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Equilibrium morphology of Au(111) vicinal surfaces revealed by scanning tunneling microscopy

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We have investigated the thermal instability of Au(111) vicinal surfaces by scanning tunneling microscopy in ultrahigh vacuum. Above an annealing temperature of 700 K, both the Au(11,9,9) and the Au(4,3,3) surfaces undergo a phase separation into (111) facets and portions of (7,5,5). In addition, the faceted surfaces present a long-range order: the superperiod is 70 Å for Au(11,9,9) and 110 Å for Au(4,3,3). Large scale images show that this structure extends everywhere on the samples. It is demonstrated that the novel periodic morphology is an equilibrium state. Comparison is made with preliminary results of the Au(4,5,5) surface that belongs to the opposite zone. Observations suggest a dramatically different behavior: The surface phase separates into large (2,3,3) portions and a more complicated vicinal surface. The superperiod seems to be greater than 2000 Å. © 1996 American Vacuum Society.

I. INTRODUCTION

The morphology of clean surfaces can be responsible for dramatic effects in a great variety of phenomena, such as surface chemical reactivity or nucleation and growth of thin films. Vicinal surfaces, i.e., surfaces regularly stepped that are generated by a slight miscut with respect to a low-index plane, are interesting surfaces in the study of the relation between surface structure and surface energy. The surface free energy $\gamma(\theta, T)$ of the vicinal surface is given by

$$\gamma(\theta, T) = \gamma_0(T) + \frac{\beta(T)}{h} |\tan \theta| + g |\tan \theta|^3, \quad (1)$$

where θ is the angle of misorientation with respect to the close-packed surface, and γ_0 is the surface energy of the terraces. The second term is the contribution of each step, $\beta(T)$ being the energy per unit length to form an isolated step of monoatomic height h . The third term accounts for the interaction between steps.¹

Relation (1) is restricted to stable vicinal surfaces, i.e., thermodynamic equilibrium surfaces presenting one type of steps and terraces. For such surfaces, the tilt angle θ appears on the equilibrium shape (ES) of the crystal.² When the ES presents sharp edges, i.e., edges across which the orientation of the tangent plane to the crystal surface changes discontinuously, the corresponding orientations are unstable towards faceting:³ they phase separate into a "hill and valley" structure. ES of gold crystallites studied by Heyraud and Métois⁴ by electron microscopy present facets [(111) and (100)] and rounded parts separated by sharp edges. They found a discontinuity close to the (111) facet about 14°. In this article is reported surface morphology of Au(111) vicinal surfaces, which are misoriented with respect to Au(111) within 10°. Therefore, the orientations studied here are thermally unstable towards faceting.

Results on the faceted morphology of three orientations are presented: (11,9,9), (4,3,3), and (4,5,5). The zone axis is $\langle 01\bar{1} \rangle$, i.e., the step edges are oriented along $\langle 01\bar{1} \rangle$. But it is well known that on a (111) surface of a fcc crystal, $\langle 01\bar{1} \rangle$ -oriented steps may form either {111} or {100} microfacets depending whether the step-down direction coincides or is opposite to the $[\bar{2}11]$ direction. The surfaces Au(11,9,9) and Au(4,3,3) display both steps having {100} microfacets, whereas steps of Au(4,5,5) form {111} microfacets (see Fig. 1). Therefore, the influence of the step structure on faceting phenomena can be addressed in this work. The article is organized as follows: The authors briefly summarize their earlier work⁵ for Au(11,9,9) and Au(4,3,3). New data are presented for these surfaces at large scales. Then preliminary results for Au(4,5,5) are described. Finally, conclusions are drawn from the comparison of results in both zones.

II. EXPERIMENT

A homemade scanning tunneling microscope (STM), described elsewhere,⁶ was used and located inside an ultrahigh vacuum chamber (UHV) (base pressure about 10^{-10} Torr). Tungsten tips are etched by electrochemical erosion and cleaned *in situ* by resistive heating up to about 1000 °C before experiments. The conditions of tunneling current and sample tunneling voltage are, respectively, about 1 nA and a few hundred mV negative. The analysis chamber connected to the STM chamber contains a standard reverse-view LEED/Auger optics and sample preparation facilities: annealing and argon ion sputtering. The *ex situ* preparation of the samples is reported in Ref. 7. Samples have been prepared *in situ* by repeated cycles of ion bombardment (400 eV Ar⁺) followed by 10 min annealing. Temperatures of annealing range from 320 to 1000 K. The samples are always observed at room temperature (RT) after a natural cooling. In this article is reported the final state of the surface observed

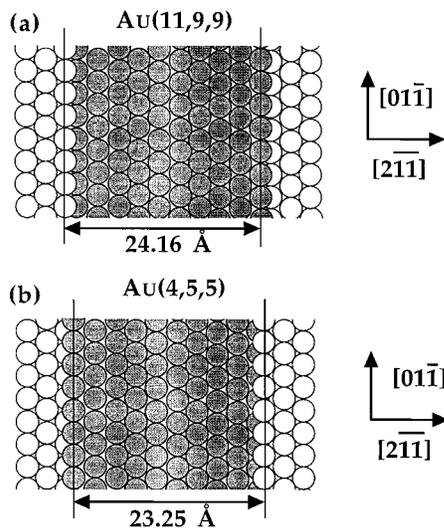


FIG. 1. Schematic diagram showing the ideal structure of the Au(11,9,9) surface (a) and the ideal structure of Au(4,5,5) (b) corresponding to a hard-sphere model.

for annealing temperatures above 700 K. Linear or quadratic background have been subtracted from the images, and images are corrected for thermal drift when necessary.

III. RESULTS AND DISCUSSION

A. Au(11,9,9) and Au(4,3,3): Thermal faceted morphology

In a notation first introduced by Lang and co-workers,⁸ the Au(11,9,9) surface [respectively, the Au(4,3,3) surface] is written $n(111) \times (100)$ with $n=10$ (respectively, $n=7$); n denotes the number of atomic rows in each terrace [see Fig. 1(a)]. The Au(11,9,9) is tilted to (111) by an angle of 5.57° , whereas the Au(4,3,3) is misoriented to (111) by an angle of 8.05° . The Au(11,9,9) ideally displays steps of monoatomic height ($h=2.35$ Å) regularly spaced by 24.2 Å. For the ideal Au(4,3,3) surface, the terrace width is 16.6 Å.

In both cases, when the annealing temperature is between 700 and 1000 K, the vicinal surfaces reach a similar final faceted state [see Figs. 2(a) and 2(b)]; a phase separation into (111) facets and portions of (7,5,5) orientation has occurred. The (7,5,5) vicinal belongs to the same zone axis as (11,9,9) and (4,3,3) orientations; it displays terraces 14.2 Å wide and it can be written $n(111) \times (100)$, with $n=6$. The LEED patterns of the faceted surfaces also present the doublet corresponding to the vicinal (7,5,5) surface, and these results are consistent with a previous LEED study.⁵ More surprising was the long-range order displayed by the faceted surfaces with a relatively small superperiod; 70 Å on Au(11,9,9) and 110 Å on Au(4,3,3) [see Figs. 2(a) and 2(b)]. In both cases, the size of the (111) facets is about 40 Å.

The samples were also observed in air with a Nanoscope III after the faceting phenomena had occurred in UHV (see Figs. 3 and 4). This allowed us to investigate the sample on a much larger scale (until about 10 μm), since the scanning range of our STM in UHV is restricted to about a maximum

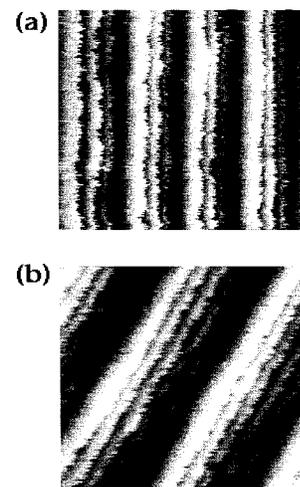


FIG. 2. Top view images of the final faceted surfaces obtained by STM in UHV at RT after annealing at temperatures between 700 and 1000 K. All steps are monoatomic, 2.35 Å high. Step edges are oriented along the $[01\bar{1}]$ direction. (a) Faceted Au(11,9,9), area 330 Å \times 290 Å, (b) faceted Au(4,3,3), area 250 Å \times 220 Å; in fact, quantitative statistical analysis indicates that the most probable number of steps within one period is 6.

size of 2 μm \times 2 μm. The superperiodicity appears almost everywhere on the surface. Even in one case, where the Au(4,3,3) sample presented long-range deformations in the three axis of symmetry of the (111) surface, the superperiod was not affected, and it is still clearly seen [see Fig. 4(b)]. These features can be due to a tip crash as observed by other authors.⁹ However, they might be due here to the fact that our sample in UHV was accidentally maintained with a large uniaxial stress during annealing. After another experiment without this artifact was conducted, the surface did not display any deformations. A careful LEED study was done on these surfaces and it demonstrated the presence of spots due to the superperiodicity.⁵

As a conclusion, both unstable vicinal surfaces, Au(11,9,9) and Au(4,3,3), belonging to the same zone, $n(111) \times (100)$, display a similar behavior under annealing; a periodic phase separation into (111) and (7,5,5) portions. The angle θ of misorientation of the (7,5,5) surface with respect to the (111) facet is 9.45° . This angle is close to the value of 14° found by Heyraud and Métois on the ES of gold crystallites. Therefore, this result, together with the fact that the surfaces do not evolve under a prolonged annealing or under an annealing at higher temperature, strongly suggests that the final states observed here are indeed equilibrium ones. It is then tempting to compare these results with observations on the opposite zone. Preliminary results on Au(4,5,5) are presented and discussed in the following section.

B. Thermal behavior of Au(4,5,5)

As mentioned before, the Au(4,5,5) surface belongs to the opposite zone than the previous vicinals described here, i.e., $n(111) \times (111)$ ($n=10$). Therefore, the terrace widths are very similar to the ideal Au(11,9,9) surface (see Fig. 1), but the step structures differ. The two first terms in the relation

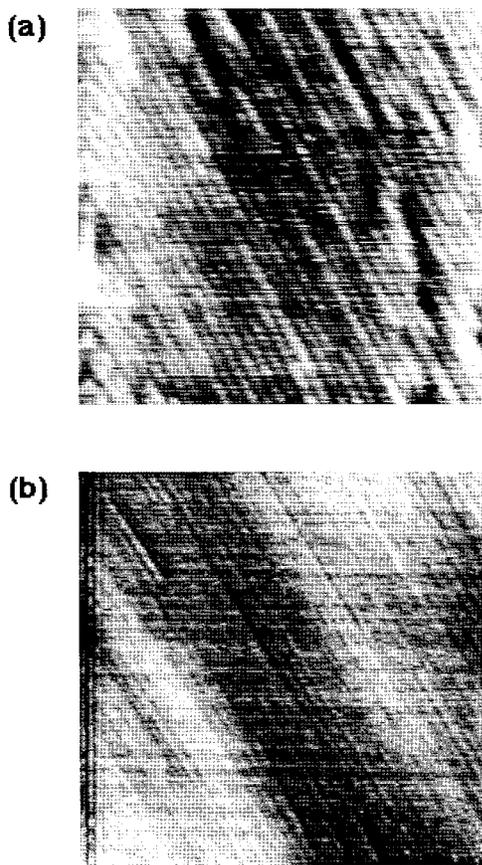


FIG. 3. Large-scale images of the Au(11,9,9) sample taken in air: (a) Area $200\text{ nm} \times 200\text{ nm}$, about 40 superperiods are seen; (b) area $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$, the surface revealed the same regularity, although the scale is too large to clearly distinguish all superperiods. Parallel stripes at the left-hand side of (b) are not real features but are artifacts due to the feedback loop.

(1) show that the surface free energies of both surfaces, the Au(11,9,9) and the Au(4,5,5), are different due to the value of the step energy β only. Indeed, the angle of misorientation of Au(4,5,5) with respect to (111), 5.76° , is again close to the one of Au(11,9,9). The question is whether this difference in β will lead to a different behavior or not.

The Au(4,5,5) first observed as it was introduced in the chamber without any further preparation reveals a regular stepped structure. The mean value of the terrace widths is about 23 \AA , as expected. Then, the sample was cleaned by repeated cycles of bombardment and annealing at 700 K . Images obtained at large scale [see Fig. 5(a)] reveals a quasi-periodic saw-and-tooth structure. Nanometer scale images confirm that indeed the surface is made of two kinds of orientations. In the following they will be referred to as “A” and “B.” On the contrary to what is usually observed in faceting phenomena, both A and B are stepped surfaces [see Fig. 5(b)]. All images obtained on A showed straight steps edges of monoatomic height separated by about 13 \AA . Structure B is more complicated to describe. Steps on B are separated by about 30 \AA . However, better resolved images reveal in addition that the steps are not straight. They are also periodically faceted (see Fig. 6) with a period of about 72 \AA .

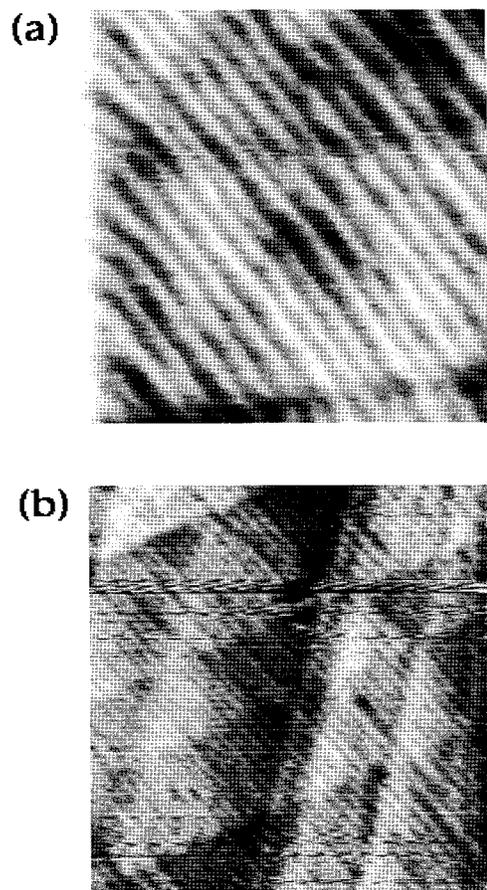


FIG. 4. Large-scale images of the faceted Au(4,3,3) sample taken in air: (a) area $196\text{ nm} \times 196\text{ nm}$, about 21 superperiods are clearly seen; (b) area $0.5\text{ }\mu\text{m} \times 0.5\text{ }\mu\text{m}$, the periodicity is apparent. Parallel stripes at the right-hand side of (b) are not real features but are artifacts due to the feedback loop. Additional features correspond to deformations in the three directions of symmetry on a (111) surface.

So far, the details of the steps edges are not clearly understood and are still under study. It seems that a misorientation of the surface in the azimuthal direction cannot account for the faceted structure of steps. The authors again checked the orientation of Au(4,5,5) by x rays coupled with an autocollimation technique: It indicates an error of $15'$ for the zone axis (one kink every 72 \AA would lead to a misorientation of 2°). In addition, the authors are studying other orientations in the same zone, and it seems that structure B appeared again on a much less tilted surface with respect to (111). On the other hand, orientation A is easier to interpret in comparison with earlier results. If we assume that surface A belongs to the same zone as the initial surface, the terraces should contain six atomic rows. Therefore, A seems to be a $6(111) \times (111)$ surface or Au(3,3,2). It has almost the same angle of misorientation close to 10° as the (7,5,5) found on the opposite zone (exactly 10.02°). When it is assumed that B may be close enough to (111), in order to be indistinguishable on the ES recorded by Heyraud and Métois, the results on Au(5,4,4) might be consistent with the ES of gold crystallites observed

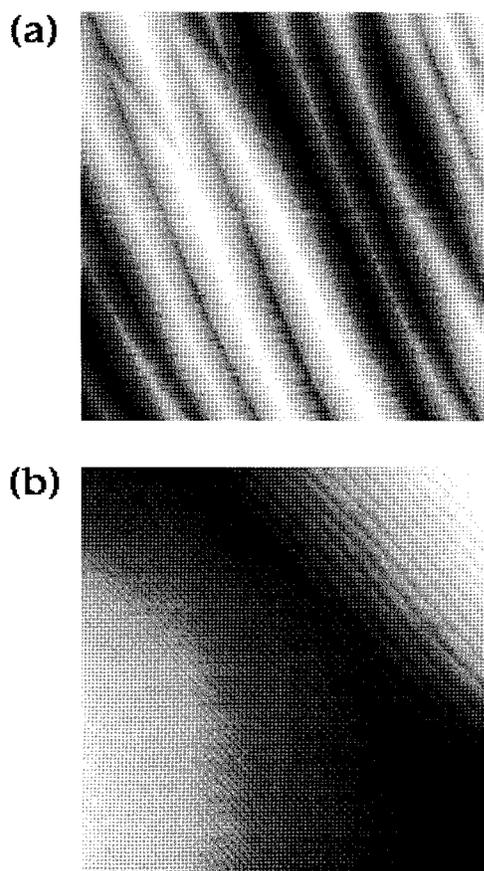


FIG. 5. STM images recorded on the Au(4,5,5) sample: (a) area $1.38 \mu\text{m} \times 1.38 \mu\text{m}$. The hill-and-valley structure presents about nine periods; (b) Area $892 \text{ \AA} \times 892 \text{ \AA}$, orientation "A" is seen on the left and orientation "B" is displayed on the right. All steps are monoatomic, 2.35 \AA high, descending from left to right.

by scanning electron microscopy. Actually, the sharp edges around the facets seemed to be isotropic. This is again an argument in favor of the fact that the morphology observed may be at equilibrium. However, since the effect of a pro-

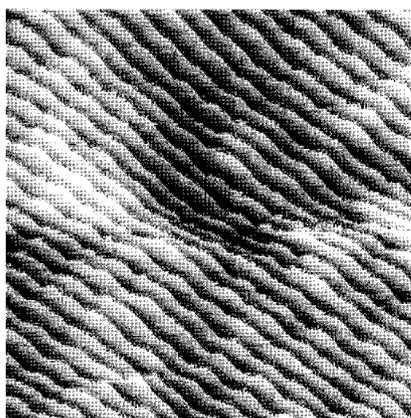


FIG. 6. STM image taken on the B orientation of the Au(4,5,5) sample. Area $680 \text{ \AA} \times 680 \text{ \AA}$. All steps are monoatomic. The steps are regularly faceted.

longed annealing or the effect of annealing at higher temperatures has not yet been studied, the authors cannot assert that this is a final state.

These preliminary results for Au(5,5,4) definitively suggest that the morphology of the surface is dramatically different from what was obtained for the opposite zone (see Sec. III A). It consists again of a quasiperiodic hill-and-valley structure, but the period seems to be much larger, about 2000 \AA [Fig. 5(a) has to be compared with Figs. 3(b) and 2(b)]. Indeed, due to the dependence of diffusion coefficients versus the temperature, it is reasonable to conclude that the surface would not evolve toward smaller facets at higher temperature.

IV. CONCLUSION

Au(111) vicinal surfaces, Au(11,9,9), Au(4,3,3), and Au(4,5,5) are thermally unstable towards faceting. Clean surfaces annealed at temperatures above 700 K separate into two phases. In all three cases, one phase is the vicinal surface of the same zone as the initial surface whose terraces contain six atomic rows each. This phase corresponds to the (7,5,5) orientation for Au(11,9,9) and Au(4,3,3), whereas it is (3,3,2) for Au(4,5,5). The reason why terraces consisting of six atomic rows are stable is not trivial. The role played by the well-known¹⁰ $22 \times \sqrt{3}$ reconstruction on Au(111) surface has been investigated in a previous work.⁵ It seems that the stability of the (7,5,5) surface cannot be interpreted in terms of the so-called "magic vicinals."¹¹ The other side of the hill-and-valley structure is a (111) terrace in both cases, Au(11,9,9) and Au(4,3,3), whereas it is a more complex vicinal surface for Au(4,5,5), which has a misorientation with respect to (111) of about 4° . In all three of the cases, the hill-and-valley structure presents a long-range order. The superperiodicity is, respectively, about 70 \AA for Au(11,9,9) and 110 \AA for Au(4,3,3), while it is at least about 2000 \AA for Au(4,5,5). Existing models¹² based on work-function variations⁷ or surface stress effects could account qualitatively for the formation of periodic domains, but more work is needed to understand the difference in behavior between the opposite zones $n(111) \times (111)$ and $n(111) \times (100)$, which differ only by the step structures.

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