Observation of Atomic Corrugation on Au(111) by Scanning Tunneling Microscopy

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This work presents the first real-space images which resolve individual close-packed metal atoms on the surface of a Au(111) thin film. Measurements made in both air and ultrahigh-vacuum environments reveal the same highly ordered, laterally extensive close-packed structure with a corrugation amplitude of $\simeq 0.3$ Å at a tip bias of +30 mV and a tunneling current of 3 nA. The possible role of surface electronic states on Au(111) in producing the corrugations imaged by the scanning tunneling microscope is discussed.

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Resolution of individual close-packed metal atoms with the scanning tunneling microscope (STM) has not previously been achieved, although images of monolayer-height steps[1-3] and corrugation effects arising from surface reconstructions[4-8] have been obtained. Close-packed surfaces such as Au(111) typically exhibit extensive terraces separated by broad steps of monolayer height, and the absence of corrugation along these terraces has been interpreted as atomic flatness of these metal surfaces.[1,2] STM images of reconstructions of other low-index planes, e.g., (110) and (100) faces of Au[4,5,8] and Pt,[7] reveal long parallel hills and channels, again with no observable corrugation along the channel direction which could be assigned to individual atoms. This inability to resolve individual close-packed metal atoms has been attributed to an intrinsic smoothing of electron-density distributions at the surface due to the free-electron nature of metals.

In this Letter, we report the first observation of atomic corrugation for a close-packed metal surface. In contrast to the measurements referenced above, individual metal atoms are clearly resolved in our images of Au(111) thin films. These novel results are obtained in both air and ultrahigh-vacuum (UHV) environments and reveal a stable, inert surface with a highly ordered, closed-packed gold lattice. The observation of a substantial corrugation, approximately 0.3 Å, has important implications for future studies of clean and adsorbate-covered metal surfaces and raises significant questions about the theoretical understanding of electronic structure and corrugation in these systems.

Au(111) samples were prepared by epitaxial evaporative deposition[9] of a 2500-Å thickness of gold onto cleaved mica substrates maintained at 300 °C. Deposition rates near 5 Å/s were monitored by a quartz microbalance. The samples were allowed to cool radiatively in the evaporator system (base pressure $\simeq 10^{-6}$ Torr) before transfer to one of two different STM systems.

Images in air were obtained with a "pocket-size" microscope[10] including a stack of stainless-steel plates separated by Viton spacers, a piezoelectric tube tripod for scanning the tunneling tip, and a micrometer for coarse approach of the sample to the tip. Samples were cemented to a quartz insulator mounted on the micrometer stage, and electrical contact was provided by the attachment of a wire to the gold surface with conductive epoxy. Tunneling images were obtained in the fast-scan mode[11] by scanning of the X and Y piezoelectric elements at rates of $\simeq 40$ and 0.04 Hz, respectively, while maintaining the tip at a constant average distance above the sample, so that the tunneling current was modulated by the corrugation of the surface electron density. Tip voltages were typically 50 to 500 mV, positive or negative, and the dc level of the tunneling current was maintained at 2 nA. Tunneling-current images were digitized and recorded directly onto video tape with an overall acquisition time of $\simeq 10$ s/frame.

Measurements were also performed in a multichamber UHV STM system with extensive surface preparation and analysis facilities,[12] previously employed to investigate structures of metal overlayers on silicon.[13] The sample was fastened by tantalum clamps lined with gold foil to a tantalum carrier, then loaded via an airlock into the UHV system (base pressure $\leq 10^{-10}$ Torr). Auger-electron spectroscopy disclosed a substantial carbon contamination on the untreated Au(111) sample. Although diffuse low-energy electron diffraction (LEED) 1×1 patterns were acquired for the uncleaned sample, Ar^+ sputtering followed by annealing to 360 °C via electron bombardment of the Ta carrier resulted in sharper LEED spots with lower background. This treatment also reduced contamination, as measured with Auger-electron spectroscopy, to levels less than 1% of a monolayer. Scanning electron microscopy disclosed a mosaic structure, with grain size varying from 0.5 to 0.02 mm depending on sample thermal history. Within such domains, previous field-emission scanning-electron-microscopy images of uncleaned samples had shown no resolvable structure ≥ 50 Å. After preparation and analysis, the sample and carrier were loaded into the STM. Images from this instrument were obtained in the slow-scan mode[14] (100 Å/s) by our monitoring the

movement of the Z piezoelectric element while maintaining a constant tunneling current of 3 nA. Acquisition times were approximately 5 min per picture. Tip voltages again varied between 50 and 500 mV, both positive and negative.

The first atomic corrugation was observed for Au(111) with the air STM. The representative tunneling-current image in Fig. 1 reveals hexagonal close packing over dimensions of $\simeq 25 \times 15$ Å.[2] The observed atomic spacing of $\simeq 2.8 \pm 0.3$ Å, as calibrated against graphite measurements from this instrument, compares well with the known gold interatomic distance of 2.88 Å. This close-packed structure persisted for tip translations of hundreds of angstroms in the lateral directions. The magnitude of the observed current modulation in this fast-scan mode was $\simeq 10\%$ of the dc tunneling current. Images with this instrument were readily obtainable from four separate Au(111) samples, at various positions on each sample and with a series of different tunneling tips. The observed corrugation may represent either the metal surface itself or an ordered contamination layer since there is no independent assessment of sample cleanliness for this air measurement. Samples coated with controlled contamination layers, in the form of organic monolayer films deposited immediately after removel from the evaporator system, were also imaged in the air microscope. Films of cadmium arachidate transferred from a Langmuir-Blodgett trough[15] and of octadecyltrichlorosilane self-assembled from solution[16] onto Au(111) presented the same highly ordered close-packed STM images over most of their surfaces as observed for the uncoated gold samples. Since atmospheric contamination seems unlikely to result in well-ordered films comparable to those formed by the Langmuir-Blodgett or self-assembly methods, we believe that the observed images originate from the gold substrate. These results are consistent with reports of imaging of gold surfaces with no interference from submersion in paraffin oil.[17]

To address the contamination question unequivocally, a Au(111) thin-film sample was transferred into the UHV STM system. Our few attempts to image the surface corrugation in the slow-scan, constant-current mode before cleaning the surface were not successful because of tip instabilities, although fast-scan tunneling-current images indicated the presence of atomic corrugation.

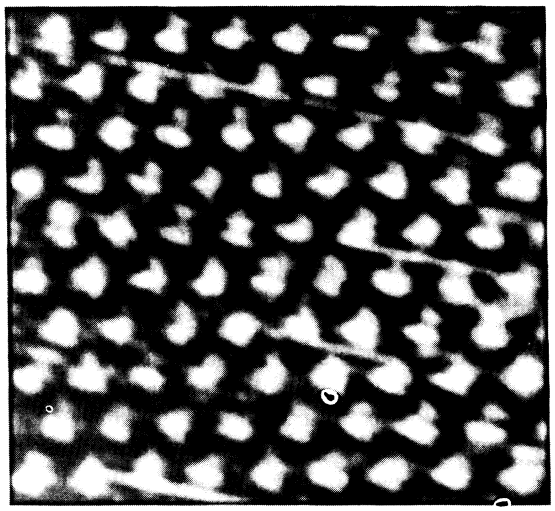
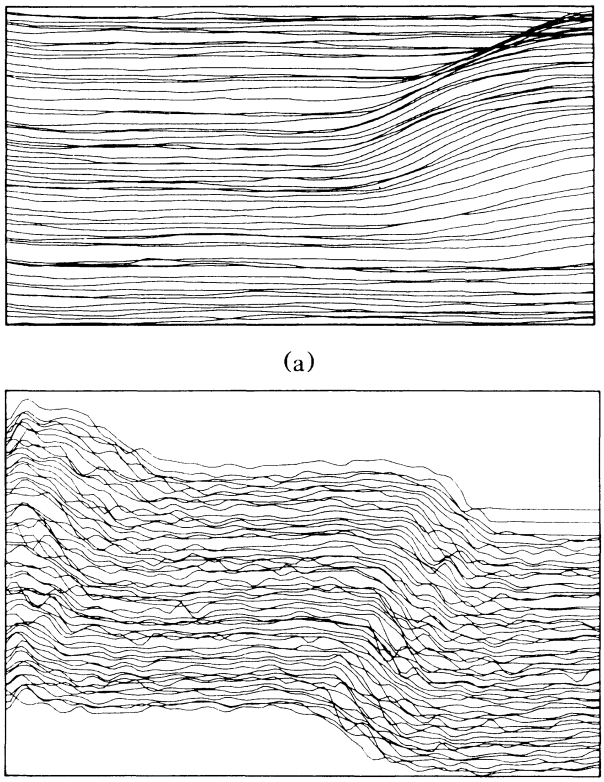


FIG. 1. STM tunneling-current image of a $\simeq 25 \times 25$-Å^2 region of a Au(111) thin film measured in air, with an atomic spacing of 2.8 ± 0.3 Å. The current modulation is $\simeq 10\%$ with a dc level of 2 nA and a tip bias of +50 mV. This figure has been corrected for thermal drift and piezoelectric creep. The diagonal streaks correspond to sudden jumps in the dc current level along scan lines in the fast direction.



(a)

(b)

FIG. 2. STM topographical line scans from a clean Au(111) surface measured in UHV, with a tip bias of +20 mV and 3-nA tunneling current. (a) In this $\simeq 150 \times 90$-Å^2 region, a step of height $\simeq 2.5$ Å and width about 40 Å is located at the right of the image. The evident low lateral resolution precludes interpretation of the lack of corrugation on the terraces as atomic flatness, even though the vertical resolution is $\simeq 0.1$ Å. (b) An area of $\simeq 90 \times 50$ Å^2, with the same vertical scale as in (a), showing two monolayer steps. Some corrugation is apparent along many scan lines, and the width of the step in the center of the image is much narrower than in (a), ranging from 5 to 10 Å for various scan lines.

After sputtering and annealing of the sample to remove the carbon contamination observed by Auger-electron-spectroscopy, initial slow scans resembled those reported by other researchers: Large terraces, often extending for thousands of angstroms, were separated by broad steps of monolayer height, as shown in Fig. 2(a). Although step-terrace structures were evident, the poor lateral resolution at the step edge makes interpretations of the terraces as defect-free, atomically flat surfaces highly questionable. Improvements in tip resolution may sometimes be induced by the enlargement of the tip bias from a typical operating value of $\simeq 50$ mV to > 1 V for several seconds, or by an increase of the tunneling current by up to a factor of 3 for $\simeq 30$ s, followed by lateral movement of the tip to a new position. Indeed, this sharpening procedure resulted in observable corrugation along the terraces and in narrowing of the step width, as demonstrated by Fig. 2(b), although tip instabilities during this transition period appear to cause many line-to-line fluctuations. Nevertheless, after we attained still higher lateral and vertical resolution, clear atomic corrugation could be stabilized over reasonable scan areas, as in Fig. 3. Images of these close-packed features were obtained while we varied the lateral tip position for many hundreds of angstroms in any direction. At a tip bias of $\simeq 50$ mV, identical images were obtained with either polarity of the tip bias. The vertical corrugation was typically $\simeq 0.3$ Å, but ranged from 0.05 Å when first becoming resolvable to over 0.5 Å during short periods of high tip instability. In comparison to the constant-current corrugation amplitude of $\simeq 0.3$ Å at a tip bias of 30 mV and a tunneling current of 3 nA, successive constant-height measurements under identical conditions showed the same 10% current modulation as obtained on the contaminated samples in air. Calibration of the Au(111) images against Si(111) 7×7 images obtained with this UHV microscope give a near-neighbor distance of 3.0 ± 0.3 Å. The absence of any measurable contamination, combined with the appropriate hexagonal packing and spacing for the Au(111) surface, conclusively supports assignment of the observed corrugation to the metal lattice itself.

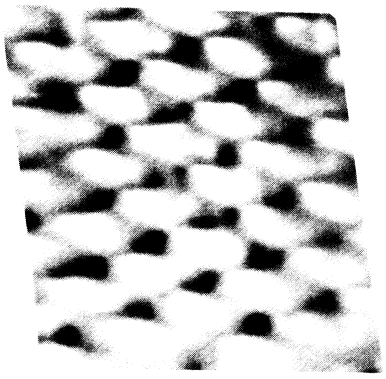


FIG. 3. STM topographical image of $\simeq 12 \times 14$-Å^2 region of a clean Au(111) thin film measured in UHV with high lateral and vertical resolution. The atomic spacing is 3.0 ± 0.3 Å. The corrugation is 0.3 Å at a tip bias of +30 mV and a tunneling current of 3 nA. This figure has been corrected for thermal drift and piezoelectric creep. We attribute the elongation of the observed atoms in the slow-scan direction to an asymmetric tip.

These images represent the first observation of close-packed atomic corrugation for a metal surface. The expectation of little or no discernible corrugation for this surface because of the free-electron nature of gold has contributed to the oversight of such structure. Other researchers[1] have indeed reported flatness down to a few tenths of 1 Å other than at steps, but lateral resolution in these experiments, as monitored by step widths, may be insufficient to observe atomic corrugation. Also, our experimental conditions of $\simeq 30$-mV tip bias and 3-nA tunneling current yield a tunneling resistance of 10^7 Ω, which is much smaller than the typical value of 10^9 Ω used in other STM experiments. Indeed, we were unable to image the atomic corruagation at a tunneling resistance of 2×10^8 Ω: With parameters of > 0.5 V and 2 nA the tip became unstable, and at 50 mV and 0.2 nA the corrugation was overwhelmed by noise. This order-of-magnitude increase in the tunneling resistance can be expected to correspond to about a 1-Å increase in the tip-to-surface distance, suggesting that the images presented here sample an electronic corrugation with spatial extent too small for previous STM studies of metals to have detected. We believe that the combination of high lateral and vertical resolution, low tunneling resistance, and excellent instrumental stability accounts for our novel observation of metal atomic corrugation.

Since our observed corrugation is much larger than the atomic corrugation for close-packed metals,[18] a significant electronic enhancement must exist. Such electronic enhancements have been described previously for semiconductor[19] and semimetal surfaces.[20] For gold, the presence of the bulk band gap at the L point[21] suggests that a surface state near the Fermi level (E_F) may contribute strongly to the tunneling current. Experimental evidence for such a surface state on Au(111) with an energy peak at -0.5 V exists from both tunneling spectroscopy[1] and photoemission.[22] Inverse photoemission studies[23] on Au(111) indicate the continuation of this surface state above E_F, so that tunneling into or out of this state under our experimental conditions is possible. Since the peak in the density of states due to the surface state is $\simeq 0.3$ eV from the bulk band edge, it seems reasonable to suggest that the state is localized to approximately atomic dimensions.

In summary, we have imaged individual close-packed metal atoms on Au(111) thin films by scanning tunneling microscopy performed with high lateral and vertical

resolution and low tunneling resistance. Thin epitaxial metal films grown on mica represent a simple way to obtain (111) metal surfaces with very large, flat terraces separated by monolayer steps, and are amenable to cleaning and analysis in UHV with standard surface techniques. The similarity between images obtained in air, both with and without adsorbed organic monolayer films, and from clean samples in UHV indicates that the Au(111) surface is valuable as an alternative system to highly oriented pyrolytic graphite to obtain atomic-resolution images in air or fluid ambients for purposes of instrumental calibration. In response to this unexpected success in the utilization of the STM to image individual atoms on metal surfaces, STM studies of metals and chemical reactions occurring at their surfaces should receive renewed attention.

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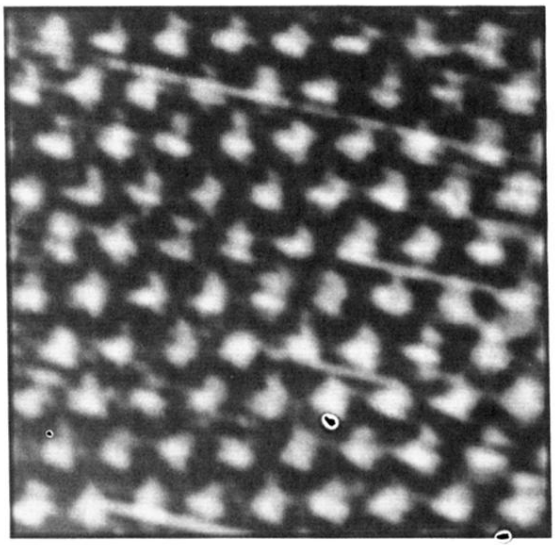

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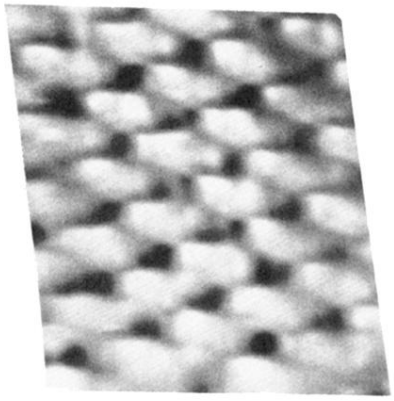

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