well as (1 \times 1) \rightarrow (hex), can be very different for both types of (hex) structure, with the transitions occurring much more slowly in the case of the large (hex) domains [21]. In this context, the role of the surface defects in the kinetics of the (hex) \leftrightarrow (1 \times 1) transitions is emphasized again, because defects can act as nucleation centres for these structure transitions. It has been shown recently by in-situ STM [21] that the (hex) phase seems to be more stable against positive potential scans in the case of the cyanide polished electrode surfaces than in the case of those surfaces which consist of small terraces and have more defects (Fig. 1). The reason for this apparent difference in stability is found in the kinetics of the (hex) \rightarrow (1 \times 1) transition, because in the former case the reaction front requires a much longer time to traverse the large (hex) domains. The influence of sample pretreatment on the kinetics of the surface structural transitions (hex) \leftrightarrow (1 \times 1) is currently under investigation and will be reported in a separate communication.

5. Conclusion

The surface of a well-prepared flame-annealed Au(100) electrode is reconstructed in very much the same way as that of a crystal prepared in UHV. Careful flame annealing yields large domains of the (hex) structure, which often extend over the whole terrace. This initial (i.e. thermally induced) reconstruction can be preserved during and after contact with the electrolyte, provided that the crystal temperature is sufficiently low at the time of contact with water (quenching) and provided that the electrode potential during immersion into the electrolyte is sufficiently negative to

prevent specific adsorption of anions. While the latter requirement has already been discussed in detail in the literature [12], the role of the crystal temperature at the moment of quenching has not. Our STM studies have shown that contact of a reconstructed surface with water at elevated temperatures will allow the (hex) \rightarrow (1 \times 1) structure transition to take place, with the extent of lifting the reconstruction increasing with temperature.

The initial reconstruction is retained in full if the crystal is cooled in air to room temperature after proper flame annealing. Quenching the crystal in water after allowing it to cool in air for about 4 s (which is long enough for the red heat to disappear) resulted in a surface which showed the initial reconstruction on about three-quarters of the total surface. The (hex)-structure had disappeared over a quarter of the electrode area. Finally, immediate quenching of the hot crystal led to a rather disordered surface, which showed no sign of the initial reconstruction, with small domains of the (hex) structure probably originating from potential-induced reconstruction. This will inevitably take place after immersion at negative potentials.

For the study of reconstructed gold surfaces it appears to be best to let the crystal cool in air (or eventually in a protective atmosphere such as nitrogen) until the red heat has completely disappeared before quenching it in water. This seems to be an acceptable compromise between thermal shock to the crystal and surface contamination by the laboratory air. The exact time lapse between flame annealing and quenching will, of course, depend strongly on the size of the crystal. It may be negligible for tiny bead electrodes, but is certainly of crucial importance for the larger crystals commonly used by those groups who employ spectroscopic techniques for further structure investigations. It should also be mentioned that details of the surface morphology, such as terrace size, number of defects (depending on polishing procedure) etc., will also determine the extent to which the quenching process will affect the reconstructed surface. In any case, the present study has demonstrated the importance of a rather gentle cooling of the crystal for preserving the initial reconstruction, a point which has not been sufficiently appreciated in the past and which has led to apparently conflicting observations as far as reconstruction phenomena at the gold|electrolyte interface have been concerned.

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