Atomic resolution scanning tunneling microscopy images of Au(111) surfaces in air and polar organic solvents

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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1991 issue.

COMMUNICATIONS

Atomic resolution scanning tunneling microscopy images of Au(111) surfaces in air and polar organic solvents

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In vacuum, atomic resolution of surface topographies has been achieved with the scanning tunneling microscope (STM) almost routinely for a number of years.[1] Although the operation of an STM in an electrochemical environment was demonstrated at an early stage,[2] atomic scale features in aqueous solutions, with electrode potential control of a single-crystal metal surface, have only recently been reported.[3,4] The differences between the STM operation in vacuum and in solution are expected to arise from the intricate interactions between electrons and a dense ensemble of polar molecules, which have been revealed by numerous experimental and theoretical investigations in the last few years.[5–8] Unfortunately, in electrochemical applications of the STM, perhaps not enough consideration has been given to the physics of electron transfer across the liquid gap and attention has mainly been devoted to environmental difficulties, such as chemical or electrochemical reactions at the tip or the sample as well as impurity effects from solution.[9,10]

In the present investigation, we have chosen liquid media which are chemically more inert than aqueous solutions. We have also tried to avoid a major source of disturbances in electrochemical studies which is the contribution to the current flow across the gap by parasitic faradaic processes originating at metal-electrolyte interfaces.[9,10] The magnitude of this interference, which essentially originates from the whole exposed surface of the tip, is dependent upon the ionic conductivity of the liquid medium and in the absence of a solute may be expected to be substantially reduced.

Organic polar solvents provide a rich variety of molecular architecture. At this early stage of our investigations, the choice of the protic solvents triethylene glycol and glycerol and the aprotic solvent propylene carbonate was mainly motivated, however, by their low vapor pressures at room temperature. This permitted operation of the STM by just placing a drop of the liquid in the region of the gap, without the need for a special cell to avoid the loss of the solvent within a matter of minutes. An additional benefit of these liquids is that their conductivity is not affected by the introduction of CO_2 from the atmospheric environment. As a result, the faradaic current of 1 nA/0.1 V observed in triethylene glycol, for example, did not change significantly over several hours and permitted the use of tunneling voltages up to $\sim$0.6 V. Atmospheric gases are, however, a potential source or problems for this type of experimental arrangement. We used mechanically polished iridium tips and the Au samples were prepared by evaporating a 2000 Å thick gold film onto tempax glass at a pressure of 10^{-6} Torr. For better adhesion a thin chromium layer ($\sim$20 Å) was evaporated onto the glass substrate before the gold was deposited. Each sample was flame annealed at $\sim$1000 K for $\sim$1 minute and subsequently quenched in methanol. This treatment produces large regions of atomically flat (111) terraces, often extending over thousands of angstroms. The beetle-type STM, designed by one of the authors,[11] was used in a liquid for the first time during this investigation. The images shown are derivative representations of the tip height above the sample.

Au(111) is the only fcc close packed surface which shows a reconstruction. The rearrangement in the topmost layer is due to an uniaxial compression of $\sim$4.3% in the ⟨110⟩ direction, which alleviates the stress induced by the different binding environment in the first layer.[12] The other low-index faces of gold also show surface reconstructions and the origins of the driving forces for these processes have been discussed in detail by several authors.[13,14] The $(\sqrt{3} \times 23)$ reconstruction of Au(111) has been studied previously by a variety of techniques[15,16] and has recently been the subject of a number of STM investigations.[12,17,18] In these studies the reconstruction is imaged as a periodic arrangement of paired lines running in the ⟨211⟩ direction. The distance between twinned lines in the ⟨110⟩ direction is approximately 25 Å, the unit cell dimension is 63 Å, and the corrugation amplitude normal to the surface is on the order of 0.15–0.25 Å. Hallmark *et al.*[17] obtained the first atomic resolution images of Au(111) in UHV and they were also able to obtain similar resolution in air. Wöll *et al.*[18] reported images in UHV which showed the surface reconstruction, but Barth *et al.*[12] produced the first images,

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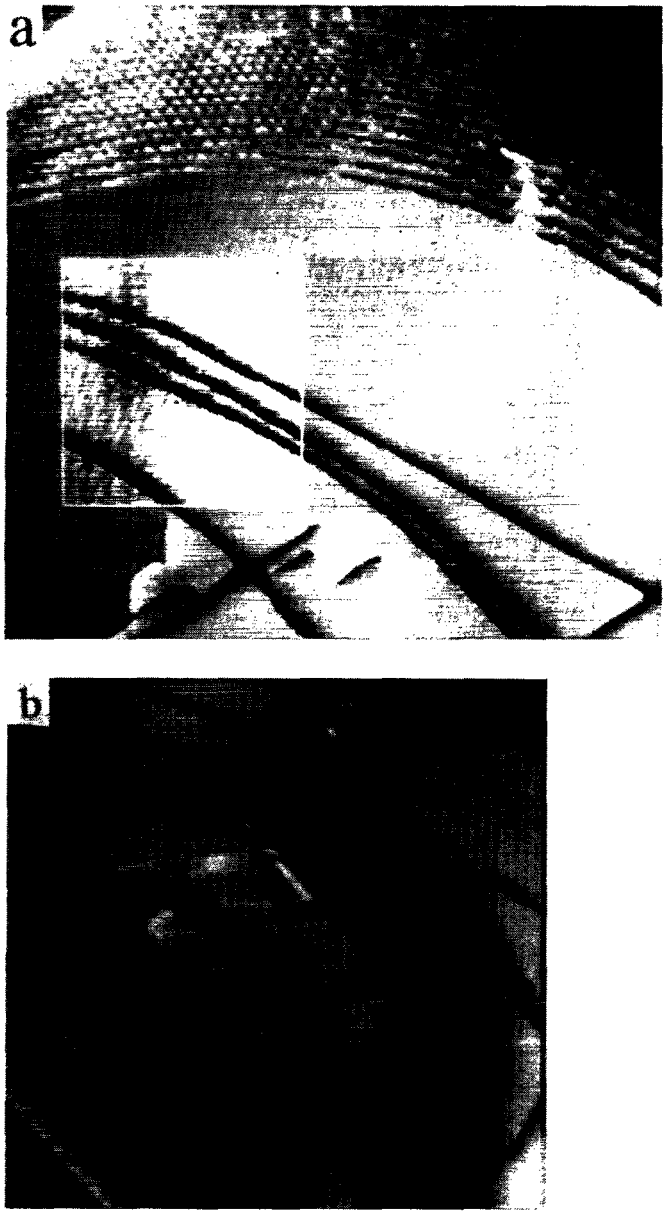

FIG. 1. Large area STM images of evaporated gold films, showing (111) terraces separated by regions of high monoatomic step density (4200×4200 Å^2). (a) In air ($V_t = +20$ mV, $I_t = 7.7$ nA); the inset shows a contrast-enhanced image. (b) In glycerol ($V_t = +100$ mV, $I_t = 20$ nA).

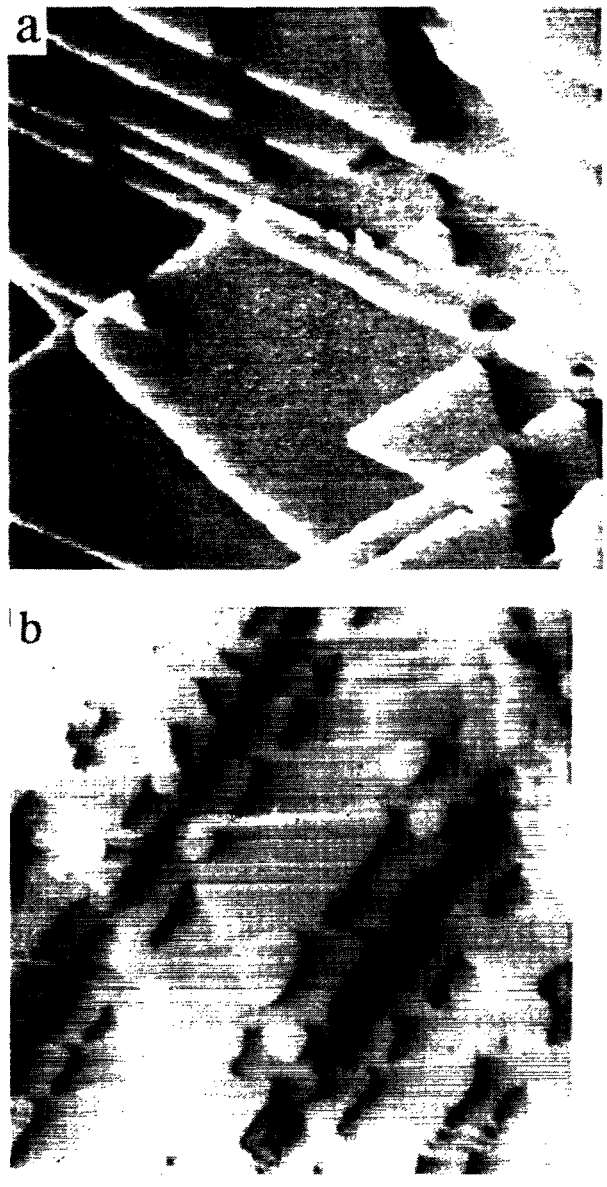

FIG. 2. Highly stepped areas of a gold film, showing regularly shaped (111) terraces of varying sizes (2100×2100 Å^2). (a) In air ($V_t = +20$ mV, $I_t = 20$ nA). (b) In propylene carbonate ($V_t = +30$ mV, $I_t = 20$ nA).

also in UHV, showing both the reconstruction and atomic resolution, such that the atomic positions within the unit cell could be determined. In this work, we present the first high quality images obtained in air and in a liquid for this system with similar atomic resolution of the surface reconstruction. Previously, only atomic step and terrace structures of Au(111) surfaces have been resolved by electrochemical STM in aqueous solutions.[19,20]

Figure 1 shows two large area images of a gold sample in air [Fig. 1(a)] and glycerol [Fig. 1(b)]. Both images show atomic scale features with flat regions interspersed with areas of high step density. The height of the monoatomic steps was determined to be ~2.4 Å in good agreement with previous observations.[12] The straight step edges are oriented along the high symmetry directions of the close packed lattice and due to the three-fold symmetry of the (111) surface, they produce triangularly shaped features. The round edges, which can be seen very clearly in the top of Fig. 1(a), are located in the region of a screw dislocation which is manifested by the growth of a step in the middle of the terrace. The contrast enhanced window in Fig. 1(a) shows corrugation lines which are due to the surface reconstruction. In this image the corrugation lines traverse the step edges perpendicularly and without any discontinuity. A similar behavior was also observed by Barth *et al.*[12] This and other details relating to the reconstruction will be the subject of a future publication. We merely mention this here to illustrate that detailed infor-

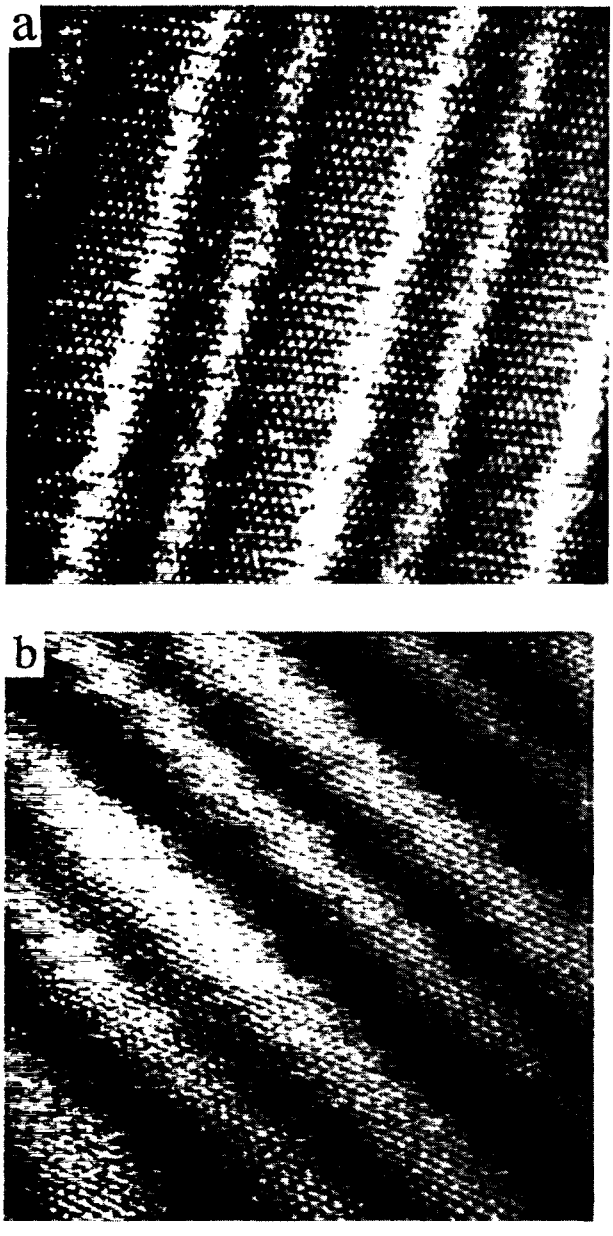

FIG. 3. STM images (130×130 Å^2) of the ($\sqrt{3}\times23$) surface reconstruction of gold (111) terraces with atomic resolution. (a) In air. (b) In triethylene glycol. [$V_t = +20$ mV, $I_t = 20$ nA, in both (a) and (b)].

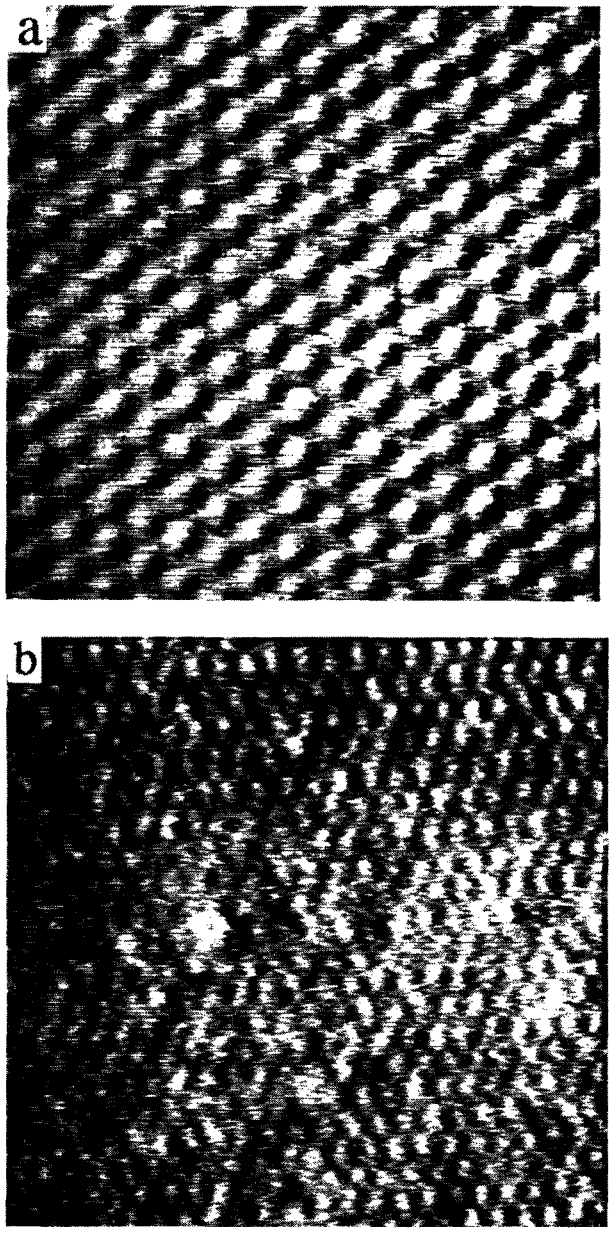

FIG. 4. Atomic resolution STM images of unreconstructed Au(111) terraces. (a) In air (37×37 Å^2). (b) In triethylene glycol (65×65 Å^2). [$V_t = +20$ mV, $I_t = 20$ nA, in both (a) and (b)].

mation on the reconstruction can be obtained in air and in liquids using this very simple preparation technique of the samples.

Figure 2 shows two images, one obtained in air and the other in a different solvent, propylene carbonate. Again, we encountered no difficulties in observing flat terraces of different widths separated by atomic steps with a lateral resolution which appears to be far superior to that reported in an aqueous environment. These images show highly stepped regions with small terrace sizes down to 100×100 Å^2. On such very small terraces, no evidence for the reconstruction was observed and this has been confirmed by comparison with a number of similar images. The medium size terraces are shaped in triangular form which shows that the step edges prefer to follow the high symmetry directions of the hexagonal structure of the topmost layer.

Figures 3 and 4 show very high resolution images of reconstructed and unreconstructed areas, respectively. Figure 3(a) was taken in air and the linear corrugation running from the top to the bottom of the picture along the $\langle 211\rangle$ direction is characteristic of the reconstructed surface. The corrugation in the z direction due to the reconstruction was determined to be 0.15–0.20 Å. It should be mentioned that the reconstruction lines in Fig. 3(a) and Fig. 3(b) are not exactly perpendicular to the compression in the $\langle 110\rangle$ direction. This must be attributed to a slight asymmetry of the piezo elongations while scanning along the surface. The image in Fig. 3(b) is of a similar region as

in Fig. 3(a), but this time under the solvent triethylene glycol. Again, both the long-range corrugation due to the reconstruction and the hexagonally close-packed structure of the surface atoms are resolved. The image in this case is not as sharp as the image produced in air, which may be related to the more diffuse tunneling trajectories of electrons in polar liquids which have recently been considered by Gimzewski and Sass.[21]

In Fig. 4 atomic resolution images of unreconstructed Au(111) terraces are presented. In both pictures the tunneling conditions are equivalent and the apparent corrugation is ~ 0.12 Å. The image in Fig. 4(b), which was taken in triethylene glycol, is again somewhat blurred compared to the measurement in air shown in Fig. 4(a).

Compared to previous studies in aqueous solutions, there are a number of differences in the experimental conditions in the present investigation. This makes it somewhat difficult to establish the origin of the excellent lateral resolution which we have obtained. There is definitely a beneficial effect of the flame-annealing procedure of the gold films on the quality of the images. Without the annealing treatment, atomic features could not be resolved. Presumably, this is related to the removal of organic impurities from the sample surface.[22] The evaluation of the other distinctions, such as not using a conducting solute and the particular physical properties of the large-molecule polar solvents, must await further studies, specifically designed to identify the influence of these parameters on the image quality.

In conclusion, we should like to mention that our results seem to provide an encouraging foundation for future atomic resolution model studies of the physical mechanisms of electron transfer across molecular layers of polar solvents.[23] It has been suggested,[21] for example, that orientational fluctuation and relaxation of solvent dipoles may manifest themselves in the nature of the electron trajectories across the gap and may determine the lateral resolution as well as the apparent barrier height[1] in polar liquid STM studies.

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