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SCANNING TUNNELING MICROSCOPY AND FABRICATION OF NANOMETER SCALE STRUCTURES AT THE LIQUID-GOLD INTERFACE

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Abstract

The Scanning Tunneling Microscope (STM) can image gold surfaces covered with a variety of liquids. This paper reviews the results obtained using the STM to image gold surfaces covered with liquid. These results include the creation of 10 nm structures, images of the electrochemical process of electroplating, and the production of atomically flat Au (111) surfaces. We conclude that in the future STM will find further application in the area of nanostructure fabrication and electrochemistry. The trend in the field is toward greater control of the electrochemical environment.

Key Words: scanning tunneling microscopy, atomic force microscopy, electroplating, liquid-solid interface, nanostructure, lithography.

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Introduction

Scanning Tunneling Microscopy (STM) [5, 13, 16, 17, 27, 41] can be used to produce three-dimensional images of surfaces with atomic resolution. The operation of the microscope is shown in Fig. 1. A sharp metal tip is brought within tunneling range (typically 0.1 to 10 nm) of the surface. Then, when a bias voltage is applied between the tip and surface a tunneling current flows. The tunneling current is a sensitive indicator of the distance between the tip and surface. For a typical surface work function of 4 eV, the current decreases by an order of magnitude for a change in tip surface distance of 0.1 nm.

In operation the tip is X-Y raster scanned over the sample while a feedback network changes the distance between the tip and surface to keep the tunneling current constant. An image consists of a z(x,y) map in which the distance between the tip and surface z is plotted versus the lateral position x,y. All of the images shown in this paper were obtained in 1 minute or less.

The STM can be used to study vacuum-solid, gas-solid, and liquid-solid interfaces. A number of reviews of STM have appeared [13, 16, 17, 27, 41]. One in particular reviews STM at the liquid-solid interface and contains over 100 references to work in this field [41]. The liquid-covered surfaces that have been imaged with the STM include: graphite [37], nickel [20], GaAs [40], DNA [22], iron [8], platinum [23], silver [39], and gold [31, 33, 34, 35 41]. In this tutorial we will review the results obtained using STM to image gold surfaces covered with liquid (in particular, the liquid-gold interface).

The liquid-gold interface was chosen for two reasons: 1) Gold is an inert material which does not form an insulating oxide layer under air or water, and 2) It is easy to prepare atomically flat single crystal gold surfaces in air.

First we will describe how to produce an atomically flat Au (111) surface [35]. Then we will describe the creation of nanometer scale features on a Au (111) surface covered with non-polar liquids [33, 35]. To image surfaces covered with conducting liquids, special tips must be used, the preparation of these tips will be described. Using these tips, electroplating on a Au (111) surface may be observed in situ with a STM [31].

Producing Flat Au Surfaces

An atomically flat surface is desirable for many

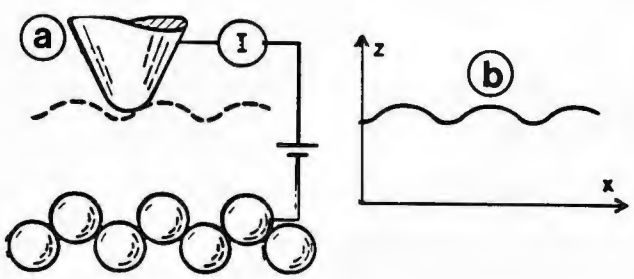

Fig. 1. Schematic representation of the operation of the STM: (a) schematic view of the operation, (b) single scan plot of tunneling current yield the z-x profile, and (c) multiple scan plot resulting in the z-x map. The images are of graphite in air taken by R. Sonnenfeld (from reference 17).

types of experiments. These include nanometer scale modification of a surface, imaging and spectroscopy of atoms and molecules adsorbed onto a surface, and electrochemistry. Most metallic surfaces intersect the small grains of different crystalline orientation of which the metal is composed. These grains result in a rough surface on the nanometer level [7, 30]. However, the surfaces of metallic glasses [42] and single crystals [35] may have large areas which are atomically flat.

Atomically flat surfaces, including gold [29], can be prepared in ultra high vacuum (UHV) but this is a time consuming procedure. Gold may be grown epitaxially on mica but this requires an elevated substrate temperature (350°C), vacuum (about 10^{-6} torr), and careful cleaving of the mica [15]. Gold deposited epitaxially on mica has been used successfully as a substrate for electroplating [31]. In addition, Hallmark et al [15] have imaged gold atoms on a surface deposited epitaxially on mica.

A simpler procedure for preparing atomically flat gold surfaces in air was developed for reflection electron microscopy (REM) [18]. A 0.5 mm thick 99.9 % pure gold wire is melted in air by pushing it slowly into an oxygen-acetylene flame (set midway between oxygen-rich and acetylene-rich). The wire forms a molten ball of gold at the end, which grows as more wire is fed into the flame. Feeding 4 cm of 0.5 mm dia. wire into the flame forms a molten sphere about 2 mm across. This sphere is then removed from the flame and allowed to cool.

Fig. 2 shows (a) optical microscope, (b) scanning electron microscope (SEM), and (c) STM images of the flat facet on a gold ball prepared as described above [35]. When the ball's surface is viewed under low magnification with an optical microscope, flat facets are visible (figs. 2a and 2b). The facets form naturally as the ball cools from its molten state [18]. All STM images we have obtained on these facets show surfaces that are atomically flat over large areas (fig. 2c), although sometimes a few steps may be present (fig. 3a). The vertical resolution of our microscope is sufficient to see atomic steps. Thus, the flatness of the surface shown in fig. 2c indicates that the surface is flat on the atomic scale. Other studies have identified these facets as (111) crystal planes [18].

Creating Nanometer Scale Structures

The STM can modify surface features as well as observe them [3, 9, 10, 12, 14, 21, 28, 29, 32, 34-36, 43]. STMs have been used to produce features on surfaces with lateral dimensions less than 10 nm in vacuum [3, 9, 12, 14, 25, 28, 29, 36, 43], air [34], and fluids [10, 21, 32, 35]. In vacuum Becker et al [3] produced a 0.8 nm diameter dot on germanium. Foster et al [10] produced a dot on graphite less than 0.5 nm in diameter. Ehrichs et al [9] produced 10 nm wide lines on silicon.

Nanometer scale surface modification has been done on a Au (111) surface covered with a non-polar fluid [35]. Non-polar fluids appear to make the surface modification process more reproducible with no net effect on the imaging process [32]. An image of a Au (111) surface covered with fluorocarbon grease is shown in fig. 3a. The tip was positioned at the location we wished to write and scanning stopped. The bias voltage was increased from the 0.1 V used for imaging until the feedback voltage, which was applied to the z-piezo to keep the tunneling current constant, increased suddenly. This increase, usually occurring at less than or equal to 3 V with the sample positive with respect to the tip, corresponded to a sudden movement of the tip away from the sample. Then the bias voltage was reduced back to 0.1 V and the same area was imaged again.

The mound formed under the tip is shown in fig. 3b. The tip was then moved 60 nm along the y-axis and another mound was formed as shown in fig. 3c. Our success at creating the mounds in figs. 3b and 3c encouraged us to try to write the letter "T". Fig. 3d and fig. 3e show intermediate steps toward this goal. The completed "T" is shown in fig. 3f.

Tips for STM under conducting solutions

Two types of current flow between the tip and the surface during STM in conducting solutions. The first type is the tunneling current used to image the surface. The second type is the ionic conduction current through the solution. If the ionic conduction current is greater than the tunneling current the STM will not work. We can minimize the ionic conduction current by insulating the shank of the STM tip, leaving the very end of the tip bare. Tips of this type allow surfaces to be imaged under conducting solutions [37].

In the work described here we used commercially available glass insulated and epoxy insulated tips (part number 30-05-1 from Frederick Haer and Co., Brunswick, ME*). The type of insulation used depends on the solution in which it is to be immersed. For example, glass insulated tips tend to deteriorate in basic solutions (e.g., KOH).

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* Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

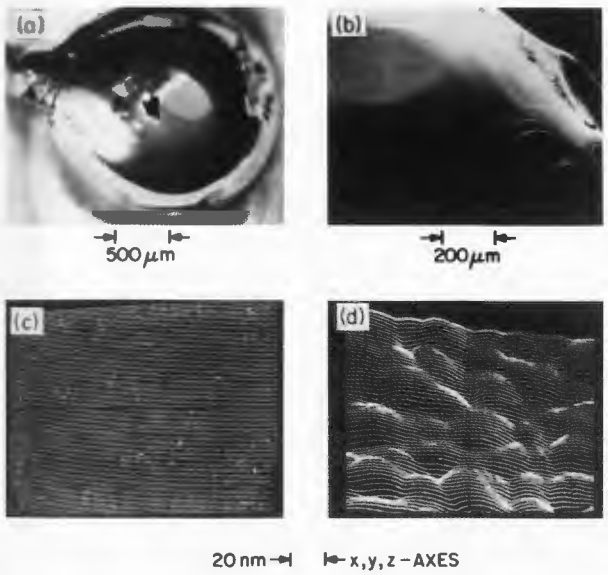

Fig. 2. Photograph and STM images of a gold ball.
a) Photomicrograph of a gold ball. The roughly elliptical grey patch in the center is an atomically flat facet reflecting ambient light. The stub of 0.5 mm gold wire from which the ball was made is visible at extreme left. Such facets occur without special treatment as the balls cool from their molten state.
b) SEM image of the same gold ball. The large flat facet of Fig. 2a is in the upper left corner. In the lower right corner is a set of facets separated by steps, which is also visible in Fig. 2a.
c) STM image of a small region on the large facet on this ball. X, Y, and Z scales are given by the scale bar.
d) STM image of a thin gold film on the same scale as Fig. 2c.

Insulated tips can be produced in the laboratory. We take the commercially available glass insulated tips and, in a vacuum system at 5×10^{-6} torr, evaporate 100 nm of SiO on the tips with the end of the tip pointing toward the source. This leaves the tips completely covered with SiO. SiO is removed from the very end of the tip by imaging a gold surface in air with 10 V bias between the tip and the surface. At this high bias voltage the SiO on the end of the tip is removed. The tips may now be used for imaging under conducting fluids [34]. Bard et al [11] use another method involving varnish to insulate their tips.

Studying Electroplating

The ability of the STM to image samples immersed in aqueous solutions has opened up the possibility for the STM to become a major new tool for in situ electrode characterization. The techniques currrently used most for in situ electrode characterization are based on visible and infrared optical spectroscopies [2]. Valuable as they are, these techniques cannot provide images of the electrode surface.

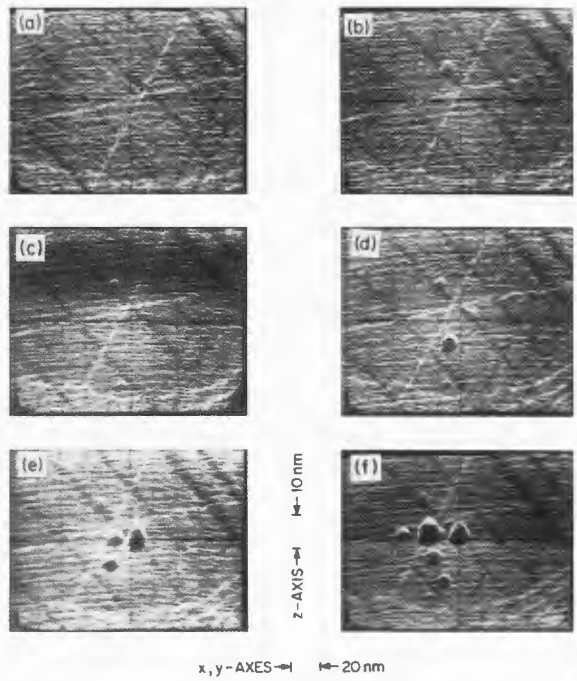

Fig. 3. **a)** Steps on the gold (111) facet which is formed as the balls cool from their molten state. The height of the steps may be used as a way of measuring the vertical calibration of the microscope.
b) A mound is formed under the tip. The mound is about 10 nm wide.
c) A second mound is formed 60 nm below the first.
d) Writing of a "T" begins.
e) Note that as more mounds are added the pattern of steps and other mounds is unaltered. This indicates that the lithography only effects the area within about 10 nm of the point.
f) The "T" is complete. The center mound on the crossbar of the "T" consists of two mounds, one on top of another.

We have used STM to study electroplating at the liquid-gold interface [31]. Fig. 4a shows a Au (111) facet on a gold ball immersed in commercially available $KAu(CN)_2$ based electroplating solution. After fig. 4a was obtained we retracted the tip and deposited 10 nm of gold. The retraction process causes the tip to move to a new region of the surface. The surface was again imaged (fig. 4b) and rolling hills 20 nm wide and 3 nm high were visible. As more gold was deposited the hills grew higher and more numerous (figs. 4c and 4d). This behavior occurred in all three trials of the experiment.

Images with the lateral resolution of fig. 4 can be obtained in vacuum with a SEM. SEM images of gold plated on Cu were obtained by Cheh and Sard [6]. In their study they varied many factors including electroplating solutions, overpotentials, thickness, and current density. They observed island formation similar to figs. 4c and 4d under some conditions and many other types of growth behavior under other conditions. Fig. 4 demonstrates the feasibility of using the STM to observe, in situ, the change in crystal form with time during the electrocrystallization process.

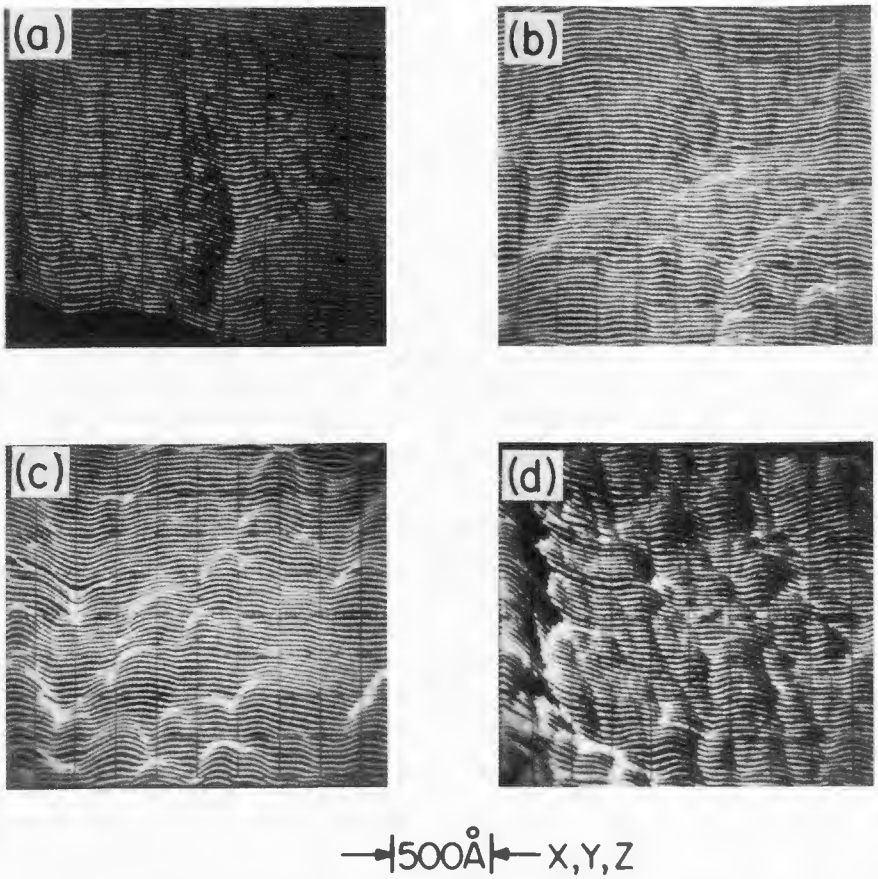

Fig. 4. **a)** A (111) facet on a gold ball imaged under electroplating solution.

b) The same surface as seen in fig. 4a after 10 nm of gold has been deposited. The largest hill visible is 3 nm high.

c) The same surface after 40 nm of gold has been deposited. The hills are now about 5 nm high.

d) The same surface after 160 nm of gold has been deposited. The hills range in height from 2 to 10 nm.

From reference 31.

Speculations on the future

One potential application of STM surface modification is to make nanometer size electronic devices. However, gold is not a suitable substrate for these devices since it is conducting. Silicon is a more promising substrate. The STM has been used to draw 20 nm conducting lines on silicon using organometallic gases [9, 24]. When the temperature of the silicon is lowered its conductivity is greatly decreased. There is hope that this technique might eventually produce nanometer size circuits.

At the National Institute of Standards and Technology (NIST), Teague et al are building an STM which uses temperature control and laser interferometry to position the tip with nanometer resolution in a 2500 mm^2 area [44]. Nanometer scale structures created with this microscope might yield rulers of unprecedented accuracy.

The liquid-gold interface is particularily easy to study because gold does not form an insulating oxide layer. Thus, in the studies discussed here the electrochemical environment was not carefully controlled. A number of groups have designed electrochemical cells for the STM which include potential control [19, 20, 22, 38, 45]. The cell described in ref. 45 allows the electrolyte to be sealed off from the atmosphere. This trend toward greater control of the electrochemical environment will continue.

The STM cannot image insulating surfaces - a severe limitation. The Atomic Force Microscope (AFM), invented by Binnig et al [4], overcomes this limitation. This microscope has recently been used to obtain atomic resolution images of insulating surfaces covered with liquid [16, 26].

Summary

1) Atomically flat Au (111) surfaces can be easily prepapred in air.

2) The STM can be used to perform lithography at the liquid-gold interface.

3) The STM can be used to study electroplating at the liquid-gold interface.

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Discussion with Reviewers

H. van Kempen: In the section "Creating nanometer scale structures" the authors describe the creation of mounds. Is it also possible to create holes? Are there effects of tip contamination as seen by Gimzewski et al. [12]?
Authors: It is possible to make holes. Sometimes mounds are formed and sometimes holes are formed. We are not sure of the reason for this. Because we are running outside of vacuum we always see low work functions which indicate tip contamination.

J.D. Andrade: Regarding the mound formation under the tip as a result of application of a high bias voltage, can the authors suggest a mechanism or at least a hypothesis related to the mound forming process?
Authors: Two possible mechanisms are mechanical contact and chemical reactions caused by the tunneling electrons.

H. van Kempen: An additional method to handle STM in conducting liquid is to use AC modulation technique. For example, a suitable DC voltage can be applied to prevent any electrolysis at the tunnel junction while at the same time an AC current is used to sense the tip-sample distance.
Authors: Thank you for your suggestion.

H. van Kempen: Are there estimates about the surface area of the part of the tip which is not covered with SiO? Do the authors know any method to determine this area?
Authors: We have no estimate of the surface area of the tip. Reference 11 describes how this can be done electrochemically.

H. van Kempen: Electroplating: Is the tip retracted out of the fluid or just backed off somewhat (how much?)? Is any electroplating observable due to the tunnel current?
Authors: The tip is not retracted out of the fluid. It is backed up about 1 micrometer. No electroplating is observable due to the tunneling current.

J.D. Andrade: It is stated that non-polar fluids appear to make surface modification process more reproducible with no net effect on the imaging process. Could the authors elaborate on the role of both non-polar and polar fluids on STM imaging?
Authors: The molecules in the fluid are moving about rapidly and so they have no net effect on the imaging process. The fluids can have an electrochemical effect. For example, they can cause band bending in semiconductors.

S. Lindsay: I add the following comments of a practical nature:
Better Substrates: We have used these melted gold spheres as substrates, but have changed to gold grown epitaxially on mica. Although this involves more work initially (we use a UHV oil-free system and heated substrates) the substrates are much more reliable, being flat to within a few atomic steps over micron distances, and free of high molecular weight contaminants (they are kept under clean argon prior to use).
Better tips: Hard coatings (such as glass and unplasticized polymers) tend to fracture near the tip during handling (increasing leakage). We now prepare our own tips with electrochemical etching in a CN solution, and insulate them by pushing them up through Apiezon wax. The temperature of the wax is adjusted to leave a few micrometers^2 of metal unexposed.
Authors: Thank you for your helpful comments.