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NANOWRITING ON AN ATOMICALLY FLAT GOLD SURFACE WITH SCANNING TUNNELING MICROSCOPE

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Abstract

We present new experimental results of writing stable features on atomically flat surfaces of gold films. By applying successive voltage pulses across the tunneling gap in controlled atmosphere, nearly 150 individual holes are produced to record one message. The writing process has a higher success rate in nitrogen gas with the presence of water or ethanol vapour. Written letters remain stable for more than 4 days in dry nitrogen gas, in contrast to some previous STM results of monatomic step movement on the gold surface. By changing the vapour pressure, pulse amplitude and polarity, we succeed in controlling the gold surface modification (feature dimensions, choice of mound or pit). The smallest stable nano-hole formed is 3 nm in diameter and 0.24 nm in depth, which represents the loss of about 100 Au atoms. The destiny of these missing atoms is unknown but the clear-cut feature of the hole indicates that they have been moved far away. We report for the first time the existence of a minimum relative humidity (18% at 22°C) for the formation of nano-hole, which implies that the reaction may be electrochemical in origin.

Key Words: Scanning tunneling microscopy (STM), nanowriting, Au(111), surface diffusion, relative humidity (Rh), threshold voltage for removal of atoms from the gold surface.

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Introduction

Recently, by increasing the interaction strength between the tip and sample in a controllable manner, scanning tunneling microscopy (STM) is being used as a means of producing nanometer scale structures. A large effort is being devoted toward the introduction of STM into the field of lithography, for reviews see [19, 23]. The fabrication of nanoscale features on the gold surface has already been reported and the formation of mounds or holes ranging in size from 3 to 6 nm has been observed by applying successive voltage pulses across the tunneling gap [3, 4, 5, 8, 9, 12, 17, 18]. The flatness of the gold surface on the atomic scale makes it an attractive candidate for nano-lithography studies as it is widely used in the electronics industry and is considered to be relatively inert to air. However, most of the up-to-date studies on the gold surface, which were performed either in a ultra high vacuum (UHV) chamber or in air, have shown no control in the formation of the hole ("etching"). Under high vacuum, it is hard to make a clean hole on a gold surface with STM. In air, the surface contamination becomes important and it is impossible to control the shape and position of the troughs by varying the voltage amplitude only. Due to the high surface mobility of gold atoms when experiments are performed in air, the gold surface modification have been done at much larger than the atomic scale by the pit formation and small holes are filled in within minutes after their creation. A little effort has been directed towards the exposition of the mechanism of removal of the gold atoms. The question of what happens during the pit formation has not been settled.

In this paper, we present an experimental technique for writing stable features on an atomically flat gold surface. Nearly 150 individual holes are produced in order to record one message. The letters are created by lines that are formed by the coalescence of the neighbouring holes. The writing process has a higher success rate in nitrogen gas with the presence of water or ethanol vapour. A time-lapse STM image study shows that the written letters are stable for more than 4 days in dry nitrogen.

We report for the first time the dependence of the pulse voltage for the formation of a nano-hole on the relative humidity (Rh) and the existence of a "critical humidity" for the gold surface modification. At room temperature (23°C), a minimum Rh of 18% is necessary to make holes on the gold surface. One interpretation of this new result can be that the hole formation on the gold surface requires an adsorbed water layer with a minimum thickness of 1.8 nm which is slightly larger than the tip-sample separation distance. Our experimental result implies that the mechanism of such a surface modification (removal of atoms from the gold surface) could be electrochemical in origin.

Experimental Procedures

A commercially available STM (Nanoscope-III, Digital Instruments, Santa Barbara, CA) is used in this study. Surface modification experiments necessitate the control of the tip-sample interface's chemical composition. It was suggested that scanning in an inert gaseous environment at atmospheric pressure can retain many of the advantages of air operation while removing much of the uncertainty caused by surface contamination [16, 21]. Our entire scanning unit is placed in a plexiglass glove box which has been purged with pure nitrogen gas for 2 hours prior to the beginning of the experiment. In order to change the relative humidity of the environment, the air-tight plexiglass chamber is continuously purged with nitrogen gas of known humidity. Ten MΩ-cm resistivity deionized water is used to produce the humidity. The desired relative humidity in the purge gas is obtained by mixing streams of dry and wet nitrogen, that are prepared by bubbling dry nitrogen gas through deionized water at room temperature in an appropriate ratio [21]. The relative humidity in the box reaches a steady-state value within 30 minutes after the adjustment of the flow ratio of gases. A digital hygrometer (Vaisala Hygrometer, HM34C, precision 1%, resolution 0.1%; supplied by Prolabo, Paris, France) is placed close to the scanning unit to measure the relative humidity inside the chamber. Similar work is performed with ethanol and the primary result obtained looks similar to the result with water.

The substrate used in this study is clear and slightly stained Muscovite, ruby red mica (supplied by Digital Instruments, Santa Barbara, CA, USA). The gold film is electron beam evaporated onto mica in a cryopumped vacuum chamber equipped with a load-lock [14]. The mica was cleaved immediately before being loaded into the vacuum chamber. About 100 nm of gold is deposited at a rate of 0.1 nm/s with the substrate placed at 20 cm from the source, and with the deposition pressures at less than 10^{-7} Torr. The substrate temperature is maintained at 300°C during the deposition. Due to the fact that the mica interlayer absorbs water, a long period of pretreatment baking of the mica in UHV (24 hours at 300°C, 10^{-8} Torr) is necessary for the growth of a high quality film [2]. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) are used in depth profile elementary analysis. No detectable carbon or potassium contamination are observed on our gold film.

It is well known that gold becomes contaminated almost immediately when exposed to air. After evaporation, the sample is removed from the UHV chamber and loaded into a clean container that is stacked into a vacuum desiccator. Direct exposure to air is restricted to less than 30 minutes. The desiccator is evacuated to less than 1 Torr and back-filled with nitrogen gas. With this precaution, gold films on ruby red mica can remain "clean" for ten days of storage under nitrogen. Occasionally, under nitrogen gas or argon-hydrogen mixing, 22 x $\sqrt{3}$ reconstructed surfaces and individual gold atoms are observed, but it is not a necessary condition for the reproducibility of pit formation. One of our criteria for a clean gold surface is based on the observation of straight single atomic steps separated by unstained (111) terraces.

Another important criterion in our study is the value of the tunneling barrier height. The expected barrier height for gold surface is about 3.2 eV under UHV condition [7]. In our surface modification experiments, the tunneling barrier height is superior to 0.5 eV which can be extracted from the expression ϕ (eV) = 0.952 $\{d(\ln I)/ds\}^2$ where I is the tunneling current and s is the tip-sample separation distance. This value is similar to that of 0.6 eV for the W-Pt system reported by Binnig *et al.* [1], under what they called a "moderate vacuum". It has been observed that for dirty surfaces, the tunneling is often unstable and the tunneling current varies less rapidly than expected with vertical displacement of the tip. For gold in air, dlnI/ds is smaller than anticipated, leading to an inferred barrier height. The obtained apparent barrier height is often less than 50 meV which is too small to be read. Surface modification on a dirty gold surface is always uncontrollable and nanowriting cannot be performed in this case.

By applying a positive voltage pulse to a stationary sample from its tunnelling value of 100 mV to a value larger than the "threshold voltage" (see **Discussion**), a net pit will be produced on a clean gold surface. In our experience, it is impossible to make a hole by applying a negative pulse. The pulse width varies between 1 ms and 2 seconds. The current servo loop is always actively maintaining the tunneling current at its 1 nA setpoint and the time constant of feed back system is less than 100 μs. The transient response of the tunnelling current

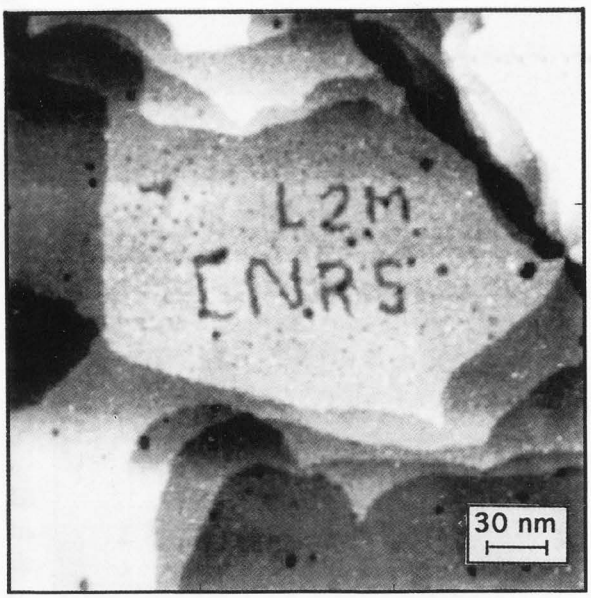

Figure 1. Nanowriting on the gold surface. Nearly 150 individual holes were produced to record the legend "L2M CNRS" on the gold surface. The letters are about 30 nm tall and 25 nm wide and are made up of lines of 5 nm in width and 0.24 nm in depth (monolayer writing). The lines are formed by the coalescence of the neighbour holes due to the fast surface diffusion.

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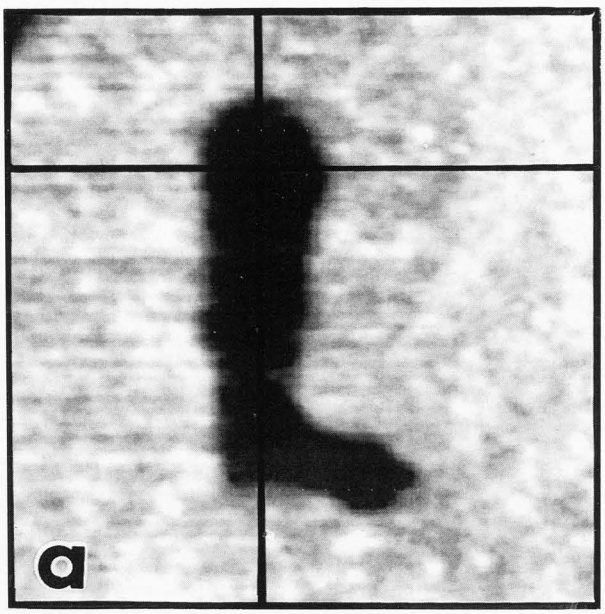
is monitored by a digital oscilloscope. No mechanical contact between tip and sample is observed in our experience. The hole created could be on an arbitrary feature at first, nevertheless, it's shape becomes nearly circular a few seconds later. The smallest stable nano-hole formed is 3 nm in diameter and 0.24 nm in depth which represents the loss of about 100 gold atoms in the surface monolayer. The destiny of these missing atoms is unknown in this study but the clear-cut feature of the hole indicates that they have been moved far away. The location of the individual hole can be controlled in a precision of $\pm$ 1 nm. When the pulse voltage is just below the threshold, some intermittent disruptions of the basal plane are noted but no monolayer hole is formed. We interpret it as a precursor of the monolayer hole formation. It could be due to the inelastic deformation of the (111) surface or due to the change of the local electronic properties of the sample.

The tips used are the commercially available Pt/Ir Nanotips (Digital Instruments). The durability of Pt/Ir tips has been demonstrated by their ability to etch holes and to subsequently supply good images of these features for days. There is, however, a gradual reduction in image and pit quality with time and an eventual failure of the tips to image the fabricated features. Due to the gradual coating of the tip apex with gold deposits, the effective tip area, from which tunnelling can take place, increases. But, the tip can be easily revived by Mamin's pulse deposition method [3, 10]. In our study, we deliberately apply 3.7-4 V pulses (just above the threshold for mound formation) to wash our tips after every 100-200 hole fabrications.

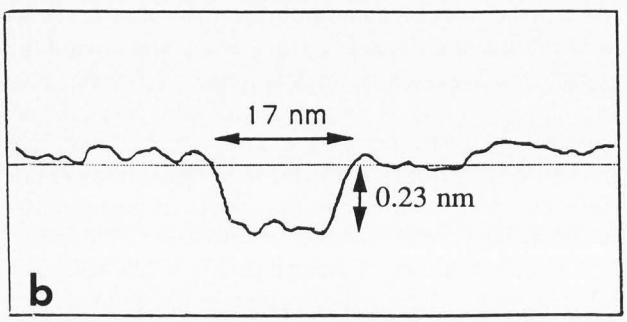
Nanowriting on Gold Surface

Figure 1 shows an image of a nanowriting feature on the gold surface. By applying successive voltage pulses across the tunneling gap in a controlled atmosphere (Rh 20%, 22°C), nearly 150 individual holes are produced separately to record the legend "L2M CNRS" on the gold surface. Only one Pt/Ir tip is used in this writing procedure. The letters are about 30 nm tall and 25 nm wide and are made up of lines of 5 nm in width and 0.24 nm in depth (monolayer writing). The lines are formed by the coalescence of the closed neighbour holes due to a fast surface diffusion. A cross-section analysis of the written letter L in Figure 2 reveals that the depths of the etching lines are quite uniform and equal to the monatomic step height. The writing process has a higher success rate in nitrogen gas with the presence of water or ethanol vapour. No debris around the trough of the written features is found. After the writing, the glove box is repurged with pure nitrogen gas and an *in-situ* time-lapse STM image study shows that the written letters stay stable for more than 4 days in dry nitrogen. For reducing the tip-sample interaction, 300 pA tunneling current is applied in time-lapse STM study.

The phenomenon of gradual healing of the holes and hillocks formed by a voltage pulse on the gold surface has been reported [3, 17]. With STM, these nano-features were observed to decay with time over a period of minutes to hours. It was proposed that the surface self-diffusion of the gold atoms leads to the healing of the formed structures. The coefficient of self-diffusion of gold atoms is about 10^{-14}-10^{-16} cm^2 s^{-1} [3, 6]. We call it fast surface-diffusion of Au atoms. The formation of our written lines by individual holes is an example of this model: in the nanowriting procedure, two neighbour pits (4-5 nm in diameter and 3 nm apart) produced by two successive pulses will merge to become a larger "hole" that has an elliptical shape with a short axis close to the original pit's diameter. An approximate volume calculation indicates that the number of atoms missing in the two holes is conserved after the coalescence. Subsequent continuous coalescence will contribute to the combination of all the neighbour holes together and form a written line. It is possible that the observed movement of the next neighbour holes and the following coalescence are due to the surface self-diffusion of gold atoms, thereby forming a relatively stable configuration. Moreover, the strain fields caused by the disturbed surface



Horizontal cross-section:



Verical cross-section:

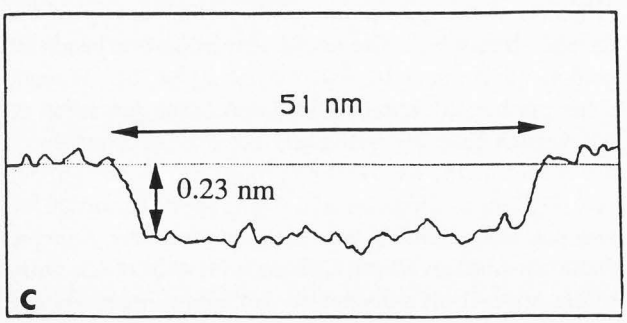
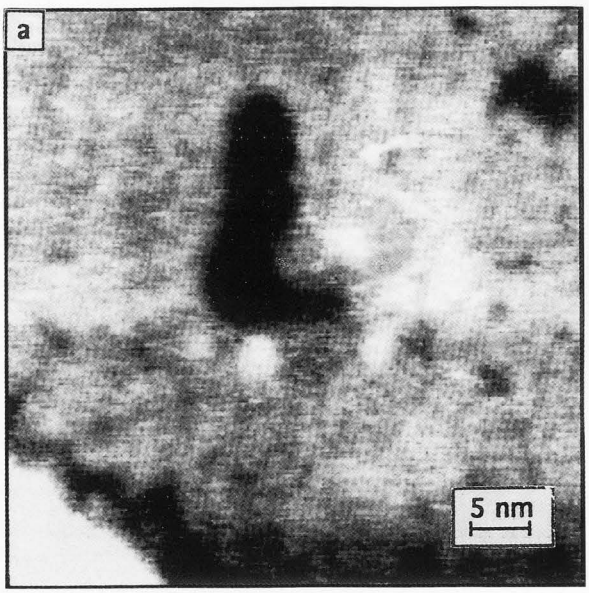


Figure 2. Cross-section analysis of writing letter L (**a**) in two directions (horizontal cross-section, **b**, and vertical cross-section, **c**) reveals the nature of monolayer nanowriting: the depth of the etching lines is quite uniform and equals to the monatomic step height. No debris around the trough was found. STM is a "good calligraphy"!



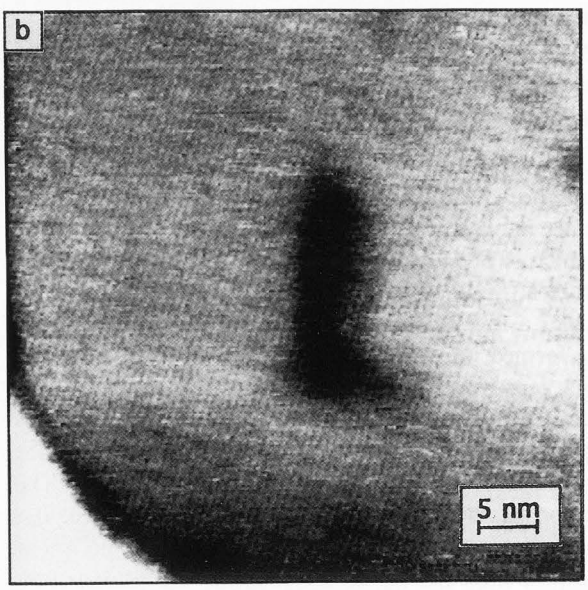


Figure 3. Time evolution of letter "L". Images were taken at different times: (**a**) Five minutes after writing; (**b**) three days later. The results show that the time evolution is less important.

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could probably be the driving force behind the observed movement. The release of the strain field could play an important role in the early decay. The merging of the two neighbour holes is favoured by the energy consideration as it reduces the total edge length of the holes by a factor of $\sqrt{2}$ and thereby reduces the total surface energy. The movement of atoms between two closed

neighbour holes is rapid. For example, some monatomic steps are observed to move as rapidly as 5 nm in 10 seconds. Diffusion velocities are estimated to be in the range of 0.01 and 0.5 $nm \cdot s^{-1}$, which is in good agreement with the result of Jaklevic [6].

However, in our STM studies on gold surface, we frequently encounter a different scenario: we do not observe any motion or any type of evolution of preexisting surface features, such as isolated small pit, although their dimensions are inferior to 10 nm (the isolated hole, defined as the minimum distance between two holes, is larger than 10 nm). In self-diffusion dogma, these structures should disappear in a period of 100 seconds ($t \approx L^2 / D / 4$, with $L = 10$ nm and $D = 10^{-15}$ cm^2 s^{-1}). Peale and Cooper [13] have observed that, under UHV conditions, nano-features of adatoms persist essentially unchanged for an extended period of time and the decay can be initiated by depositing certain adsorbates on the gold(111) surface. They argued that the decay on gold surface belongs to the interface-transferee-limited mass flow regime and that the appearing diffusion coefficient under UHV could be five orders of magnitude smaller than Jaklevic's result [6]. Our time-lapse STM image study in dry nitrogen gas (Fig. 3) shows that the written letter stays stable for more than 4 days which means the diffusion rate is less than 0.1 $nm \cdot h^{-1}$ even though our experiments take place in nitrogen atmosphere. This diffusion velocity is 1000 times lower than that in the early period of decay. It is constructive to distinguish two kinds of decay in the nanowriting on gold surface: fast decay with the diffusion coefficient as high as 10^{-14}-10^{-16} cm^2 s^{-1} (Jaklevic's [6] surface diffusion) and slow decay with the diffusion coefficient as low as 10^{-22} cm^2 s^{-1} (Peale's [13] mass flow). During the process of creating layered features, the original stable configuration of the surface atomic arrangement is disturbed by the voltage pulse applied across the tunneling gap and a number of the free energy minima of total system are created. Since the energy barriers between these free energy minima are so small, after the voltage pulse, atoms start to rearrange their positions rapidly until they find relatively stable ones. Then the fast atomic movement becomes rather slow upon the attainment of the metastable configurations which corresponded to a deeper energy minimum. The strikingly long-lived nature of written letters implies that the system settles into a very deep valley in the free-energy landscape. The coexistence of two decay rates in one system is very popular in nature and a number of complex systems far away from their equilibrium configuration can have more than one relaxation mechanism. We have to consider them separately in the relaxation study [22]. The detailed mechanism in the transfer of atoms onto and away from the step edge of the gold film should be clarified in the future.

Due to the strong electric field that is being applied and the high current density under the STM tip, the presence of the STM tip raises the issue of it's influence on diffusion processes [11]. In some experiments of time-lapse STM image study, the deterioration of the written feature is clearly induced by scanning the tip, which indicates that the influence of the STM tip is another possible factor that must be taken under consideration. Reducing the tunneling current can minimise the tip-sample interaction. The real diffusion coefficient could be lower than the value reported in this paper.

Threshold Voltage and Humidity

Figure 4 presents the dependence of the etched pit depth (or the deposited mound height) on the positive pulse voltage at different relative humidity (note: the sample is in positive polarity). The mound height is often superior to 10 nm and varies abruptly with the pulse voltage. However, the formed pit depth varies more slowly and regularly than the formed mound height does when the pulse voltage increases. Consequently, it is possible to control the etching depth in the numbers of monatomic layer. The bias threshold voltage (Vt) for pit formation is defined as necessary to produce a **monolayer** hole on the gold surface which could be subsequently observed by STM. The similar Vt definition is applied for the mound formation except for the mound height requirement. The strength of the threshold voltage for the making of a monolayer hole depends on the relative humidity. Rabe *et al.* [15] have suggested that the presence of water is a necessary condition for the surface fabrication process to occur on graphite with STM. We find that this assertion is also valid for the nanowriting on gold even though the nature of the reaction could be different. The samples grown on different batches have the similar threshold voltage-humidity (Vt-Rh) dependence behavior. A slight change of less than 0.2 V of the threshold value is noted in different samples, though, it could be due to the changing of the tips. A careful study of Vt-Rh dependence in Figure 5 demonstrates the existence of a critical humidity (Rhc) for pit formation. When above Rhc, the threshold voltage for pit formation is nearly constant. When below Rhc, however, it increases rapidly with reducing the relative humidity until it becomes higher than the threshold voltage for mound formation. It is impossible to make a clean hole with STM by increasing the pulse voltage in the lower relative humidity atmosphere. Instead, it results in the formation of a mound on the surface. Sometimes, a tiny pit was found on the top of the mound. No relationship between the mound formation and Rh is observed. The threshold voltage for the mound formation is approximately constant in all the humidity range. The variation

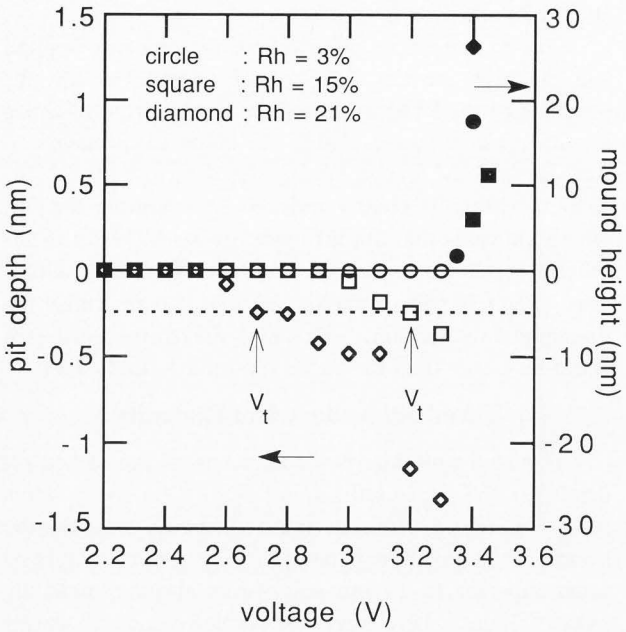

Figure 4. The dependence of the etched pit depth (or deposited mound height) on the pulse voltage at different relative humidity. Discontinuous line indicates the monolayer depth in (111) direction of gold. White symbols represent the pit and black ones represent the mound. The bias threshold voltage (Vt) is defined as that necessary to produce a monolayer hole on the surface of gold which could be subsequently observed by STM. Some intermittent disruption of the basal plane below Vt is noted but no monolayer hole is formed.

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of Vt as a function of Rh presented in Figure 5 is reversible and reproducible by intentionally increasing or reducing the humidity. But, if the sample stays too long in high humidity (more than 40%) the risk of gold surface deterioration is high. At room temperature Rhc for pit formation equals 18% and the transition width is about 3-4%. Measurements from four different samples gave the same Rhc even though their threshold voltage could be slightly different.

It is well established that water is smoothly adsorbed onto a clean gold surface, initially in a rapid physisorbed stage. The adsorption isotherms correspond to multilayer adsorption and have been termed Type II isotherms according to Brunauer's scheme [20]. Thomas and Sharma [20] had investigated the effects of relative humidity on the water adsorption. They reported that the amount of water on the gold is proportional to Rh for Rh less than 30%. They suggested that, at low humidity, the adsorption isotherms can be described by the BET equation:

$$h = 10\ Rh\ /\ \{(1 - Rh)\ /\ (A + B\ Rh)\} \qquad (1)$$

where h (in nm) is the thickness of water layer adsorbed on gold surface, the coefficients A and B equal 0.595 and 4.40 respectively (values at 23°C, deduced from Thomas's [20] experimental result). The curve in Figure 5 presents the result of calculation of h using BET equation. For 18% relative humidity at 23°C, we find h to be 1.8 nm, which approaches the tip-sample separation distance. With the tunneling parameters V equal to 50 mV, I 1 nA, and ϕ 3.2 eV, Kuk and Silverman [7] detected their tunneling gap distance to be 0.4 nm directly. Suppose the value of (s x $\sqrt{\phi}$) in our experience (where ϕ equals to 0.5 eV, V 100 mV, and I 1 nA) is similar to that of Kuk's [7], our tunneling gap distance is calculated to be 1.0-1.2 nm.

To our knowledge, the existence of the critical relative humidity for the pit formation has never been reported. This new result can be interpreted as that the hole formation on the gold surface needs a minimum thickness (1.8 nm) of water which is slightly larger than the tip-sample separation distance. Does it just meet at random or is it providing an electrolyte necessary for an electrochemical reaction process under the STM tip to arise if the thickness of the layer is larger than the gap? Nevertheless, our experimental results imply that the mechanism of such a surface modification (removal of atoms from the gold surface) could be electrochemical in origin.

In conclusion, we have demonstrated a technique that produces controlled topographic changes on a gold surface. These features are stable for more than 4 days. Monolayer nanolithography on an atomically flat gold surface can be realised with STM. The existence of a critical humidity value (Rhc) is important in the surface modification. The fact, that the etching process is dependent on the polarity of the pulse and on the thickness of the adsorbed liquid layer, could shed some light on the nanowriting process with STM for a better understanding.

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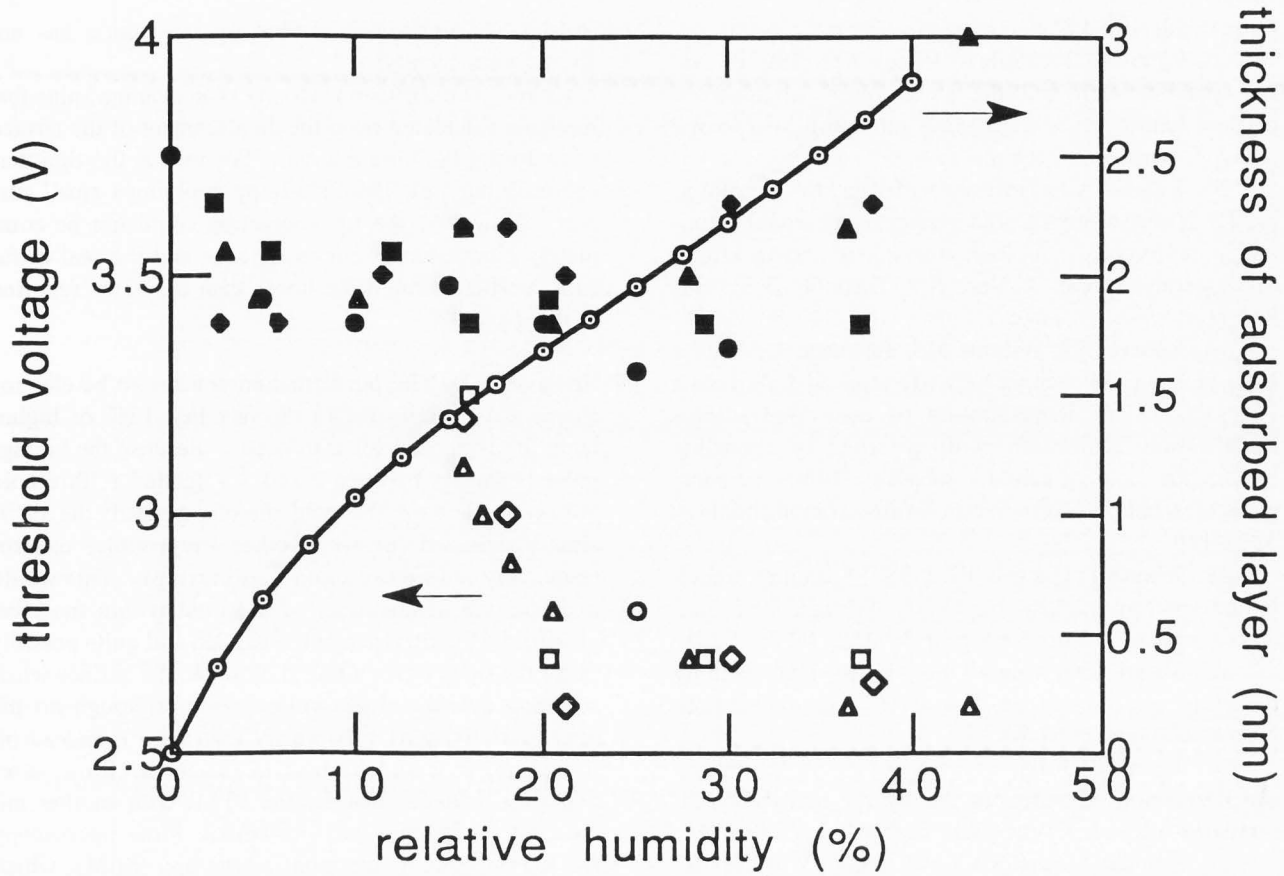

Figure 5. The relationship between threshold voltage (Vt) and relative humidity for four samples. The existence of a critical humidity value (Rhc) at 18% is clearly presented. White symbols represent the pit and black ones represent the mound. The curve in the Figure, calculated from Thomas's experimental result [20], illustrates the relationship between the thickness of adsorbed water layer and relative humidity at 23°C.

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Discussion with Reviewers

Reviewer I: How is tunneling barrier measured and with what are you comparing this number in order to determine surface cleanliness?

Authors: As stated in the text, in our surface modification experiments, the tunneling barrier height is superior to 0.5 eV which can be extracted from the expression ϕ (eV) = 0.952 $\{d(\ln I)/ds\}^2$ where I is the tunneling current and s is the tip-sample separation distance. We measured the apparent tunneling barrier while the tunneling conductance was being varied over a decade. With v = 100 mV, I = 1 nA and ϕ = 0.5 eV, our tip-sample distance is estimated, from the experimental result of Kuk and Silverman [7], to be 1.2 nm.

Reviewer I: How did you measure your diffusion velocities and are you sure that tip interaction has not altered your results?

Authors: Our diffusion velocity is an average value that has been calculated from the displacement of the terrace edge during the time interval. We reduce the tip interaction in our time-lapse study by applying a small current. However, the tip interaction could not be completely eliminated in our experience and the real diffusion coefficient might be lower than the value reported in this paper.

Reviewer II: The pit formation appears to be electrochemical in origin due to the fact that 18% or higher humidity is needed for it to occur. Because the voltage pulse is usually between 2 and 3 V (called a "threshold voltage"), perhaps the gold directly beneath the tip is simply oxidized (or some other irreversible, electrochemically induced reaction is occurring). This would decrease the conductivity of the gold within the local area below the tip (change the LDOS) and quite possibly cause the tip to move a few Å closer to the surface when scanning over a voltage pulse region, although **no pit may actually exist**. To verify that there is indeed pit formation, it would be best to image the films, after doing the voltage pulse by the STM, with another microscopy technique, such as atomic force microscopy (AFM) or scanning electron microscopy (SEM), which utilizes a different principle of operation.

Authors: Your suggestion to image the written feature with other microscopy technique is a good one and we are working in this direction. We have been concerned about the local conductivity change of the sample below the tip. However, due to the fact that the "etching depth" measured by STM varied discontinuously in a step of 0.25 nm and that no change of ϕ value in the center of the hole was observed, we believe that the change of the LDOS (if it exists) is not relevant in our experiment. Recently, we succeeded in imaging the written letter on gold film with tapping mode AFM, just after writing and imaging by STM. The AFM image observed is identical to that of STM. Our experimental result confirms that the gold surface topography is irreversibly changed and the written letters do actually exist.