

Scanning-Tunneling-Microscope Observation of Surface Diffusion on an Atomic Scale: Au on Au(111)

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(Received 5 August 1987)

Time-lapse topography has been done with a scanning tunneling microscope on a clean, annealed Au(111) surface showing the effects of surface diffusion of Au atoms at room temperature. Within several minutes, features such as marks made by a gentle touch of the tunnel tip are seen to change as a result of the diffusion of Au atoms over the surface. The diffusion does not depend on the magnitude or sign of the tunneling current and voltage parameters. These experiments demonstrate the unique ability of the scanning tunneling microscope to obtain directly information about surface diffusion on an atomic scale.

PACS numbers: 61.16.Di, 68.35.Fx

We report here the first direct observation with the scanning tunneling microscope (STM) of surface self-diffusion on a metal. This experiment demonstrates the use of the STM as a tool to study microscopic details of the diffusion process, in this case at room temperature. Previous methods of studying surface diffusion on macroscopic samples, such as the scratch-decay method, are usually performed at higher temperatures.¹ Field emission and field-ion emission are microscopic methods capable of observing individual atoms or clusters of atoms diffusing on a very sharp emitter tip.^{1,2} Recent experiments have shown that the transmission electron microscope is capable of observing motion of rows or clusters of atoms on surfaces.³

The STM is capable of producing high-resolution topographic images of surfaces with a lateral resolution of about 10 Å on metals and vertical resolution of about 0.1 Å.^{4,5} This resolution results from scanning of a tunneling tip which is effectively a single atom maintained at constant altitude about 5–7 Å above the surface. Regions thousands of angstroms in extent can be scanned. Images showing atomic structure have been obtained from reconstructed semiconductor and metal surfaces. Adsorbed molecules and atoms are resolved and the time-dependent diffusion of oxygen atoms on Ni has been studied.⁶

From previous STM studies it is known that the topography of the clean Au(111) surface is composed of single or multiple atomic steps along low-index $\langle 112 \rangle$ or $\langle 110 \rangle$ directions separated by flat (111) terraces.⁷ In the present work, by using time-lapse topography with the STM, we see surface features change with time. Individual steps move by acquisition of atoms diffusing across terraces or along the steps themselves. Marks can be made on the surface by a controlled tip touch and the gradual change in their shape with time is monitored. In one particularly interesting case (Fig. 1), a pair of shallow circular craters are created and then observed to fill in gradually in a visually striking way that gives infor-

mation about the diffusion processes. It is foreseen that this method will be used to study surface diffusion in a variety of applications and will be extended to observe real-time motion of individual atoms or vacancies.

Experimental details of our STM have been described before.⁷ Topographic images are produced in the constant-current mode with use of tungsten tips made by electrolytic etching. The tunneling voltage is set in the range 0.05 to 0.40 volts with both polarities and the current in the range 0.2 to 2.0 nA. The STM operates in a baked ultrahigh-vacuum chamber and sample preparation and characterization are done without breaking vacuum. The Au single crystal is sputter cleaned with 2-kV Ar ions at about 500°C and is annealed by cooling to room temperature over several hours. The surface was found to be free of significant contamination by Auger spectroscopy and showed a clean, stable LEED pattern. Although all data presented here refer to clean Au surfaces in ultrahigh vacuum, atomic steps and surface self-diffusion are observable in vacuum after exposure of a cleaned Au(111) surface to dry room air for many weeks.

Topographic images are made by plotting the X -piezo drive voltage on the horizontal axis versus the sum of the Y -piezo voltage and the variable part of the Z -piezo voltage on the vertical axis. A decrease in the vertical signal signifies a depression in the Au surface. Frames are scanned from left to right starting from the bottom and one frame requires several minutes to scan. Time-lapse images of a region of the surface are made by repeated scanning over the region. When desired, a mark can be made on the surface by a gentle touch of the tip. This is done most simply by tapping the outside of the vacuum chamber, or in a more controlled manner by adding a short-duration voltage pulse of set amplitude to the Z -piezo control voltage. In either case the tip reacts with an amplitude too great for the feedback circuit to control it. The result is a tip touch which leaves a slight depression in the surface. A significant change in tip behavior

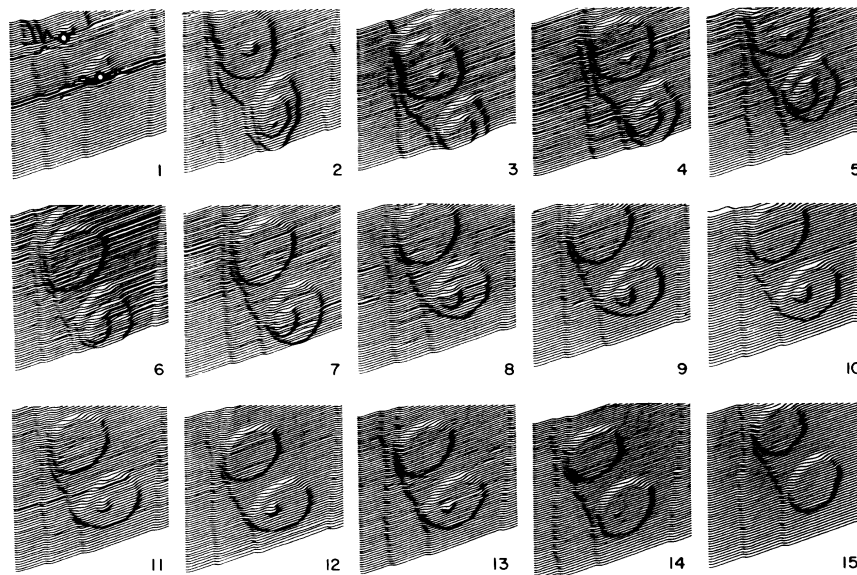


FIG. 1. A series of time-lapse STM topographic images at room temperature showing a $400 \times 400\text{-}\text{\AA}^2$ area of a Au(111) after cleaning and annealing. The time per frame is 8 min and each requires about 5 min to scan. The Z -piezo voltage is added to the Y -piezo voltage and is plotted vs the X -piezo voltage. The steps shown are one atomic unit in height (2.5 \AA) and the flat terraces are (111) planes. The initial scanning region of frame 1 (lower half) shows three parallel steps of single-atom height running vertically. The two circles indicate tip touches. Frame 2 shows two "footprints" left by the tip touches which appear as craters two and three atom levels deep. During a 2-h period the smaller craters are completely filled with diffusing atoms. The two large remaining craters continue to fill. The large slope of the scan lines is due to a tilt in the mounting of the Au crystal.

sometimes accompanies this event but often this change is slight and the scanning region of the STM does not change.

Many topographic images of the Au(111) surface have been obtained after cleaning and annealing.⁷ These show large flat (111) terraces bounded by single steps one layer (2.5 \AA) in height. Individual metal atoms on clean metals have not been observed^{5,7} but features such as steps and rows of atoms may be seen. We have observed, using time-lapse topography, that for temperatures of about 30°C surface details change with time. Steps appear to move, recessed regions tend to fill in, and initially crooked steps gradually become straight. These observations show that there are mobile atoms on the Au(111) surface at room temperature. However, it was not clear from initial observations whether atoms were diffusing along steps exclusively or were also crossing the flat (111) terraces.

The sequence of fifteen topographic images in Fig. 1 provide direct visual information about this process. In the first frame, the initial scanning in the lower half shows three steps running vertically along a $\langle 112 \rangle$ direction. Circles are drawn to indicate locations where the tip was deliberately touched to the surface. For some tip touches atoms are lost from or added to the tip, causing a discontinuous shift in the Z -piezo voltage and a shift in

the field of view. This does not happen for the cases shown in Fig. 1 and the image produced in subsequent scans shows that the two outer steps continue to be imaged indicating little or no change in the tip. The center sections of the image show obvious modifications of the surface after both tip touches. Surprisingly, the new structure shows well-formed single steps only a few seconds after touching. A damage region characterized by more disordered structure with less recognizable features might be expected. Evidently local annealing occurs very rapidly for Au after the touch event.

The second frame of Fig. 1, taken after 8 min, shows clearly the result of the two tip touches. Two craters have formed; the upper one is two atom layers deep while the lower is three. The shapes of both craters are very similar, suggestive of a tip "footprint." The size of each is nearly the same and represents the loss of about 3200 atoms. The fate of these missing atoms is not known but the absence of any tip change indicates that they were either splashed out of the craters and moved to remote regions of the sample or tip or were forced down into the bulk as interstitials. The following frames show no evidence of any clumps or ridges of atoms near the craters to indicate which of these possibilities occurs. The possible presence of a large number of bulk interstitial atoms in the vicinity of the craters might be expected

and these would rapidly diffuse back to the surface. However, as mentioned above, time-dependent changes are observed even for annealed surfaces which are not first perturbed by a tip touch. Therefore the presence of bulk disturbances resulting from the tip touch is not necessary for surface diffusion.

In subsequent frames it is evident that the craters are filling in. In the lower crater, the third level can hold about 25 atoms and is filled within 8 min (frame 3). After about 30 min the second level in the upper crater, which can hold about 125 atoms, disappears (frame 6) and then the second level of the lower crater, with room for about 900 atoms, is filled after 120 min (frame 15). Area measurements of the craters were made and plots of crater volume show that these decrease linearly with time. The rate for both large craters is about 9 atoms/min and for all three sublevels is about 6 atoms/min.

Many examples of surface diffusion were observed and a number of additional experimental tests were made. Several other tip touches were followed by similar changes of topography with time. Generally, depressions tend to fill up and mounds of atoms tend to smooth out, in agreement with scratch decay experiments made on a macroscopic scale.^{1,8} The power delivered to the substrate by the tunneling electrons was varied by a factor of more than 20 without any qualitative change from the described behavior. Thus diffusion effects driven by localized heating of the surface by the tunneling current are ruled out. After an initial tip touch, a second one was made in a nearby field of view about 600 Å away. The second mark was scanned for about 100 min and then the first touch region was revisited. The first mark showed signs of drastic changes similar to the behavior observed with many other marks. This indicates that the scanning motion and proximity of the tip is not necessary for surface diffusion to occur.

Although the craters are nearly circular in shape, their peripheries show angular features. The two low-index ($\langle 110 \rangle$ and $\langle 112 \rangle$) step directions on the fcc (111) face allow for polygonal crater shapes with external angles of 30°. The nearly circular shape indicates little preference for the $\langle 110 \rangle$ steps (fivefold site coordination) over the $\langle 112 \rangle$ (sixfold site coordination) steps. In the low-temperature limit the shape of the craters should be hexagonal as determined by the lowest-index $\langle 110 \rangle$ steps, contrary to observation. The position and shape of the craters is not fixed by changes with time. These facts indicate that the rate-determining process for filling is the capture of atoms arriving from remote regions of the Au surface.

No events were observed which might be interpreted as localized single atoms, vacancies, or clusters of atoms. A single atom in close proximity to a tip would be a significant perturbation to the tunneling current and therefore might be observed. Occasional isolated noise pulses in topography or in time-dependent current sig-

nals occur, but not with sufficient frequency that they can be interpreted as itinerant atoms. Unsuccessful attempts were made to observe time-dependent current pulses by positioning the tip near steps. Either the diffusing atoms jump too rapidly from site to site for the circuitry to respond or their density is so low that the probability of encountering a diffusing atom is too small.

A value for the surface diffusion coefficient D_s as measured by the scratch-decay method may be used to estimate the jump time and density of diffusing atoms. The mean time t that a diffusing Au atom spends at a site will be $t = d^2/4D_s = 0.12$ sec where d (about 2.5 Å) is the jump distance.² This jump frequency would be on the borderline for measurement with the existing control circuit. It is also estimated that there will be approximately 100 diffusing atoms scattered over one frame area on the assumption of uniform surface properties. This density is probably too large because the assumed value for D_s is representative of a macroscopic surface containing many steps and other sites of high occupation probability while the present surface is composed largely of (111) terrace regions whose diffusion sites have low (threefold) coordination and therefore very rapid diffusion across these regions is expected.

That these observations must be interpreted in terms of a surface diffusion phenomena is supported by the following: (1) The volume self-diffusion coefficient of Au at room temperature is insignificant (10^{-40} cm²/sec) on the basis of data obtained at elevated temperatures. Volume self-diffusion in bulk Au is believed to occur by a simple vacancy mechanism even at room temperature⁹ and other mechanisms such as grain-boundary diffusion are not observed. (2) Even if there were a significant volume contribution at room temperature, surface diffusion nevertheless plays an important part in these experiments because of the tendency for regions of the surface enclosed by atomic steps to fill in preferentially. (3) The vapor pressure of Au at room temperature is negligible so that there is no atomic redistribution by evaporation and condensation. (4) Mechanisms of volume diffusion which might depend upon local interstitials caused by the tip touch can be ruled out because tip-touch damage is not necessary for surface diffusion to occur. (5) Heating of the surface by the tunneling tip or other disturbances caused by its presence are ruled out by the power level and tip proximity experiments.

From these experiments we see that the changing topography of a metal surface resulting from diffusion can be monitored with resolution sufficient to see surface features on the scale of single atomic steps. This method is clearly very useful because one can produce a surface with specific topographic features or composition, examine the initial state of the surface accurately, and then watch the surface features change with time. The area can be as large as 3000×3000 Å² or more—enough to contain complicated structures such as depressions, hill-

ocks, and very large multiple steps. Changes occurring locally at individual steps, kink sites, etc., can also be seen and the relative contribution of each component to overall surface diffusion determined.

Obvious extensions of this technique would make it even more useful. The ability to resolve individual diffusing atoms would allow detailed study of their positions with time and provide a value for the local diffusion coefficient.² An extension of techniques used in field-emission experiments to the STM has recently been analyzed in detail.¹⁰ Faster scanning rates are possible with improved STM design and adjusting the temperature will allow individual atoms or groups of atoms to be slowed or frozen in place. Microscopic data would allow for a comprehensive theoretical description of diffusion on a macroscopic scale. Extension of the technique to alloys or adatoms is also possible.

The authors wish to express thanks to A. D. Brailsford and M. A. Tamor for very valuable discussions.

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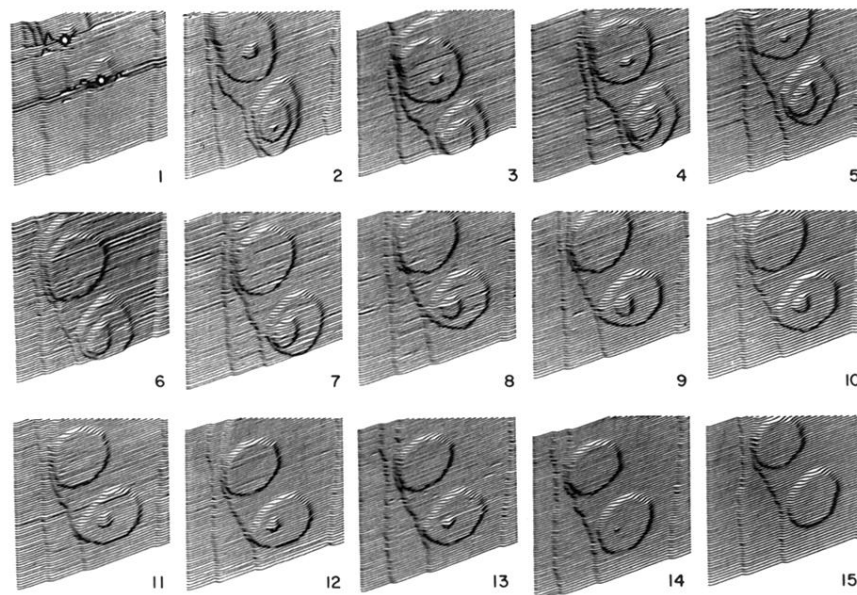


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