Determination of atom positions at stacking-fault dislocations on Au(111) by scanning tunneling microscopy

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The determination of atom positions around Shockley-type partial dislocations [Burgers vector $\frac{1}{6}(1,1,-2)$] at the (111) surface of gold has been achieved by operating a scanning tunneling microscope with atomic resolution on regions containing several unit cells of the $(23\times\sqrt{3})$ stacking-fault reconstruction of this surface. The data show directly the occupation of both hexagonal-close-packed and face-centered-cubic sites in the surface layer, verifying earlier reconstruction models.

Gold takes a unique place among the metals showing the phenomenon of reconstruction at single-crystal surfaces because it is the only face-centered-cubic (fcc) metal whose (111) surface reconstructs. Experiments using low-energy electron diffraction (LEED),[1] reflection high-energy electron diffraction (RHEED),[2] and helium atom scattering (HAS)[3] have observed a $(22\pm1)\times\sqrt{3}$ reconstruction on Au(111). Transmission electron microscope (TEM) real-space images of small Au(111) platelets grown on MoS_2 revealed two bright stripes within the reconstructed unit cell, leading to a model for the surface-atom rearrangement which involves an ordered array of boundaries between surface regions with fcc-type stacking (*ABC*) and hexagonal-close-packed (hcp) stacking (*ABA*).[4]

We have measured the reconstruction of the Au(111) surface by scanning tunneling microscopy[5] (STM) and have made the first direct observation of atomic occupation of hcp sites on an fcc metal. These measurements are the first atomic resolution images of the partial dislocations at the surface which cause this reconstruction. Although STM studies of this surface have been performed earlier,[6–8] they have not clearly resolved the reconstruction. Previous STM measurements[7] on this surface associated an "ordered array of steps" with the reconstruction, in disagreement with earlier work on this surface. We have extended earlier measurements of the first observation of atomic corrugation on Au(111) thin films[8] to well-ordered surfaces on a bulk Au(111) single crystal. The good agreement of our atomic resolution images with previous models of the reconstruction[3,4] suggests that the STM measures spatially localized electronic states near the atomic cores. Our measurements can then be used directly to obtain the precise relative positions of the atoms in this large reconstructed unit cell. In addition, even in images without atomic resolution, we observe very clearly the domain boundaries between regions with hcp and fcc type atomic stacking.

The proposed model for this reconstruction[4] includes one stacking fault per unit cell. The top layer regions with hcp and fcc stacking are connected by partial Shockley dislocations,[9] which are described by Burgers vectors of $b_1=\frac{1}{6}(-2,1,2)$ and $b_2=\frac{1}{6}(1,-2,1)$. These two partial misfit dislocations add 0.5 atoms each, giving one extra atom per reconstructed unit cell, resulting in an average 4.2% contraction of the surface layer along the $[1\bar{1}0]$ direction. An investigation employing the scattering of thermal He atoms[3] with high energy and angular resolution revealed new structural information on the detailed shape of the boundaries and showed that the widths of the regions with fcc stacking are not equal to those with hcp stacking; the measured ratio of the widths was 0.7. The helium-scattering data could be described successfully by a Frenkel-Kontorova model[10] employing a sine-Gordon (SG) potential, giving a soliton lattice with two subsolitons (modeling the partial dislocations) per unit cell centered at the stacking fault edges. This model is shown in Fig. 1. Although the SG potential does not give different *ABC* and *ABA* domain sizes, the shape of the soliton boundaries agreed very satisfactorily with the information extracted from the He-scattering data.[3] Recently, a more appropriate theoretical treatment of this problem was performed, allowing for a slight difference in energy for *ABC* and *ABA* stacking by introducing a double-sine-Gordon (DSG) potential.[11] As a result, the different domain sizes observed experimentally were reproduced in the model, providing information on the

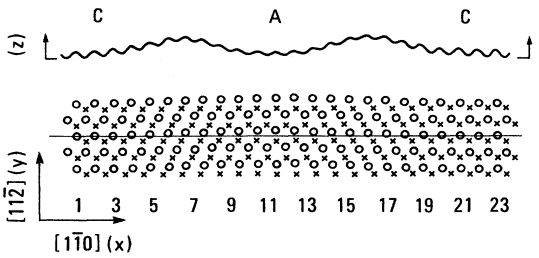

FIG. 1. Model for the reconstruction of the Au(111) surface (Ref. 3). The crosses denote the positions of atoms in the second layer, whereas open circles denote the positions of atoms in the reconstructed top layer. *C* and *A* mark the regions of *ABC* (fcc) and *ABA* (hcp) stacking, respectively. The lattice defect at the boundary between these two regions corresponds to a bulk Shockley partial dislocation with Burgers vector $\frac{1}{6}(1,1,-2)$. The displacement of the atoms from the straight line which has been drawn in the $[1\bar{1}0]$ direction is clear.

difference in energy between fcc and hcp sites. Although a thorough examination of relative excitation probabilities of surface phonons in He-atom time-of-flight spectroscopy gave some indication of surface regions with *ABA* stacking,[12] the occupation of hcp sites in the top plane was not confirmed directly.

Our STM measurements on Au(111) have been performed using an ultrahigh vacuum (UHV) instrument connected to a surface preparation and analysis system chamber by internal transfer mechanisms.[13] Electrochemically etched tungsten tips have been used for all tunneling experiments reported here. In addition to the thin epitaxial films of Au(111) grown on mica used in our earlier work, we also studied the surface of a Au(111) single crystal cut from a boule and prepared by standard methods, including prolonged cycles of Ar-ion sputtering (500 eV, ~ 2 μA/cm^2) and annealing at 1000 K. The sample was transferred to the STM chamber only after LEED reconstruction patterns resembling those reported in Ref. 14 were observed.

In Fig. 2(a) we show a low-resolution STM picture obtained from a $\sim 250 \times 90$ Å^2 region on the surface of the Au(111) single crystal at a tunneling tip voltage $V_T = 0.31$ V and a constant-tunneling current $i_T = 0.5$ nA. Pairs of stripes are clearly observed, with the distance between stripes ~ 22 Å and the distance between pairs ~ 44 Å. The stripes are interpreted as domain boundaries between the regions of ABC and ABA type stacking. In Fig. 2(b) a scan along the black line in the STM picture is given and shows a corrugation height of 0.15 ± 0.04 Å, in agreement with the helium-scattering data. For a hard-sphere model, a difference in height of 0.15 Å is expected between atoms in hollow and bridge sites.

The ratio of the regions between the domain boundaries in Fig. 2 is 0.5, thus confirming the observation of the different region widths reported in Ref. 3. However, there is a discrepancy from the previously reported ratio of 0.7, which was extracted from the He-scattering data by a fitting procedure involving several approximations.[3] In particular, the use of a simple hard-wall potential for simulating the He-atom surface interaction may give rise to problems, as the attractive van der Waals interaction is completely neglected. Since the relative size of the two different regions can be extracted from the STM images without any data analysis other than the subtraction of a planar background, the STM results should be more reliable.

STM images obtained for other regions of the surface looked very similar, although the orientation of the stripes was found to differ by multiples of 120° for different spots on the surface, thus confirming the earlier TEM[4] observations of three equivalent rotational domains at the surface. We have also observed boundaries between these different domains within single STM images, as well as imperfect reconstruction patterns, with lattice defects consisting of atoms pushed out of the surface at intersecting domain boundaries. In addition, our observations of atomic steps on this surface include images of the reconstruction continuing across a step and the possible effects of diffusion near a step. These topics will be presented in a forthcoming publication.[15]

In Fig. 3(a) we display an STM image which was obtained by reducing the scan range of the x piezoelectric element to 90 Å. As a result, the resolution visible in the STM images was considerably improved, and we were able to resolve the positions of ~ 500 atoms within the scanning region. The image was taken at $V_T = 0.31$ V and $i_T = 0.5$ nA. Figure 3(b) presents the corrugation along the black line in the STM picture, again providing a value of about 0.15 Å for the height of the solitons. A close look at Fig. 3(a) reveal that, in the smaller of the re-

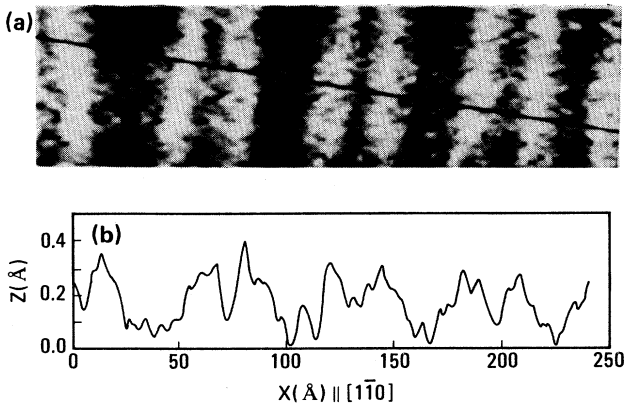

FIG. 2. (a) Low-resolution STM image of Au(111) single crystal, measured for $V_T = 0.31$ V and $i_T = 0.5$ nA, showing an area of 300×90 Å^2. The solitons, which separate the stripes of *ABC* and *ABA* stacking, respectively, are clearly visible. (b) A single-line scan along the black line denoted (a). From the corrugation along the solitons, a unit cell size of 63 ± 0.5 Å and a corrugation height of 0.15 ± 0.04 Å can be determined.

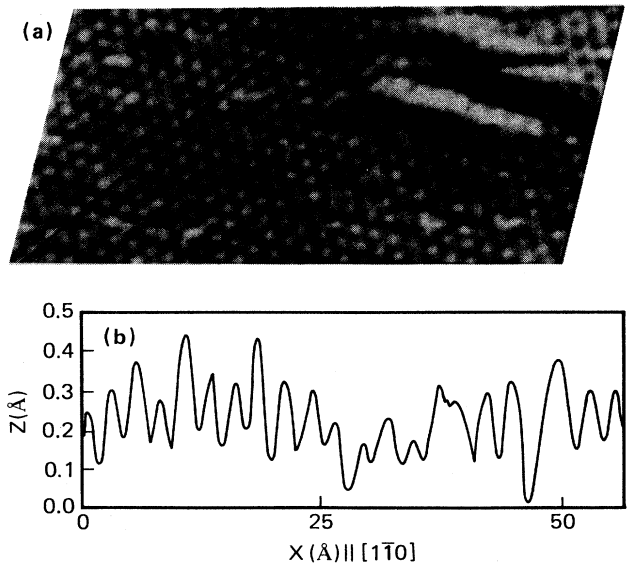

FIG. 3. (a) Atomic resolution STM image of Au(111) single crystal, measured for $V_T = 0.31$ V and $i_T = 0.5$ nA, showing a region of 90×40 Å^2, allowing the determination of the positions of single atoms in the reconstructed unit cell, with the domain boundaries appearing as bright stripes. (b) A single-line scan along the black line denoted in (a).

gions between the stripes, the atoms are gradually displaced along the direction parallel to the domain walls by about 0.7 ± 0.3 Å. This agrees with the value of 0.83 Å, obtained from a hard-sphere model, which assumes occupation of ABA sites in the smaller region between the stripes. This bending of the rows of surface atoms was present in all STM images which exhibited atomic resolution. The same effect is more obvious in the larger area atomic resolution image shown in Fig. 4. The atoms in the figure are clearly displaced from the indicated line, analogous to the line in the model of Fig. 1.

FIG. 4. STM image, taken in UHV at $V_T=0.611$ V and $i_T=0.3$ nA, for an epitaxially grown Au(111) thin film on mica, showing a region of 100×40 Å^2. The atomic resolution of the image allows the determination of the positions of single atoms, and the displacement of the atoms from the straight line in the $[1\bar{1}0]$ direction can be directly compared to the model in Fig. 1.

The stability of the tip appears to be the most important parameter for atomic resolution imaging on Au(111). We have now measured atomic resolution images at gap impedances as high as 8×10^8 Ω, corresponding to voltages of 1.6 V and currents of 0.2 nA, as well as in the low-gap-impedance regime $\sim10^7$ Ω reported previously.[8] Although we do not presently understand the differences between these measurements, we speculate that a single atom tip may be necessary in order to observe the small atomic corrugation on a metal surface. In contrast, the observation of larger periodic structure associated with the domain boundaries between regions of different stacking does not depend strongly on the gap impedance or the voltage polarity and can be observed both in images with atomic resolution and those without it.

A closer look at the corrugation profile in Fig. 3(b) reveals another interesting effect, namely that the atomic corrugation is larger in the regions where the atoms are raised above the surface because of the dislocation at the stacking fault edge. A detailed theoretical analysis of this difference may provide insight into the relative importance of contributions from localized electronic d states and from the delocalized (sp) states. A similar drain of sp charge has also been observed by Rieder *et al.*[16] for a stepped Ni(113) surface. The differences in the observed amplitude of the atomic corrugation may be similar to the asymmetries observed in the STM corrugation observed in the two halves of the unit cell on the Si(111) 7×7 surface,[17] which are believed to be associated with electronic structure differences in the faulted and unfaulted halves of the unit cell.

A detailed analysis of the core positions around a dislocation can give important information on the validity of the descriptions of metal-metal interactions on surfaces. Recently, several groups have reported their ability to describe single-crystal surfaces of gold in the framework of an embedded atom theory[18–20] or using a first-principles approach.[21] The atomic positions around a dislocation can be inferred from the STM data and can be used to test the theories. They should be an especially strong test of the long-range part of the interatomic potentials because the energy of a stacking fault in fcc metals is zero for a model incorporating only nearest-neighbor interactions. In this context, it should be noted that a recent study of the Au(111) surface within the embedded-atom approach[20] was able to reproduce some details of the reconstruction (e.g., the presence of regions with hexagonal stacking), but could not get the right value for the unit cell length. Although at present only qualitative arguments discussing the origin of the reconstruction on Au(111) are available,[22,23] our determination of the precise atomic arrangement at this surface should allow more quantitative theoretical descriptions of this reconstruction.

In conclusion, our results demonstrate that the STM can be used to study lattice defects at surfaces with atomic resolution, a subject of considerable importance in the study of crystal growth. The STM images presented in this work strongly substantiate earlier reconstruction models for the Au(111) surface.[3,4] As atomic resolution was obtained over large areas, the determination of atomic positions within a unit cell is unambiguous. The reconstruction has been confirmed to be describable by a regular array of partial Shockley dislocations. Future theoretical treatments of this Au(111) reconstruction may be possible, even though they would require a correct description of atomic interactions, not only between atoms at regular lattice positions but also at interstitial positions. It is hoped that this work will stimulate further theoretical investigations of this system.

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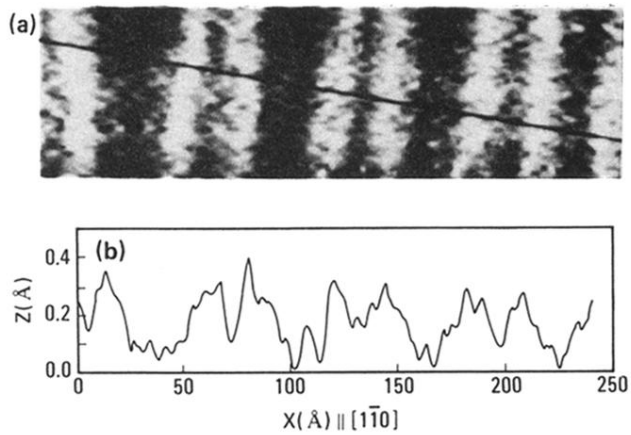

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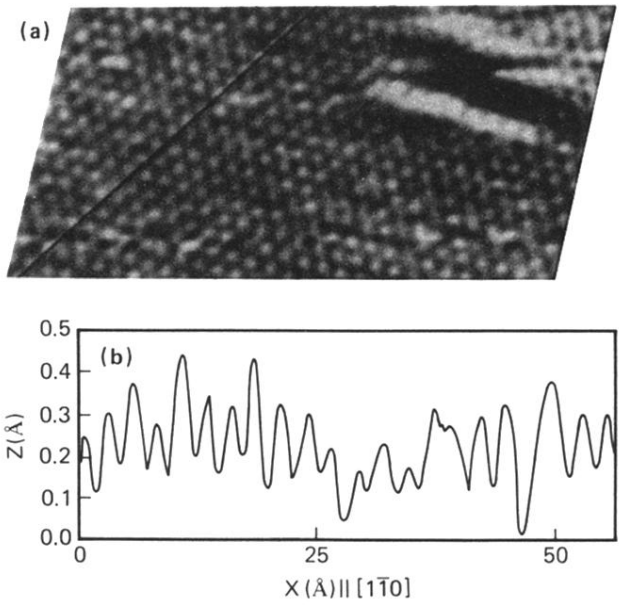

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