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Citation: Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena **14**, 1117 (1996); doi: 10.1116/1.588411

View online: https://doi.org/10.1116/1.588411

View Table of Contents: https://avs.scitation.org/toc/jvn/14/2

Published by the American Institute of Physics

Tip-induced lifting of the Au{100} (hex)-phase reconstruction in a low temperature ultrahigh vacuum scanning tunneling microscope

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(Received 24 July 1995; accepted 17 January 1996)

The clean Au{100} surface is known to be reconstructed, forming a pseudohexagonal (5×27) outermost layer. This structure is observed both in ultrahigh vacuum (UHV) and in the electrochemical environment at potentials corresponding to small negative surface electronic charges. Using a UHV scanning tunneling microscope (STM) at 77 K we have observed that the reconstruction can be lifted at large positive sample biases. The 20% less dense bulk-terminated surface is produced and the excess material appears as irregularly shaped gold clusters. Over a period of a few minutes, however, the surface relaxes back to the pseudo-hexagonal phase, a process that can also be followed with the STM. © *1996 American Vacuum Society.*

I. INTRODUCTION

It has been known for many years that clean metal surfaces in ultrahigh vacuum often exhibit the phenomenon of reconstruction: the outermost layer, and possibly underlying layers, rearrange to give a new surface periodicity.[1] The formation of such a phase relieves the tensile strain associated with the bulk-terminated, or (1×1), structure. The {100} surfaces of Ir,[2] Pt,[3] and Au,[4] for example, reconstruct to form an almost hexagonal close-packed top layer, although the details of the structure for each metal are subtly different. In the gold case various periodicities have been reported, e.g., (1×5), (5×20), and $c(26\times28)$, although in a recent high momentum resolution low-energy electron diffraction (LEED) study it was reported that the superlattice period is ~(5×28).[5] The authors noted that this was also the most frequently reported periodicity when the results of all the various experimental methods were considered. (In common with other articles in the literature we will refer to the reconstructed surfaces as the (hex) phase). Au{100} has also been studied in aqueous electrochemical environments using both the scanning tunneling microscope (STM)[6–10] and the grazing-incidence x-ray diffraction technique.[11] As on other low-index gold surfaces the reconstruction can be induced or lifted by applying electrode potentials corresponding to negative or positive surface charge densities. On the basis of one detailed STM study,[8] it was concluded that the normal periodicity of the reconstructed surface is (5×27), but that the same structural unit rotated by 0.7° also occurs and enables the ''rows'' of the structure (nominally oriented in the ⟨110⟩ direction) to ''circumnavigate'' surface defects.

Although the (hex)↔(1×1) transition on the Au{100} surface in the electrochemical environment is well established, it is not clear to what extent adsorption of ions or even of neutral species simultaneously plays a role. Thus, Kolb and co-workers have established that the reconstructed surface is only stable as long as the specific adsorption of anions is avoided.[12] More recently, Weaver and co-workers have demonstrated the importance of hydroxide adsorption, in that the (hex)→(1×1) transition occurs at lower potentials in an alkaline electrolyte than in a weakly acidic medium.[9] At the metal-vacuum interface there is of course no possibility of independently varying the surface charge density via the electrode potential, but at least the surface can be kept free of adsorbates. One possibility of inducing the surface modifications is then to use the bias voltage in an STM to produce a very high local electric field and thus, in a less well-defined way, to change the surface charge density. Schott and White[13,14] have recently shown that on Au{111} in air the (1×1)↔($\sqrt{3}$×22) phase transition can be induced by changing the bias voltage. However, it is known that STM studies on gold in air are probably affected by an ultrathin film of water on the surface.[15] In the present article we investigate this effect under ultrahigh vacuum (UHV) conditions on a Au{100} surface and follow the subsequent relaxation of the surface, which at 77 K is sufficiently slow to observe with the STM. In previous work at room temperature in UHV[16–19] these processes were found to occur too fast to be observed on the atomic scale.

II. EXPERIMENTAL DETAILS

The measurements have been performed in a low-temperature STM, the design of which resembles that of Eigler,[20] but differs in that a mechanical coarse approach is used. An important factor for the stability of the Eigler instrument is the pendulum suspension for the vibrational decoupling of the STM chamber (resonance frequently <1 Hz). The complete chamber can be cooled to 4.2 K. Helium gas provides the thermal coupling between the Dewar and the STM flange as well as acoustic insulation. By varying the He pressure (and by changing from liquid He to liquid N_2) the temperature of the STM can be set between 4 and 300 K.

The mechanical coarse approach is based on a lever system with a reduction ratio of 11:1 which gives an exact perpendicular displacement of the tip relative to the surface. A tripod configuration of the piezoelements has been chosen

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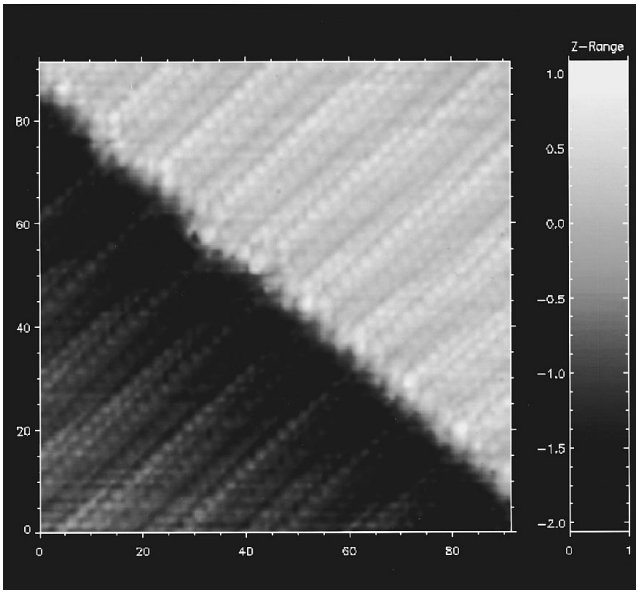

FIG. 1. STM topograph (z image) of a monatomic step on the Au{100} surface. The (hex) reconstructed structure is visible on both terraces with atomic resolution ($U_{\text{bias}}=30$ mV, $I=5$ nA, 64 Å×64 Å).

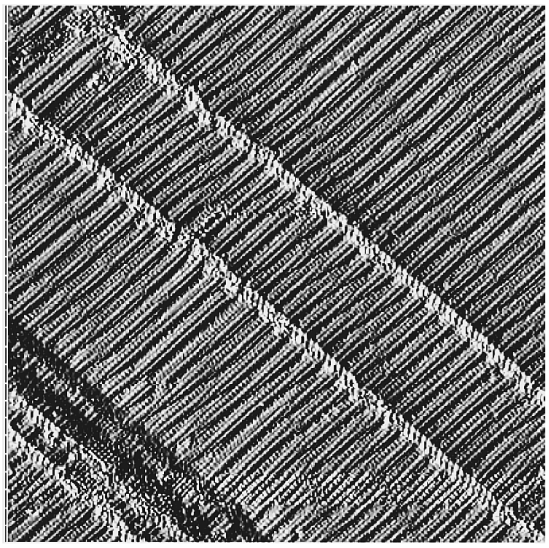

FIG. 2. STM ΔI image (see the text) of the Au{100} surface. Nearly all of the surface exhibits the (hex) reconstruction. Parts of the very narrow terraces (bottom left) are not reconstructed and show the bulk-terminated (1×1) structure ($U_{\text{bias}}=30$ mV, $I=5$ nA, 330 Å×330 Å).

for the fine approach and for scanning. The highest possible resolution perpendicular to the surface is a few 1/1000 Å and the drift is less than 5 Å h^{-1}. The base pressure in the upper UHV chamber (equipped with usual surface science instrumentation) is 5×10^{-11} mbar. A manipulator with a travel of 1.20 m allows the sample to be prepared in the upper chamber and transferred to the STM chamber.

The Au{100} crystal was prepared in the usual way by mechanical polishing, electropolishing, and *in situ* sputter/anneal cycles. For comparison, a flame-annealed surface was also prepared and examined directly after transfer into the system via a sample lock. In this way a partially reconstructed surface could be prepared.

All the micrographs shown in the present article have been taken in the constant current mode with the tip at earth potential. During the scan two measurements are made simultaneously. The first records the z profile, which gives the surface ''topography'' (high areas are bright and low areas dark on the gray scale). The second is a signal which can be interpreted as the differential of the z profile, i.e., $\Delta I=I_a-I_n$. I_n is the nominal, or set, current and I_a is the actual current measured at some point in time before the nominal value has been reached. The two measurements are compared in Figs. 1 and 2. The z profile shows two terraces of the Au{100} surface separated by a monatomic step. The dynamic range of the gray scale is set such that ''atomic'' resolution is just visible on both terraces. This represents, however, the limits of this display mode; if the step height were larger, the atomic fine structure would no longer be resolvable over the whole surface. Typically the fine-structure corrugation is two to three orders of magnitude less than the height of a step or of an adsorbate atom or molecule. This problem is avoided in the ΔI measurement of Fig. 2. The height information is lost and the picture is perhaps not so readily interpretable, but the fine structure can be observed across the whole surface.

III. RESULTS AND DISCUSSION

The Au{100} surface prepared in UHV appears to be almost completely reconstructed in the STM. As reported in the electrochemical studies,[6–10] the (hex) phase consists of parallel rows oriented approximately along the ⟨110⟩ directions. The terraces are normally separated by monatomic steps and exhibit only one of the two rotational domains. In Fig. 2 (bottom left) three particularly narrow terraces, which are not completely reconstructed, can be clearly seen. Also visible (center left) is a different structural unit, in which the unit cell is rotated by 0.7°, as described by Gao *et al.*[8] As mentioned in the Introduction, the occasional occurrence of this feature allows the rows of the (hex) phase to adjust to the presence of surface defects with the consequence that the rows are not strictly parallel to the ⟨110⟩ directions. That the rows are not perfectly oriented in the ⟨110⟩ direction is also shown in the micrograph of Fig. 3 which was measured on a flame-annealed Au{100} crystal with a larger field of view. The surface in this case is incompletely reconstructed; the (hex) phase areas appear bright and the (1×1) areas dark. The contrast is presumably due not only to differences in corrugation, but also to the different electronic structure of each surface. Figure 3 indicates that the rows can deviate by at least 10° from the preferred substrate direction.

The structure of the reconstructed overlayer is pseudohexagonal (Fig. 1). The rows are six atoms wide, corresponding to five atoms of the square array of the underlying (1×1) second layer. The first atom and the sixth atom are positioned between the rows of the (1×1) structure, so that a buckling occurs in the direction perpendicular to the rows. This configuration results in the observed separation between the

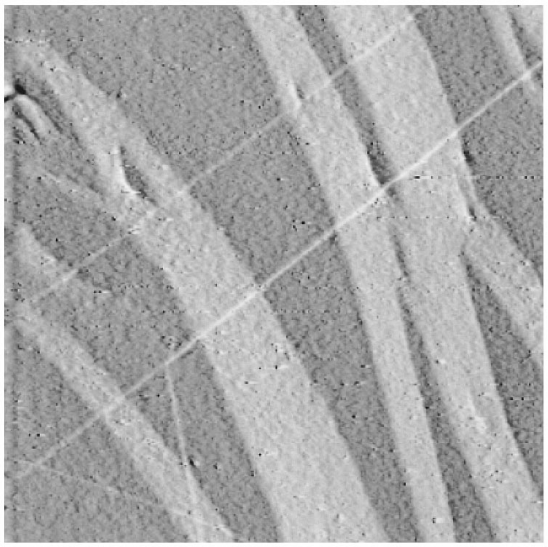

FIG. 3. STM image of a flame-annealed Au{100} surface, cooled in air and subsequently transferred into UHV. The surface is only partly reconstructed (bright areas) (U_{bias}=100 mV, I=1 nA, 6000 Å×6000 Å).

ridges of 14.5 Å. The STM also shows a further undulation along the ridges, due to the fact that the atoms in the reconstructed phase vary in their registry between the atop and fourfold hollow sites. This leads to a periodicity of approximately 75 Å. The observed maximum corrugation in the STM topographs (e.g., Fig. 1) is 0.6 and 0.4 Å perpendicular to the rows, and along the rows, respectively. This result agrees essentially with the images of Au{100} (hex) in the electrolytic environment,[6–10] and in particular with the detailed observations of Gao *et al.*[8]

On increasing the tunnel bias (+1.4 V relative to the tip) at a resistance of 10^8 Ω, the reconstruction can be partially lifted during the scan. This process can be seen in Fig. 4(a) on the upper edge of a monatomic step. The high tunnel voltage gives rise to the rather distorted picture; displaced, and presumably mobile, atoms also contribute to the generally high noise level. The reconstruction is not lifted below the step or in the top half of the scanned region. The tip-induced structural transition is apparently initiated at the step: in the top half of the picture the scan starts and ends on the upper terrace. This demonstrates the importance of the step for the nucleation of the structural phase transition. In the electrochemical experiments[7,10] it was observed that homogeneous nucleation does not normally occur, but that the potential induced transition (in either direction) is initiated at surface steps or other defects.

Figure 4(b) was taken 2 min after the picture in Fig. 4(a) with the same tip separation, but at the more normal bias voltage of 100 mV. The field of view has been shifted down by 20 Å compared to Fig. 4(a), in order to place the (1×1) region in the center. Irregularly shaped gold clusters can be seen at the border of the central (1×1) region (top left). These form because the (1×1) layer is 20% less densely packed than the (hex) phase. The clusters are not observed in Fig. 4(a), presumably because they only form subsequent to

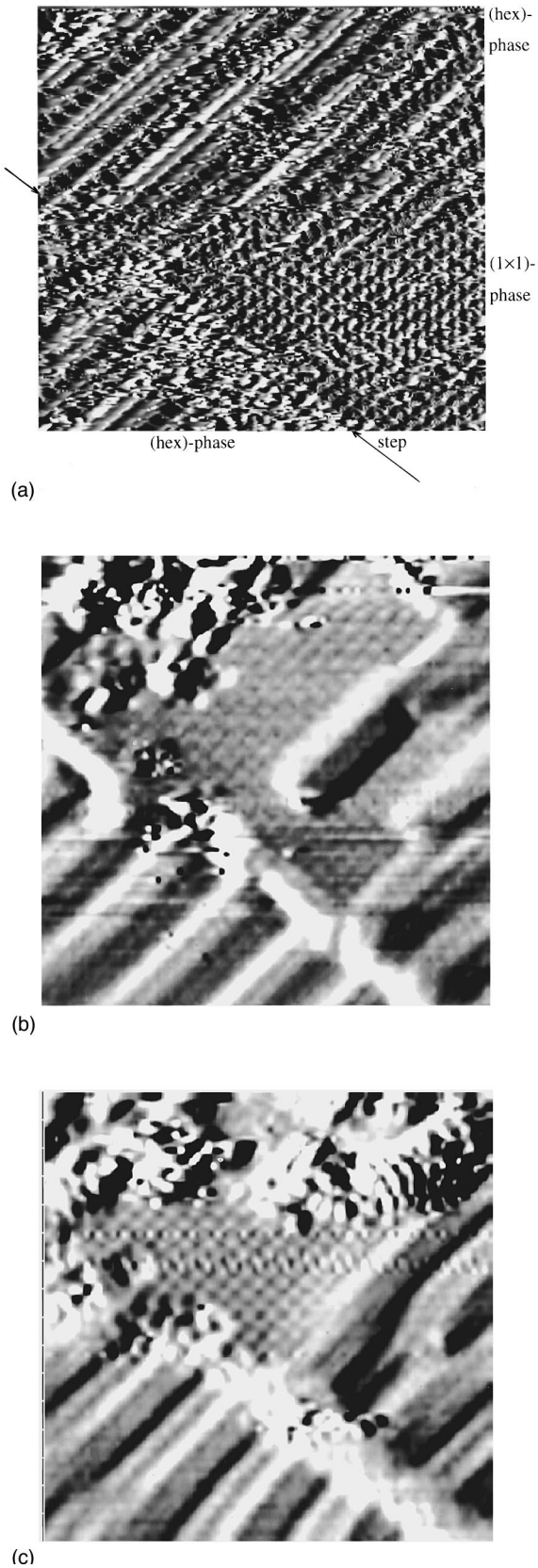

FIG. 4. (a) STM ΔI image recorded during the tip-induced lifting the Au{100} reconstruction. The bias voltage at the sample was +1.4 V (R_{gap}=10^8 Ω, 80 Å×80 Å). (b) STM ΔI image taken 2 min after (a). The image is shifted 20 Å downwards compared to (a) to focus on the central (1×1) area (U_{bias}=100 mV, (R_{gap}=10^8 Ω, 80 Å×80 Å). (c) STM ΔI image taken 3 min after (a) (U_{bias}=100 mV, (R_{gap}=10^8 Ω, 80 Å×80 Å).

the lifting process or, alternatively, because they are moved around by the tip under the extreme tunneling conditions. In the middle of the central (1×1) region of Fig. 4(b) a six-atom-wide island of the (hex) phase remains. In Fig. 4(c), taken after 3 min, this whole island has diffused across the (1×1) region to join up with a larger (hex) region. A similar behavior for single, relatively long rows of the (hex) phase has been observed in the electrolytic environment.[7] At the same time, the (1×1) region has become considerably smaller and the gold clusters have diffused further downwards, presumably acting as the supply of Au atoms necessary to create the (hex) regions.

Although the present data show that strong local fields created via the STM tip can be used to produce surface structural transformations it is not clear whether this process is equivalent, or even similar, to that observed under electrolytic conditions. In the latter experiments the surface charge density is independently varied via the electrode potential; the tunneling conditions can be kept essentially constant. In a study of Au{111} in air it was found that the strong tip-surface interactions led not only to structural changes but also to ''mound formation'' which was ascribed to tip deformation.[14] In the context of the present experiments this may be understood as follows. It has now been shown in several laboratories that atomic resolution on close-packed metal surfaces is often only obtained by picking up atoms or clusters on the tip. In such a situation the local density of states at the Fermi level is no longer sampled, but rather some parameter associated with the formation or breaking of bonds between the tip and the surface. It is likely that such a process is also occurring in the present case so that a simple explanation in terms of increased (or decreased) surface electronic charge density as a function of local field strength is difficult to apply. Similarly, it is not possible to easily assess how such a modified tip would affect the tensile strain in the surface layer.

IV. CONCLUSIONS

Using a low-temperature STM we have imaged the pseudohexagonal Au{100} (hex) surface at 77 K and shown that the reconstruction can be lifted at large positive biases of the sample relative to the tip. The effect is qualitatively similar to the same phase transition in the electrolytic environment where the surface charge density can be varied independently via the electrode potential. However, because of tip modification effects at the high local fields needed to induce the lifting of the reconstruction with the STM, the analogy may not be complete. We note that the subsequent relaxation process back to the reconstructed surface is nonetheless independent of the tip-surface interaction, so that future, more detailed investigations at low temperature may reveal interesting information on diffusion processes and mass transport.

ACKNOWLEDGMENT

The authors thank J. Wintterlin for useful experimental hints.

[1]B. W. Dodson, Phys. Rev. Lett. **60**, 2288 (1988).
[2]T. Grant, Surf. Sci. **18**, 228 (1969).
[3]S. Hagström, H. B. Lyon, and G. A. Somorjai, Phys. Rev. Lett. **15**, 491 (1965).
[4]D. G. Fedak and N. A. Gjastein, Phys. Rev. Lett. **16**, 171 (1996).
[5]Y.-F. Liew and C.-C. Wang, Surf. Sci. **227**, 190 (1990).
[6]X. Gao, A. Hamelin, and M. J. Weaver, Phys. Rev. Lett. **67**, 618 (1991).
[7]X. Gao, G. J. Edens, A. Hamelin, and M. J. Weaver, Surf. Sci. **296**, 333 (1993).
[8]X. Gao, A. Hamelin, and M. J. Weaver, Phys. Rev. B **46**, 7096 (1992).
[9]G. J. Edens, X. Gao, M. J. Weaver, N. M. Markovic, and P. N. Ross, Surf. Sci. **302**, L275 (1994).
[10]O. M. Magnussen, J. Hotlos, R. J. Behm, N. Batina, and D. M. Kolb, Surf. Sci. **296**, 310 (1993).
[11]B. M. Ocko, J. Wang, A. Davenport, and H. Isaacs, Phys. Rev. Lett. **65**, 1466 (1990).
[12]P. Skodula and D. M. Kolb, Surf. Sci. **260**, 229 (1992).
[13]J. Hossick Schott and H. S. White, Langumir **8**, 1955 (1992).
[14]J. Hossick Schott and H. S. White, Langmuir **9**, 3471 (1993).
[15]H. J. Mamin, E. Ganz, D. W. Abraham, R. E. Thomson, and J. Clarke, Phys. Rev. B **34**, 9015 (1986).
[16]Y. Kuk, F. M. Chua, P. J. Silverman, and J. A. Meyer, Phys. Rev. B **41**, 12393 (1990).
[17]F. Besenbacher, F. Jensen, E. Laegsgaard, K. Morgensen, and I. Stensgaard, J. Vac. Sci. Technol. B **9**, 874 (1991).
[18]D. J. Coulman, J. Wintterlin, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **64**, 1761 (1990).
[19]A. Borg, A.-M. Hilmen, and E. Bergene, Surf. Sci. **306**, 10 (1994).
[20]See, e.g., P. S. Weiss and D. M. Eigler, in *Nanosources and Manipulation on Atoms Under High Fields and Temperatures: Applications*, edited by V. T. Bink *et al.* (Kluwer, Dordrecht, the Netherlands, 1993), p. 213.