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Observation of Atomic Corrugation on Au(111) and Iodine on Pt(111) in Air

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Synopsis. The STM images acquired in the constant current mode were found to resolve individual close-packed gold atoms on Au(111) and iodine atoms on Pt(111). Measurements were made in air on the facets formed on single crystal spheres. Single crystals were prepared by melting pure metal wires with a hydrogen–oxygen flame.

The resolution of individual close-packed gold atoms has previously been achieved on Au(111) films on mica in both ultrahigh vacuum (UHV) and air environments.1,2) More recently, adlattices of iodine irreversibly adsorbed on Pt(111) have been clearly resolved in an air environment.3)

Au films were prepared for a previous study1,2) by epitaxial deposition of cleaved mica in a UHV. These films were also used for in situ STM studies in electrochemical environments.4,5) Atomically flat surfaces of Pt(111) after being polished were usually prepared by an annealing method in a flame;3,6,7) this method was originally developed by Clavilier et al.8) It was reported in our previous paper that carefully prepared Pt single crystal spheres always consist of eight fairly large facets of (111) in an octahedral configuration.7) STM images obtained on a Pt(111) facet indicated that the surface of Pt(111) is atomically flat with a few monatomic steps.7) Schneir et al. presented STM images of Au(111) facets prepared by a similar method employed for the Pt(111) facets.9) The resolution of individual metal atoms has not yet been achieved on these facets, although images of monatomic steps have been obtained in both air and aqueous electrolyte solutions.7,9)

In this letter we report on the atomic corrugations for Au(111)(1×1) and an adlattice of iodine on Pt(111). Single crystals of Pt and Au spheres were prepared by a method of Clavilier et al.,8) as described in our previous paper.7) Spheres 2—3 mm in diameter comprise eight facets of the (111) surface in an octahedral configuration. In order to expose clean surfaces, Au and Pt spheres were annealed in a hydrogen–oxygen flame near 500 and 1000 °C for 1 minute, respectively, and then quickly brought into contact with ultrapure water (Millipore-Q) saturated with hydrogen.7)

The STM unit used was similar to that described by Hansma et al.9,10) A fine mechanical approach was achieved by a 10:1 reducing lever. A piezo-electric tube scanner was kindly supplied from Seiko Instruments Inc. A digital data acquisition and image processing system (Seiko I.) was employed, as described previously.7) Mechanically polished tungsten wires were used as the tip electrode. The single crystal sphere was firmly held on a holder and mounted on the STM unit. The Au sphere emmersed from water was kept under a nitrogen stream and subjected to STM measurements. The Pt sphere was either exposed in an I_2–nitrogen stream or immersed in a KI solution (1×10^{-4} M, 1 M=1 mol dm^{-3}), as described by Schardt et al.3) and Hubbard et al.,11,12) respectively.

Figure 1 shows an STM topographic image showing 80×80 nm^2 area of an Au(111) facet in air. Very flat terraces and a few steps were consistently observed. The height of each step was ca. 0.23 nm, in accord with the monatomic step height of 0.235 nm on the Au(111) surface. Figure 2-a shows an STM topographical line scan over a dimension of 3.5×3.5 nm^2 obtained at a constant tunneling current of 3 nA. The sample voltage and the x-scan rate were 50 mV and 50 ms/line, respectively. The z-direction was calibrated with the heights of monatomic steps on Au(111) and Pt(111) surfaces. The x- and y-directions were calibrated against graphite measurements. Figure 2-b is presented as a top-view image of the same data as in Fig. 2-a, revealing a hexagonal close-packed structure. The observed spacing is comparable with a gold interatomic distance of 0.288 nm. A similar value was reported in a previous report.1) We found that the corrugation heights are in the range of 0.03—0.05 nm, as shown in Fig. 2-a, acquired in the constant current mode. The close-packed structure can also be clearly observed on a

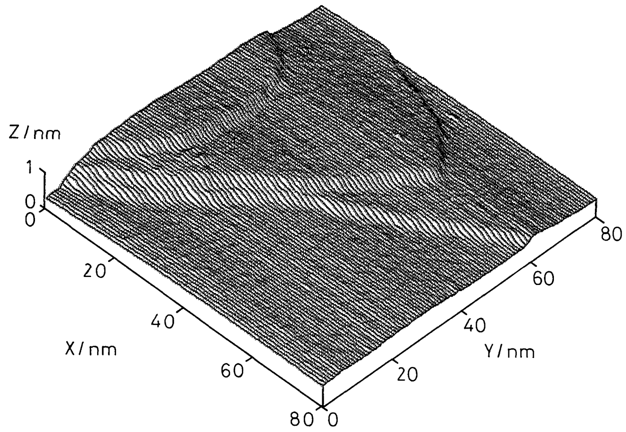

Fig. 1. An STM image of an 80×80 nm^2 region of an Au(111) facet surface observed in air. The sample voltage and the x-scan rate were 50 mV and 500 ms/line, respectively.

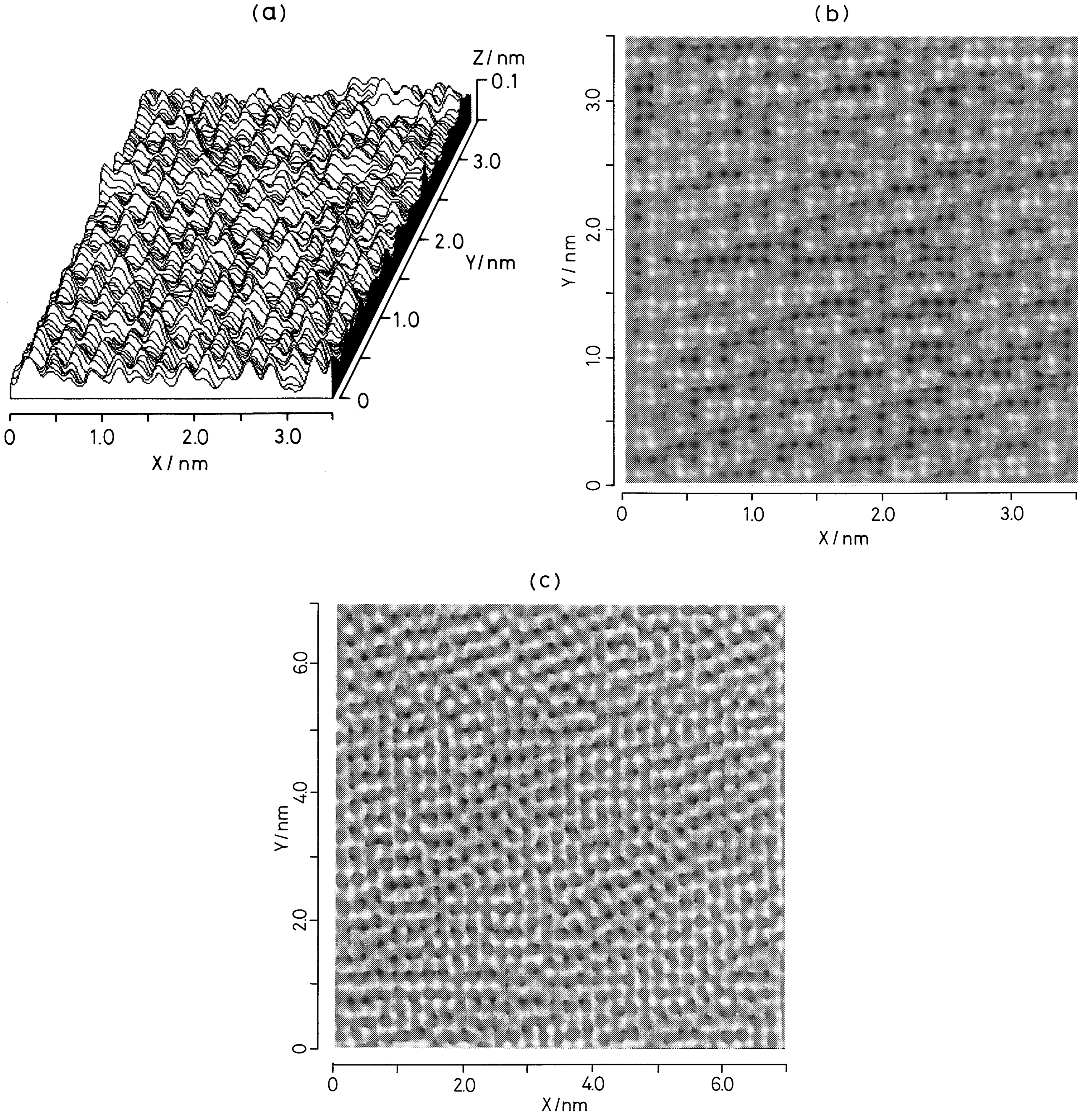

Fig. 2. STM topographic line scans (a), and a topview (b) of a 3.5×3.5 nm^2 region of an Au(111) facet. (c) is a topview of a 7×7 nm^2 region. The sample voltage and the x-scan rate were 50 mV and 50 ms/line, respectively. The tunneling current was 3 nA.

larger area of 7×7 nm^2, as shown in Fig. 2-c. As pointed out in our previous paper,[7] observations of the atomic corrugation of platinum in air seems to be more difficult than those of gold, because of a stronger tendency of Pt surfaces to absorb various impurities. However, the close-packed structure on Au(111) persisted in air for at least several hours. We can now conclude that the Au(111) facet prepared by the present method has an ideal (1×1) structure in air. D'agostino and Ross previously showed using a UHV-electrochemical system that reconstructed Au(111) surfaces were transformed to the (1×1) structure upon contact with water.[13]

Although we have not yet obtained images with a resolution of individual Pt atoms in air as discussed above, adlattices of iodine adsorpted on a Pt(111) facet could be relatively easily seen in air. Figure 3-a shows a typical image of topographical line scans over a dimension of 3.5×3.5 nm^2 obtained at a constant current of 2 nA. The hexagonal close-packed structure can be more easily recognized in a top-view image of Fig. 3-a, as shown in Fig. 3-b. The observed atomic spacing of ca. 0.4 nm compares well with the iodine interatomic distance of 0.415 nm, as expected for both $(\sqrt{7}\times\sqrt{7})$ and (3×3) structures.[12)] Images of the iodine adlattice on Pt(111) have been previously measured in the constant height mode.[3)] Two types of iodine atoms were distinguished, which seemed to be located on top of a Pt atom and at a three fold hollow site, respectively.[3)] However, it is interesting to note that all iodine atoms seem to show a similar corrugation height (ca. 0.05 nm) in the image acquired under the present condition using the constant current mode, as shown in Fig. 3-a. A detailed comparison of images obtained with the different modes are required for a further discussion of the structures of iodine adlattices.

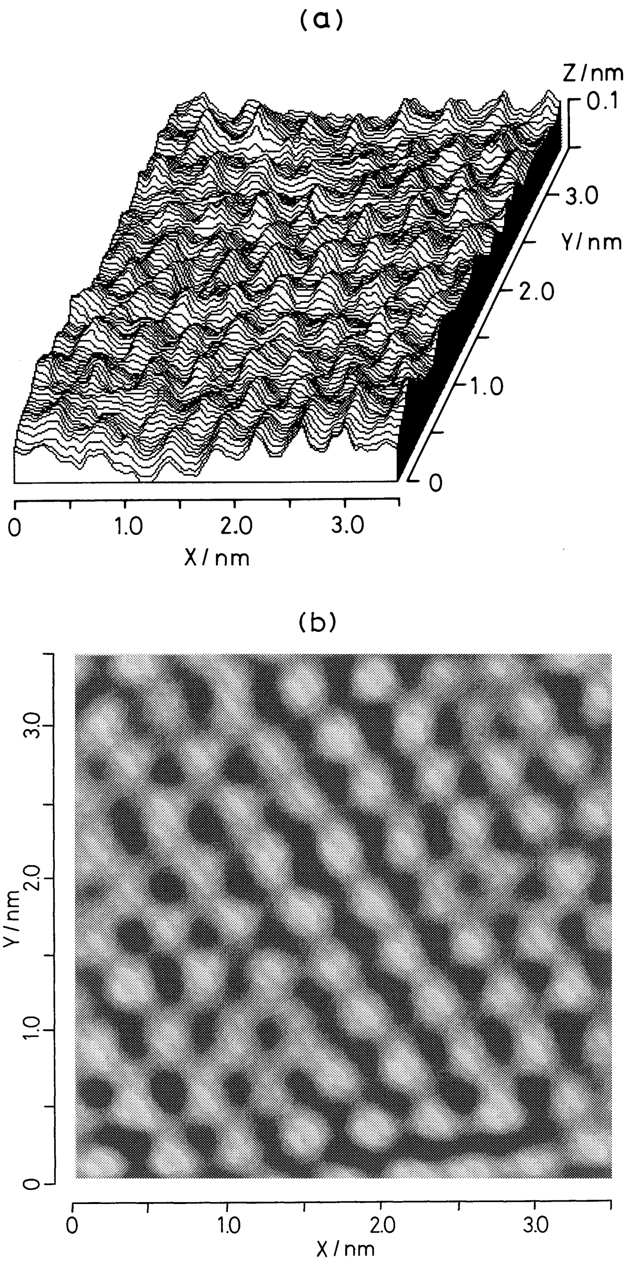

Fig. 3. STM topographic line scans (a), and a topview (b) of a 3.5×3.5 nm^2 region of an iodine adlattice on a Pt(111) facet. The sample voltage and the x-scan rate were −5 mV and 50 ms/line, respectively. The tunneling current was 2 nA.

In summary, we could resolve individual gold and iodine atoms on atomically flat facets with the constant current mode of microscope operation. Atomic resolution images of other adsorbates are now of special interest.

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