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Metastable Phase of the Au(111) Surface in Electrolyte Revealed by STM and Asymmetric Potential Pulse Perturbation

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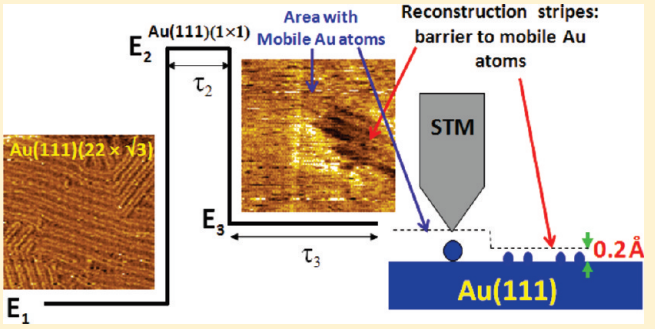
ABSTRACT: We report, for the first time, a new phase of the Au(111) surface that is different from the well-known reconstructed $(22 \times \sqrt{3})$ and the unreconstructed (1×1) states. This new metastable phase is characterized by a high density of highly mobile atoms, the absence of islands, and a paucity of reconstruction stripes. This phase results from the lifting of the reconstruction in the 0.1 M $HClO_4$ interface that is induced by an asymmetric potential pulse perturbation and observed as the potential is stepped down, into the range from 0.3 to 0.45 V_{SCE}, where the potential is neither high enough to form a stable unreconstructed Au(111)-(1×1) with islands nor low enough to form stable reconstructed Au-(111)-$(22 \times \sqrt{3})$ stripes. Our experiments demonstrate that the reconstruction process can be independent from Au island decay. Furthermore, we discovered that the formation of the $(22 \times \sqrt{3})$ phase from the metastable phase is a fast process, which indicates that previous reports of slow Au(111) reconstruction, i.e., $(1 \times 1) \rightarrow (22 \times \sqrt{3})$, may result from the rate limiting process of island decay. This observation enhances our understanding of the dynamics of surface phase transitions



INTRODUCTION

It is reported that Au(111) surfaces can exist in either a reconstructed $(22 \times \sqrt{3})$ structure or an unreconstructed (1×1) structure. In the reconstructed phase, the hexagonal top layer is compressed by ~4.5% in the $(1\bar{1}0)$ direction, so that every 23rd surface atom is in registry with the 22nd atom of the underlying bulk.[1,2] Electrochemistry provides an easy way to control and observe the transition between the reconstructed and the unreconstructed phases.[3,4] It has been believed that adsorption and surface charge are two important factors determining the stability of reconstructed surfaces.[5−12] A recent publication demonstrated that the lifting of the reconstruction is induced by the positive charge on the surface and not by specifically adsorbed ions.[13] Negative surface charge stabilizes the reconstructed surface, while positive charge stabilizes the unreconstructed surface.[5−9,13]

The potential induced $[(22 \times \sqrt{3}) \leftrightarrow (1 \times 1)]$ phase transition on Au(111) and its kinetics have been extensively investigated in the past decades.[14] However, our understanding of the mechanism and kinetics of this phase transition is still limited, and sometimes contradictory. For example, second harmonic generation experiments indicate that the $(1 \times 1) \rightarrow (22 \times \sqrt{3})$ transition is faster than the lifting of the reconstruction,[4] in disagreement with most other reports that the lifting of the $(22 \times \sqrt{3})$ reconstruction is the faster transition.[3,9,11,12] The contradictory observations may be caused by a number of factors, such as surface history[14] and local surface properties,[15] that may affect the rates of surface phase transitions. However, the more critical reason may be that the dynamics of the phase transition is always coupled with the dynamics of nanoscale island decay. This coupling makes the Au(111) surface phase transition dynamics complex and difficult to study as an independent process. The rate limiting step in the $(1 \times 1) \rightarrow (22 \times (3)^{1/2})$ transition is not clear. Is it island decay or the formation of the reconstructed structure? Can we decouple the two processes? These are the questions that motivate this study.

In $HClO_4$ solution, the reconstructed Au(111) surface transforms to the Au(111)-(1×1) phase at potentials above ~440 mV_{SCE}, and the reverse transition occurs for potentials below ~240 mV_{SCE}.[3,6] Therefore, when the potential is higher than 440 mV_{SCE}, the reconstruction is not stable. Likewise, when the potential is lower than ~240 mV_{SCE}, the unreconstructed Au-(111) surface is not stable and a phase transition from Au-(111)-(1×1) to Au(111)-$(22 \times (3)^{1/2})$ occurs. The question is what will happen after a potential step to between 240 and 440 mV, following a potential pulse that lifts the Au(111) reconstruction?

In this paper, an asymmetric potential pulse perturbation, combined with scanning tunneling microscopy (STM), was used to investigate the dynamics of the Au(111) reconstruction. Initially, starting from a potential at which the Au(111) reconstruction is stable, a positive potential pulse perturbation is applied to lift the reconstruction. Then the potential is stepped down to between 440 and 240 mV, where the potential is neither high enough to form the stable unreconstructed Au(111)-(1×1)

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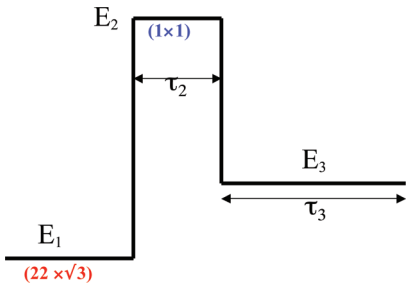
Scheme 1. Asymmetric Potential Pulse Perturbation Experiment



with islands nor low enough to form the stable reconstructed Au(111)-(22 × √3) stripes. This asymmetric potential pulse perturbation leads to the observation of a new metastable phase, characterized by highly mobile Au adatoms on the surface that coexist with a low density of reconstructed stripes in "holes" over a potential range from 0.3 to 0.45 V.

EXPERIMENTAL SECTION

Materials and Methods. An Au(111) single crystal (Monocrystals Co., Ohio) and a single crystal gold bead were used as substrates. Prior to the experiments, the substrate was cleaned by immersion in hot piranha solution [1:3 H_2O_2 (J. T. Baker, CMOS^{TM}) and H_2SO_4 (J. T. Baker, CMOS^{TM})] for 1 h and immersion in hot HNO_3 (EM SCIENCE GR) for 30 min. (*Caution! The piranha solution is a very strong oxidizing agent and can be extremely dangerous. Eye protection and gloves should be used during handling.*) After each step the sample was rinsed by ultrapure water (>18 MΩ·cm) produced by a Barnstead, Nanopure Infinity system. After chemical cleaning, the crystal was hydrogen flame annealed and then transferred to the STM electrochemical cell and immersed under potential control (0.1 V) in 0.1 M $HClO_4$ solution (perchloric acid, OPTIMA, Fisher Chemical).

STM Imaging. STM images were obtained by using a PicoScan STM system (Molecular Imaging Co.) with a bipotentiostat to control the sample and tip potential independently. The electrochemical cell was made of Teflon. All potentials in this paper are referenced to the standard calomel electrode (SCE), though a silver wire or a Pt wire was actually used as the quasi-reference electrode. A platinum wire was used as a counter electrode. All cell components were chemically cleaned in the same way as the crystal. STM tips were prepared by electrochemically etching 0.25 mm diameter tungsten wires using 10 V AC in 3 M KOH solution. Tips were coated with paraffin wax, yielding less than 10 pA faradic current. All the STM images were obtained under constant current mode at tunneling currents <1 nA. The tip potential was fixed at 0 V_{SCE}, unless otherwise indicated. All the images are presented unfiltered.

The asymmetric potential pulse perturbation (Scheme 1) time resolved scanning tunneling microscopy (AP^3 TR-STM) experiment is a simple extension of the P^3 TR-STM experiment.[16] The sample was initially held, in all the experiments reported here, for several minutes at a potential (0.1 V) at which the reconstructed (22 × √3) structure is stable. A short positive potential pulse (Scheme 1) to a potential E_2 (0.7 or 0.8 V of duration 0.1 s) was applied to the sample during STM imaging. This results in the rapid lifting of the surface reconstruction and the generation of nanometer scale islands.[16] After the perturbing pulse, the sample was stepped to a potential, E_3, chosen to be between 440 and 240 mV, where the potential is neither high enough to form a stable unreconstructed Au(111)-(1 × 1) with islands nor low enough to form stable reconstructed Au(111)-(22 × (3)$^{1/2}$) stripes. The STM follows the dynamics on a frame by frame basis. The scan direction, indicated by an arrow at the right of each image, also serves as a time axis.

RESULTS AND DISCUSSION

At 0.1 V the Au(111) reconstruction is stable. The characteristic herringbone pattern of the reconstructed surface with pairs of stripes, each pair separated by ~6.3 nm, is clearly seen in the STM image (Figure 1A), in agreement with previous observations.[2,16] After the 0.1 s, 0.8 V potential pulse perturbation was applied near the top of the image (Figure 1B), the potential was stepped down to 0.3 V (E_3). The lifting of the reconstruction appears to be complete and rapid as the characteristic herringbone pattern of the reconstructed stripes disappears entirely and islands appear. As time increases, i.e., as the scan proceeds down the image, the islands rapidly disappear as shown in the lower part of Figure 1B and the whole Figure 1C. The surface is "noisy", with a few isolated areas having the signature reconstruction stripes of the substrate. The noisy area is higher than that of the reconstructed area, so that these small reconstructed regions appear to be buried in "holes" in the surrounding substrate rather than raised above the substrate as observed in the normal reconstructed surface (Figure 1A). This is made clear by inspection of the line scan (Figure 1E) of a region that contains reconstructed stripes.

The reconstruction stripes in holes do not grow significantly with time, as they appear similar in extent in successive images. However, when the electrode potential is dropped to 0.1 V, the reconstruction stripes appear almost immediately, Figure 1 D, covering almost the entire surface. Comparing Figure 1D and Figure 1C, the stripes in the holes (Figure 1C) at 0.3 V (E_3) and the reconstruction stripes (Figure 1D) have the same double line structure and same direction. Therefore, we deduce that the stripes in the holes are characteristic of the reconstructed Au structure, and they may serve as the nucleation sites of the new Au(111) reconstruction when the potential is stepped down to 0.1 V.

There are three striking characteristics in the observations of the Au(111) surface after the asymmetric potential pulse perturbation:

1. The holes, i.e., reconstructed regions, are lower than the surrounding noisy background (e.g., Figure 1C). Typically, the reconstructed stripes are higher (~0.2 Å) than the unreconstructed area.[1,2] Noise in STM images has been reported to be caused by mobile diffusing adatoms.[17−21] The observation of a "noisy background" higher than the reconstructed (22 × √3) structure suggests that the surface may be covered with high density highly mobile adatoms, which is different from both the well-known reconstructed structure and the unreconstructed structure.
2. The absence of either islands or reconstructed stripes. The reconstructed Au(111) surface contain ~4.5% more atoms than the unreconstructed surface; thus, lifting of the reconstruction will release the 4.5% extra Au atoms. Typically, the released Au atoms will either form islands on the

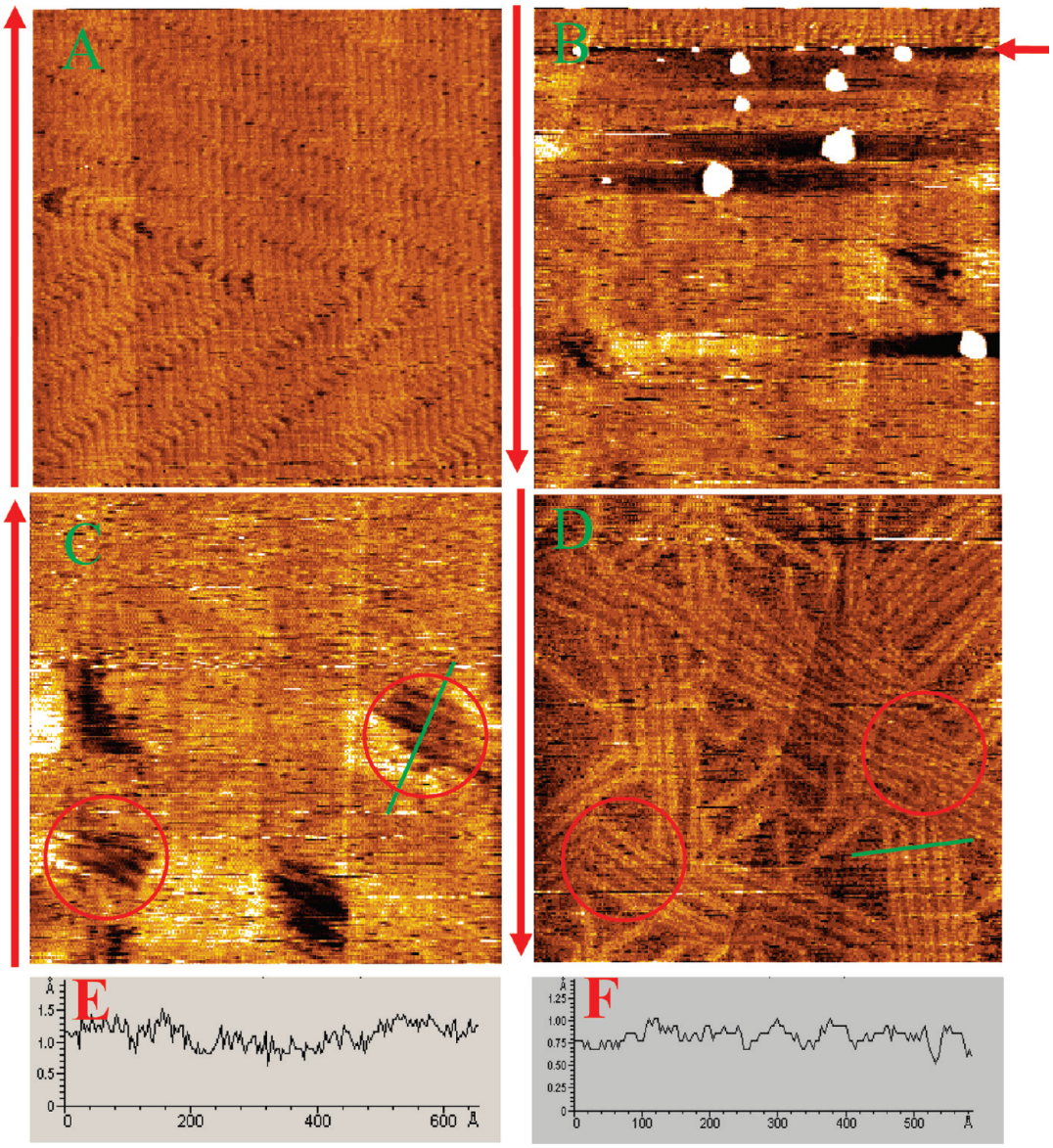


Figure 1. STM images (230 × 230 nm^2) for a 100 ms asymmetric potential pulse experiment on Au(111) in 0.1 M $HClO_4$ solution, about 72 s/image. (A) At 0.1 V (E_1). (B) At 0.3 V (E_3), 0−65 s after a 0.1 s, 0.8 V potential pulse, indicated by (←). (C) At 0.3 V, 66−137 s after the potential pulse, the stripes in the "holes" (red circles) serve as nucleation sites of the new Au(111) reconstruction. (D) 0−75 s after the potential is stepped down to 0.1 V, the reconstruction stripes (red circles) have the same double line structure and same direction as in the red circles in (C). (E) Cross section of the reconstructed domains in holes, indicated by the green line in (C). (F) Cross section of the reconstructed domains, indicated by the green line in (D).

unreconstructed (1 × 1) structure or incorporate into the substrate to reform the (22 × $\sqrt{3}$) structure, depending on the potential.[16] However, the surface is characterized by a lack of islands, and only limited residual evidence of the reconstructed structure, i.e. the "stripes in holes" (e.g., Figure 1C). So the noisy background is neither the unreconstructed (1 × 1) structure nor the reconstructed (22 × $\sqrt{3}$) structure; it has higher atoms density than that of the normal unreconstructed Au(111) surface.

3. Rapid reappearance of the reconstructed phase as the potential is stepped to 0.1 V. It is observed that the reconstructed Au(111) phase, characterized by the stripes, appears almost immediately after the potential is stepped to 0.1 V_{SCE} (Figure 1D). This observation of a rapid formation of the reconstructed Au(111) surface indicates that most of the surface Au adatoms exist as highly mobile species at the potential 0.3 V after the asymmetric potential pulse lifting the reconstruction. This provides further evidence that the noisy background is a surface state that is covered by highly mobile Au adatoms, which is a different surface state from both the known unreconstructed (1 × 1) structure and the known reconstructed (22 × $\sqrt{3}$) structure.

These three findings suggest that the noisy Au(111) surface, observed at 0.3 V after a short potential pulse lifting the reconstruction, is a previously unreported metastable phase constituted by a two-dimensional "gas" of highly mobile Au adatoms. While a structure that was neither the unreconstructed (1 × 1) nor the reconstructed (22 × $\sqrt{3}$) has been observed at surface charge densities between −5 and 28 μC in recent a report,[13] the three

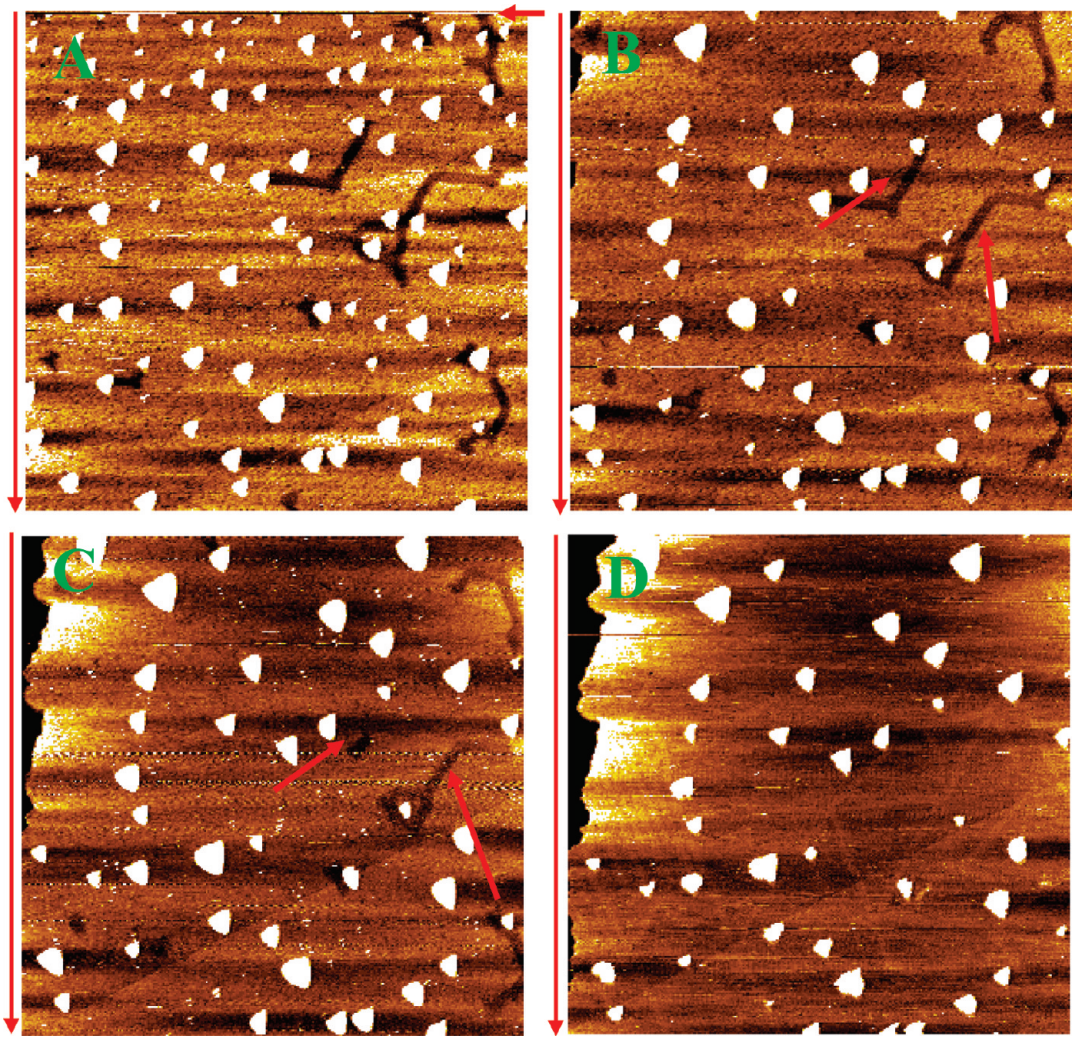
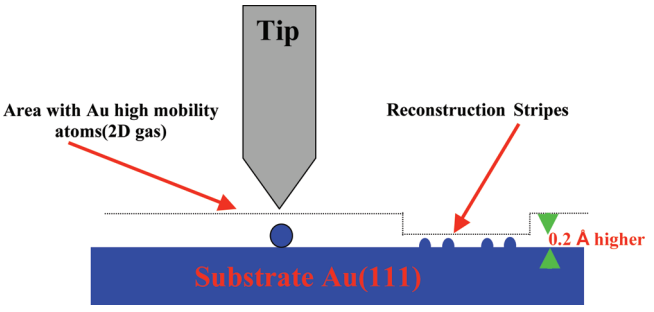


Figure 2. STM images (375 × 375 nm^2) for 100 ms asymmetric potential pulse experiment on Au(111) in 0.1 M $HClO_4$ solution, about 192 s/image. (A) At 0.45 V, 0−192 s after a 0.1 s, 0.8 V potential pulse, indicated by (←). (B) At 0.45 V, 385−576 s after a 0.1 s, 0.8 V potential pulse. (C) At 0.45 V, 981−1152 s after a 0.1 s, 0.8 V potential pulse. (D) 0−192 s after the potential is stepped down to 0.1 V. The arrows indicate reversed stripes.

Scheme 2. Proposed Model for the STM Images of the New Metastable Phase



striking characteristics identified above, which suggested that this could be a new novel phase, were not elucidated.

The presence of reconstructed stripes in holes suggests that the highly mobile adatoms diffuse mainly on the unreconstructed surface area, and that the reconstructed stripes, due to their higher corrugation and anisotropy, serve as a barrier to prevent the diffusion of the adatoms; therefore, the stripes do not appear noisy. (Additional experiments in our laboratory show the decay of islands can be hindered due trapping in corals formed by reconstructed Au(111) stripes (*unpublished results*).) In addition, the reconstructed area and unreconstructed area have different surface charge density; the potential of zero charge (PZC) of the reconstructed surface in 0.1 M $HClO_4$ (PZC = 0.32 V) is 0.09 V higher than the unreconstructed surface (PZC = 0.23 V).[14] The differences in local surface charge density may also affect atomic diffusion. Thus, when the electrode potential is 0.3 V, locally the reconstructed surface is close to neutral, while the surrounding unreconstructed surface is positively charged. Atomic diffusion on Au surfaces has been shown to increase with increasing positive surface charge.[22−25]

A simple model is proposed (Scheme 2) to explain the observations. In this model, the majority of the surface is covered by a sea of highly mobile atoms that diffuse mainly on the unreconstructed surface area, while the reconstructed stripes serve as a barrier to prevent the diffusion of the adatom. Hence, regions with reconstructed stripes appear clearly, i.e. with less noise. Electron tunneling through an adiabatically time-dependent barrier, e.g., due to the movement of adsorbed atoms on a surface, can cause fluctuations of the STM current.[17−21] To a first

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approximation, if the density of mobile adatoms is high enough, the sea of mobile atoms will appear higher than the reconstruction stripes. Accordingly, the STM image renders the reconstructed region lower than the surrounding areas.

It is clear that, in the experiments described above, the process of island decay and the process of reconstruction formation were decoupled. At 0.3 V, the unreconstructed (1 × 1) phase created by the 0.8 V, 0.1 s potential pulse perturbation is not stable and the islands disappear rapidly (Figure 1C). However, 0.3 V is also not low enough to form the reconstructed (22 × $\sqrt{3}$) phase. Thus, except for a very small amount of Au atoms that form reconstructed structures, i.e., the "stripes in holes", most of the extra Au atoms remain on the surface in a high mobility state, i.e., a dilute two-dimensional gas of Au adatoms on the surface. These atoms are available to form a high coverage of reconstructed stripes in a short time (Figure 1 D), once the potential is stepped down to 0.1 V. This observation indicates that both the island decay and the reconstruction can be very fast processes and that these two processes are not necessarily coupled.

The potential E_3 is a critical factor that determines the coverage of each phase. The upper limit of stability of the two-dimensional gas of Au adatoms is 0.45 V, where STM images (Figure 2) reveal a few isolated reversed stripes, i.e., the reconstructed phase, some islands (covering about 3.8% of the surface) representing the unreconstructed phase, and the noisy background representing the 2D adatom gas (Figure 2). The reversed stripes in Figure 2 from the holes in Figure 1 are elongated and appear to contain only a single pair of reconstruction stripes, embedded in the noisy background characteristic of the 2D adatom gas. These reversed stripes are the nuclei of the reconstruction stripes, as demonstrated by the observation that the reversed stripes appear raised with respect to the surrounding surface after the potential is finally dropped to 0.1 V. On the other hand, the appearance of the reversed stripes, i.e., features characterized by a lower tunneling current than the background, suggests that mobile Au atoms are moving around the reconstructed stripes on the surface (Scheme 2). The presence of islands indicates that some of the Au atoms arising from the lifting of the reconstruction are present as the unreconstructed phase. As time increases, the average single island area increases while the overall island coverage does not change, providing evidence for Ostwald ripening. The reversed stripes seem very stable, with only a small number disappearing (indicated by the arrows in Figure 2B and C) from the images over a 30 min time span. This result indicates that the potential 0.45 V may be close to the upper potential limit of stability of the two-dimensional gas of Au adatoms.

A systematic investigation of the effect of E_3 indicates that, in the potential range between 0.45 and 0.3 V, the 2D adatom gas and the reconstructed phase (in holes) coexist. The fractional area covered by the holes increases as the potential decreases to 0.3 V. Outside the range 0.3 V $\leq E_3 \leq$ 0.45 V, the 2D mobile adatom gas was not observed. The normal reconstructed stripes are observed when E_3 is lower than 0.3 V, and only islands (i.e., no holes) are observed when E_3 is greater than 0.45 V, consistent with previous results.[3,16,26]

In conclusion, a new metastable phase of the Au(111) surface which is different from the well-known reconstructed (22 × $\sqrt{3}$) and the unreconstructed (1 × 1) states has been detected by STM in combination with asymmetric potential pulse perturbations methods. The new metastable phase, a two-dimensional "gas" of mobile atoms resulting from the lifting of the Au(111) reconstruction, is stable in the potential range from 0.3 to 0.45 V. These experiments also reveal that the island decay and the formation of the Au(111) reconstruction can be two independent processes. Furthermore, the present results clearly show that the reconstruction is not necessarily a slow process, as had been previously assumed. This observation enhances our understanding of the dynamics of surface phase transitions and is of potential importance to surface science, materials science, and nanotechnology.

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