

The Scanning Tunneling Microscope

Nanolithography and Morphology

by

Chunxi Guo

A thesis

Presented to the University of Manitoba

in partial fulfillment of the requirement for the degree of

Master of Science

in

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**THE SCANNING TUNNELING MICROSCOPE
NANOLITHOGRAPHY AND MORPHOLOGY**

BY

CHUNXI GUO

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

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ABSTRACT

A Scanning Tunneling Microscope is used to deposit nanometer scale features onto metal surfaces. Tip position versus time data clearly show the transfer of material between the tip and the substrate. A theoretical study is performed to determine the mechanism for feature formation. In our situation, thermal melting is excluded based on the current energy dissipation calculation. Another possible mechanism is field evaporation of the tip during the voltage pulse. The threshold pulse amplitude has a linear dependence on the log of the gap resistance, in agreement with the field evaporation mechanism. However, the threshold pulse amplitude is essentially independent of the tip material in disagreement with the field evaporation mechanism. We are proposing that large electrostatic forces between the tip and substrate may be responsible for feature formation.

The surface of epitaxial gold on mica and a gold ball is characterized by STM in air. We find that these surfaces are simple to prepare, are relatively inert to exposure to air, and have atomically flat terraces extending for up to several hundred angstroms. The observed atomic resolution topography is consistent with the Au(111) surface. Self-diffusion of gold is observed in the movement of feature edges.

Gold and silver films have been evaporated onto mica at substrate temperature ranging from room temperature to 450°C . STM images are obtained in air. The films exhibit an increasing grain size together with a grain flattening as the substrate temperature increases. The pre-heating process could improve the quality of the films. The nucleation process and the pre-heating process are discussed. In conclusion, epitaxially grown Au(111) films evaporated at 450°C and Ag(111) films evaporated at 300°C on mica with hours of pre-heating process have been shown to exhibit large flat terraces suitable for nanoscale modification studies with the STM.

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CHAPTER 1

SURFACE MODIFICATION

1.1 INTRODUCTION

Nanometer-scale surface modification has important potential applications in areas such as high-resolution lithography for solid state devices or high density data storage. Optical lithography is used to manufacture the commercial integrated circuits. The resolution of this process is limited by diffraction to dimensions of a few times the wavelength of light. This limit can be extended by using X-ray or electron beam lithography [1]. The lateral resolution of conventional high-energy electron beam lithography on thin substrates with thin resists is ultimately limited to $100\text{\AA}$ because of second-

ary electron effect [2,3], although features as small as 20Å have been created on thin membranes [4]. However, the ultimate in miniaturization will require devices made on the scale of individual molecules or atoms. The Scanning Tunneling Microscope (STM) seems to have a new impact on microfabrication of semiconductors and superconductors. The STM could yield a new tool for nanometer lithography.

Although this is primarily due to its extremely small beam diameter, it has several other important advantages. The STM can provide a very high current density, limited only by destructive heating of the target rather than by source brightness or lens aberrations. The low beam energy reduces or eliminates the proximity effect as well as any radiation damage. Finally its low cost and simplicity offers the possibility of making arrays of STM's for increased throughput.

For the purposes of this thesis, the expression 'lithography' will be applied as a synonym for a whole pattern generation processes, even if there are no proper exposure and development sub-processes involved.

Every instrument that images a sample has to interact with its object. With this interaction, an energy or a momentum transfer is effected and, hence, the sample is affected or probably even modified in some way. From this point of view, each instrument that is supposed to image a sample is at first a lithographic tool. Only when the transferred energy or momentum is small enough that the sample is not permanently modified, can it be looked upon as a microscope in the proper sense.

Researchers working with STM have all observed sudden changes in the resolution of the microscope or random changes of the scanning area. This is often attributed to a change in the tip, which means nothing else than that a surface has been accidentally

modifications have often turned out to be the starting point for the development of new kind of lithographic process. It did not take a long time after the invention of the STM until the first intentionally made surface modification was created.

1.2 SURFACE MODIFICATION HISTORY

In 1985 Ringger et. al. [5] used a glassy alloy, $Pd_{81}Si_{19}$ for a substrate. They were able to draw lines simply by scanning the surface at a bias of 100mV with a current of 10nA. Scan speed was $0.1\mu m/s$. The resulting lines were less than 500Å wide. Originally these modification happened accidentally and were discovered during an inspection after some STM measurements had been performed on that sample. They believed that a polymerization of a hydrocarbon combination film may have occurred.

In the same year, prior to that work McCord and Peace [6,7,8,9] outlined how the STM could be used for low energy electron beam lithography and successful resist exposure was demonstrated the following years. They successfully exposed a variety of different e-beam resist including PMMA and alkali-halide films. They run the STM usually in the field emission mode with the sample at positive potential. The bias voltage usually ranged from 1V to 100V and the emission current from 10pA to 100nA. They generated a variety of different patterns. Applying the lift off technique they even fabricated a thin film resist which has resistance of $2.5k\Omega$. A common problem arising in any kind of e-beam lithography is the exposure contributed by the backscattered or the secondary electron. Based on the work of McCord and Peace, Zhang[10] demonstrated that reversing the polarity of the STM can overcome this problem. Furthermore

they explored the application of very thin resist film which had been deposited onto the substrate by the Langmuir–Blodgett technique. Such films are probably required for STM lithography involving electrons emitted from the sample.

Using thin insulating films as a kind of resist McCord and Pease [11] generated line shaped structures by scratching the surface with the STM tip. The $0.36\mu\text{m}$ wide lines were in $200\text{\AA}$ thick films of calcium fluoride and aluminium fluoride which had been vacuum deposited onto to silicon. The process did no apparent damage to the tip nor the substrate.

Another technique for manipulation of an e–beam resist was used by Albrecht et. al. [12] and Dovek et. al. [13]. They split PODA fibers by applying 100ns pulses of 4V across the tunnel gap. During this short time the current rose up to 200nA because the feedback loop was too slow to maintain a constant current.

While investigating the transition from the tunneling regime to point contact Gimzewski and Moller [14] observed the creation of plastic deformation of the sample during contact. They found that depending on the cleanness of the iridium, adhesion between the silver sample and the tip led to hillock formation upon retracting the tip from the surface.

Abraham et. al. [15] reported the creation of holes drilled in Au by touching the surface with a polycrystalline tungsten tip. They could also observe a subsequent relief of the stress which had been induced by the formation of the indentation. Working at high currents and small tip to sample distance they deposited material from the tip onto the sample resulting in the formation of a hillock typically 20nm across. Since before that experiment the tip had touched the sample several times, they concluded that a lot

of material was first transferred from the sample to the tip. This material could be redeposited in small fractions afterwards during the lithographic process.

A very simple technique for the modification of a Au(111) surface was introduced by Jaklevic and Elie [16]. They gently tipped the UHV chamber while the STM was imaging the sample, leading to a soft tip 'crash'. The indentation which had typical diameter of 20 to 100Å formed by this technique annealed out within a few hours by surface diffusion. The rate of atom diffusion into the hole was calculated to be between 6 to 9 atoms per minute.

Schneir et. al. also produced both holes and mounds on a gold surface [17,18]. The instrument worked in air, with the gold surface covered with a fluorocarbon grease. To modify the surface, the scan was stopped and the bias was raised above the nominal level of 0.1V until the Z voltage increased suddenly. Holes were usually formed if the bias reached 1.5 to 3V before the Z voltage changed, whereas mounds usually formed if the Z voltage increase occurred at 0.7V. Mounds were typically 100Å wide, while holes were usually smaller with widths of approximately 50Å. The researchers could not influence the type of feature formed. No modifications were possible if the grease was not present. In addition, not every attempt in the presence of the grease was successful.

Li et. al. also increased the bias voltage in order to modify a gold surface [19]. However, they pulsed the bias, and continued to scan the surface during the pulse. They operated in air, with no substances deliberately introduced onto the surface. Their millisecond duration pulses typically formed craters which were 20 to 80Å in diameter. Sometimes, mounds with diameters approaching 200Å were formed. If mounds did

form, the measured current saturated at approximately 90nA for up to 2ms, while it would only momentarily peak at the saturation value if craters were formed. In addition, observation of the voltage on the Z piezo indicated that, following a surface modifying pulse, the piezo returns the tip to a different nominal distance from the substrate in an attempt to maintain a constant current. The direction of the change in separation following formation of a hole is opposite to that following formation of a mound. They also found that a threshold voltage of approximately 2.7V must be exceeded for any modification to occur. They speculated that explosive evaporation caused by rapid heating may cause the craters. This suggestion has been discounted by others [20], as the heat generated by the pulse is conducted away from the surface too quickly to allow for explosive evaporation.

Emch et. al. [21] also used voltage pulses while scanning to modify a gold surface. They too created both craters and, less frequently, mounds. Like Li, they noted a voltage threshold of around 3V. In addition, they found the threshold would approach 5V if the tip was blunt or dirty. Besides a voltage threshold, they also determined that a minimum pulse width was necessary. This was approximately 10ns. Their smallest features were on the order of 50Å wide.

Becker et. al. [22] performed surface modification experiments on germanium in UHV. They deposited material onto the surface by increasing the bias voltage with the scan halted. The diameter of the deposition was approximately 8Å with a height of 1Å. Not every attempt was successful; however the success rate could be increased by lightly contacting the tip with the surface. Because of this, they attribute the deposi-

tion mechanism to an electrostimulation of Ge atoms adhered to the tip back onto the surface.

Emission of atoms from an STM gold tip was used by Mamin et. al. [23] to deposit small mounds of gold onto a gold sample. To cause hillock formation, 600ns voltage pulses of 4V were applied, while the tip was within tunneling range. The humps were typically 9nm across at the base and 2–3 nm high. For a successful modification, a threshold value of the pulse height observed for both polarities. This value turned out to depend logarithmically on the gap impedance. This led Mamin and co-workers to conclude that the modification took place at a critical value of the electric field. A comparison of the apparent field strengths with those where field evaporation of tip atoms had been observed in a FIM, showed that the observed modification slightly lower values were necessary. However, in the STM the proximity of the sample might change the field strength for field evaporation to lower values, since atomic orbits start to overlap.

Surface modification attributed to localized heating and melting was explored by Stauffer et. al. [24,25,26]. The substrate used was a glassy $Rh_{25}Zr_{75}$ alloy. Hillocks were formed by increasing the bias voltage to 2V and the tunneling current to 315nA, with the scan stopped. After approximately 5 seconds, the current began to oscillate, and the control system withdrew the tip. This behavior is attributed to the movement towards the tip of a molten portion of the surface; the melt is attracted because of the strong electric field, forming a cone. Hillocks formed in this manner had diameters of 350Å and heights of 100Å. Lines and complex patterns were also created. Typical line widths were 200Å. Structure size could be controlled by application of variable biases,

yielding a range of diameters from 40 to 115 Å. Structures were also formed on other glassy alloys, such as $Fe_{86}B_{14}$, and the ferromagnetic $Co_{35}Tb_{65}$.

Localized healing and subsequent Taylor cone formation was supposed to be the origin of bias voltage induced surface modifications on gold surface reported by Naga-hara et. al. [27]. They increased the bias voltage from 0.1V to 1.4V in a step like function, while scanning of the tip was continued. This created small hillocks 1.0 to 1.5nm in diameter all over the surface. After a certain scanning time at increased bias voltage the hillock formation stopped and the surface became stable again.

Decomposition of an organometallic gas in the STM was shown by Silver et. al. [28]. They leaked dimethyl cadmium between the tip and the sample. By this, a kind of microscopic plasma was formed out of which material was deposited onto the copper sample.

McCord et. al. [29] used $W(CO)_6$ and dimethyl-gold-trifluoro-acetylacetonate as reagent for the decomposition. They also pulsed the bias voltage for decomposing the gas. Lines with 10nm in width were fabricated with this method. An analysis of the chemical composition of deposits that had been made with different fabrication parameters showed that the amount of metal in the structure depended on the tip voltage and the emission current.

Reactive graphite etching with the STM was reported by Rabe et. al. [30]. While investigating the interphase between octylcyanobiphenyl and graphite, they found that tip voltages more negative than 2V resulted in hole formation in the graphite lattice. If the voltage is only increased to 1.6V to 2V they observed material to be metastably

bonded onto the sample. They assumed, that this material consisted of the same highly reactive molecules which etched the graphite at voltages more negative than 2V.

Another nanometer scale hole formation on graphite was reported by Albrecht et. al. [31]. In this experiment, a chemical process was suggested to be responsible for the surface modification. The holes were produced by applying a voltage pulse of 3–8V and 10–100 μ s in time across the tunneling gap in an STM. This locally removed one or more layers of graphite. An investigation of the influence of the surrounding atmosphere showed, that the presence of water vapor was needed for successful hole formation. Therefore Albrecht and co-workers concluded that some kind of chemical reaction took place,

Schneir et. al. [32] deposited gold onto a gold sample with an STM working in a commercial electroplating solution. In order to generate a line-shaped structure they retracted the STM tip about 1 μ m starting in the tunneling regime, increased the tip potential to 3V and moved the tip back and forth along the lines. They ended up with a line 0.3 to 0.5 μ m in width and more than 0.1 μ m in height.

Ehrichs and de Lozanne [33] tried to etch silicon with STM. Based on their experience on the decomposition of organometallic gases, they tried to etch the silicon sample with a localized dry etch process. For that purpose WF_6 was applied as a reagent. Depending on the surface temperature, either tungsten was deposited onto the substrate or the silicon was locally etched as soon as a voltage pulse was applied to the tip.

Heinzelmann et. al. [34] modified $HoBa_2Cu_3O_{7-x}$, a high T_c superconductor, with the STM. For that purpose they increased the bias voltage with the sample positive

from 1.5V to 4V and the current from 1nA to 10nA. They observed formation of holes which had a depth that changed from 43nm to 3.5nm during the first 10min after their creation. Beside mechanical hole drilling, also a local change of conductivity, possibly due to loss of oxygen, was discussed as a possible process creating the structures. In the later case, the changing depth would be explained by oxygen diffusing into the hole making the modified region again more conductive.

1.3 INSTRUMENT.

The instrument used in our experiments was a modified Digit Instrument Nanoscope I STM, which was manufactured by Digit Instruments of Santa Barbara, California. the Nanoscope I consisted of these parts: (Fig. 1)

1. the microscope,
2. the control unit and
3. the display oscilloscope.

1.3.1 THE MICROSCOPE

The mechanism of STM can be found elsewhere.[35]

The microscope consists of following parts:

1. the head which holds the piezo and the first preamp mounted. The scanning piezo which controls the motion of the tunneling tip in three dimensions. The tube scanner can be driven with voltages up to $\pm 150V$ in all three dimensions., yield a scanning area of approximately $0.6\mu m \times 0.6\mu m$ or $9\mu m \times 9\mu m$, respectively, for two different piezo tubes we have.

2. the base which supports the head and sample,
3. the support structure for the base,
4. the stepper motor to control the fine adjust screw,
5. the second preamp.

1.3.2 THE CONTROL UNIT

The control unit contains the low voltage power supply, the high voltage power supplies, the feedback board, the X-Y driver board and the stepper motor board.

The feedback loop [36] uses the current as an input to control the height of the tip by applying a voltage to the scanning piezo (the Z drive voltage). The operator controls the tunneling current and the bias voltage on the sample, so the height of the tip above the sample is adjusted by the feedback loop automatically. The tip-sample separation height is typically less than $10\text{\AA}$.

The X-Y board generated triangular scan voltages whose frequency and amplitude can be varied by the operator.

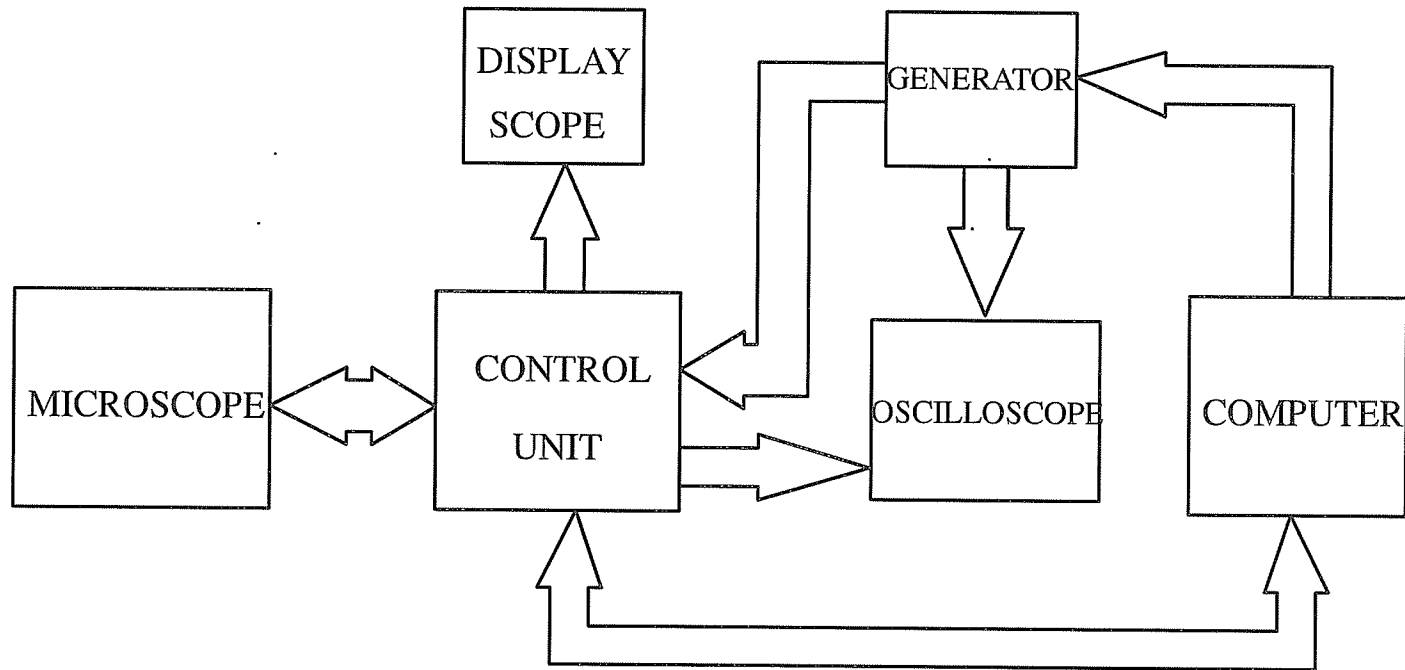


Fig.1. Component interconnecton

1.3.3 DISPLAY OSCILLOSCOPE

The Nanoscope I was designed to display its images directly onto a storage oscilloscope. The Kikusui oscilloscope is used for this purpose. The scope trace is moved across the screen in unison with the movement of the tip above the surface of interest. The vertical motion of the scope trace is controlled by a combination of the y scan voltage and the z control voltage. A third signal is used to control the intensity of the trace on the scope screen. It is derived from the z proportional control voltage.

1.4 EXPERIMENTS

Both gold balls and gold films were used for surface modification. We prepared the gold balls following a procedure developed by Hsu and Cowley for reflection electron microscopy.[37] A 0.5mm thick 99.95% pure gold wire was melted in air by pushing it slowly into an oxygen-acetylene flame (set midway between oxygen rich and acetylene rich). The wire formed a molten ball of gold at the end which grew as more wire was fed into the flame. Feeding 4cm of 0.5mm diam wire into the flame formed a molten sphere about 2mm across. This sphere was then removed from the flame and allowed to cool.

The cooled ball with wire was then put under an optical microscope to examine whether there were good facets to be used. The facets occurred without special treat-

ment as the balls cooled from their molten state. Good facets were easy to find as they reflected the incident light in one direction. The wire (with the ball at the end) would be cut and inserted into a hole on a metal block of the stage. Before setting the stage on the STM it should be examined under the optical microscope again to make sure that the chosen facet upward and lied horizontally by twisting the wire, otherwise the slope of the scan lines would be too large to be digitized

The stage we used is finely movable in both X and Y directions. The fine adjustment screws should be adjusted carefully to make sure that the facet is located right underneath the tip. The sample holder is a block of metal with a hole, in which the gold ball is inserted, and a small screw for holding the wire. The holder is glued to the stage by conductive epoxy. The small screw on the block should be tightened to hold the gold ball firmly.

Gold films were also prepared by evaporation onto heated mica substrates in 2×10^{-7} Torr vacuum. The mica was cleaved just before loading into the vacuum system. The evaporating rate and total film thickness were measured with a quartz crystal oscillator monitor. The flatness of the film was dependent on the sample temperature, evaporating rate and film thickness. The best quality film we have got was deposited at the temperature about 450°C . After evaporation the films were kept in the vacuum system at the same temperature and annealed.

The samples were imaged in constant current mode. Imaging was typically performed with a steady-state voltage of 100mV and a constant current of 0.5nA. The separation between the tip and the substrate was in the range of a few angstroms. To cause surface modification voltage pulses were applied while the tip was within tunneling

range. All imaging was performed in air. The current and Z-piezo voltage were monitored during and after the voltage pulse using a storage oscilloscope.

In order to study the size dependence of the written nanometer scale structures on the applied sample bias voltage the pulse amplitude was varied from 2V to 10V. McBride et. al. [38] reported that the shape of the features formed after pulses were dependent on the width of pulses applied so in our experiments different width pulses from 20ns to 20ms were used. As we know[39] that noise inherent in the tunneling current is an uncertainty in the vertical position of the tip, which eventually causes the tip crash. This uncertainty should be maintained below 100Å if the noise is in a bandwidth limitation of 1MHz at a setpoint current of 1nA. But for single pulse such an uncertainty should not be considered. Unfortunately we did not observe the dependence of the feature size or shape on the pulse height or width.

Several materials were used to make tips including W, Mo, Pt-Ir and Ni tips and all were prepared by electrochemical etching. A threshold curve was drawn for each material.(see 1.5.4 and Fig.9–12) For each voltage 20 trials were made to evaluate the probability for forming a feature.

To observe the relation between threshold and gap distance different tunneling currents and bias voltages were set. It is difficult to assign a distance scale to the horizontal axis, since the conversion requires knowledge of the tunneling barrier height. But the tunneling impedance as the horizontal scale to represent the tip– surface separation. The impedance varied from $10^8\Omega$ to $5 \times 10^9\Omega$. It meant that the tunneling current and bias voltage were in the range of 0.1nA to 10nA and 0.32V to 3.2V respectively.

Both positive and negative voltage pulses were used.

1.5 RESULTS

1.5.1 SURFACE MODIFICATION

Three different kinds of features have been obtained. Those were hills(Fig.2), craters(Fig.3) or holes(Fig.4) and hillocks accompanied with holes(Fig.5). The size of the features varied from 50Å to hundreds of angstroms. The size and the shape of the individual feature were tip dependent. The threshold amplitudes for different tips varied from about 3V to 8V.

The oscilloscope traces of tunneling current and z-piezo voltage were obtained while the tip was operating in air. We could estimate the change in tip sample separation from the trace and it gives strong evidence of material transfer. Bernhardt *et al.* demonstrated such results earlier[40]. When a hillock was formed the tunneling current finally remained constant after the pulse but the piezo moved the tip closer to the surface. That means that a corresponding amount of tip material must have been removed by the pulse. On the contrary when a hole was formed the tip was withdrawn by the piezo further from the surface following the pulse, which implied that some material has been transferred to the tip. But in some cases the piezo was at the same position after pulsing even though there was a feature formed. It is believed that the tip material came from a location on the tip which was not involved in tunneling.

The following describes a typical experiment with a W tip. All the following 105 features were formed by the same tip. Among 105 features 30.5% of them were

hillocks. All of them corresponded to positive z-piezo position change (Fig. 2.(c)) i.e. material was removed from the tip to the sample. 66.7% of 105 features were craters, some of them were holes, which corresponded to z-piezo withdrawn from sample(Fig. 3.(c)). It was believed that material was transferred to the tip.

Efforts were made to write patterns formed by small mounds. Figure 6 shows an array of nine mounds written on gold substrate by a gold tip in air using the modification technique. Each mound is about 500Å across.

1.5.2 FEATURE DIMENSION AND Z DISPLACEMENT

The dimensions features was proportional to the absolute value of the Z-piezo change. (Fig. 7) Obviously the bigger the Z-piezo change was the more material was transferred and the bigger the feature formed should be. Such a consistent correspondence between the feature and Z-piezo change, either qualitatively or quantitatively, was strong evidence that the mechanism for the formation of feature was the material transferal between the tip and the sample.

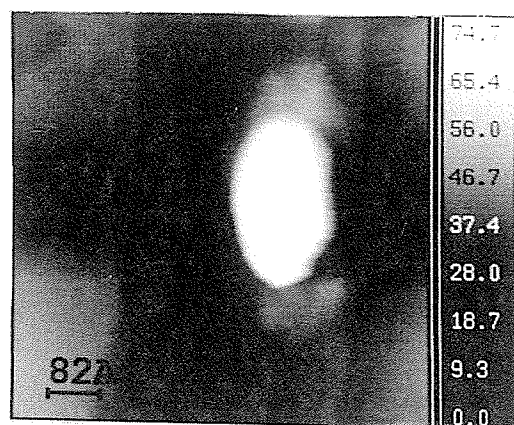
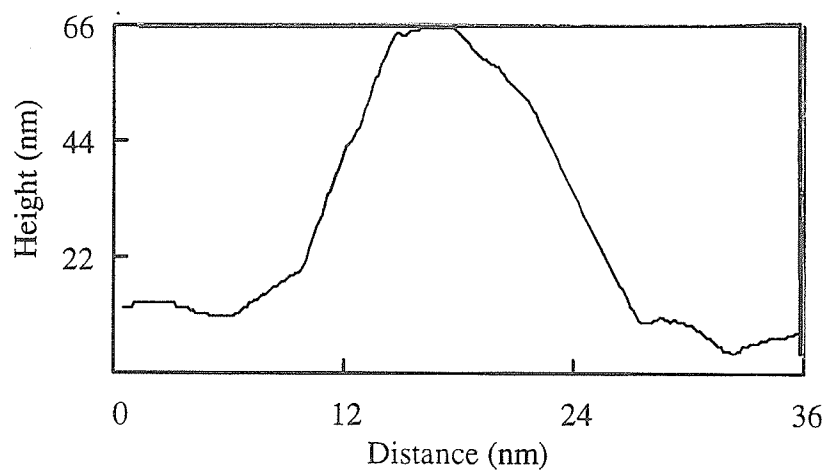


Figure 2(a) A hillock formed after pulsing



(b) The profile of the feature

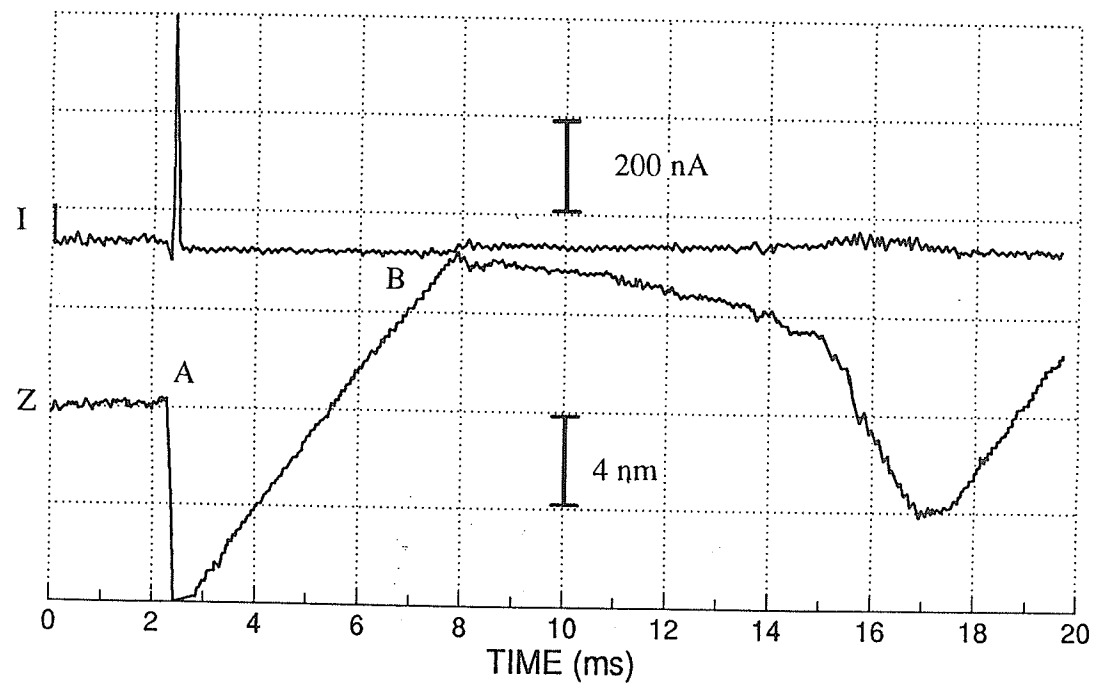


Fig.2(c) Vertical piezoelectric drive voltage Z and tunneling current I for forming a hillock. The scope trace shows that the tip moves closer to the surface because of the material transfer from the tip to surface. At point A the voltage pulse is applied resulting in a current pulse and a retraction of the piezo. During the period from A to B the tip contacts the surface and material is transferred and then the tip moves to its new equilibrium B.

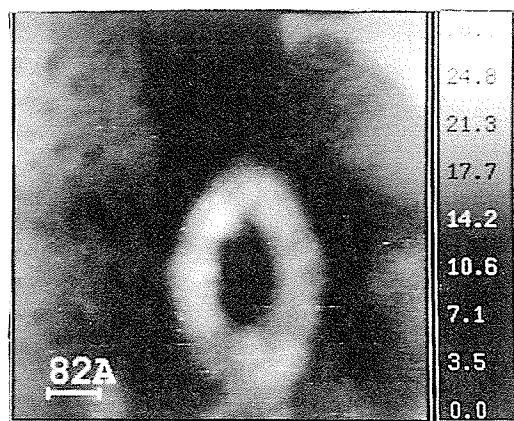
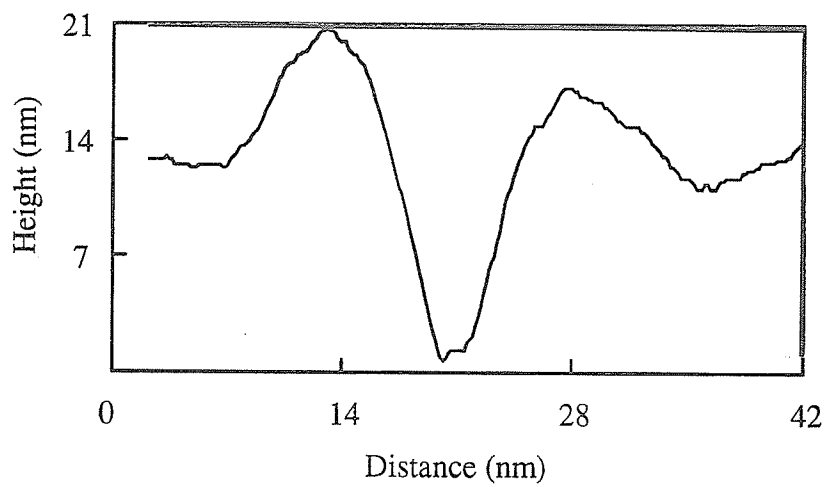


Figure 3(a) A crater formed after pulsing



(b) The profile of the feature

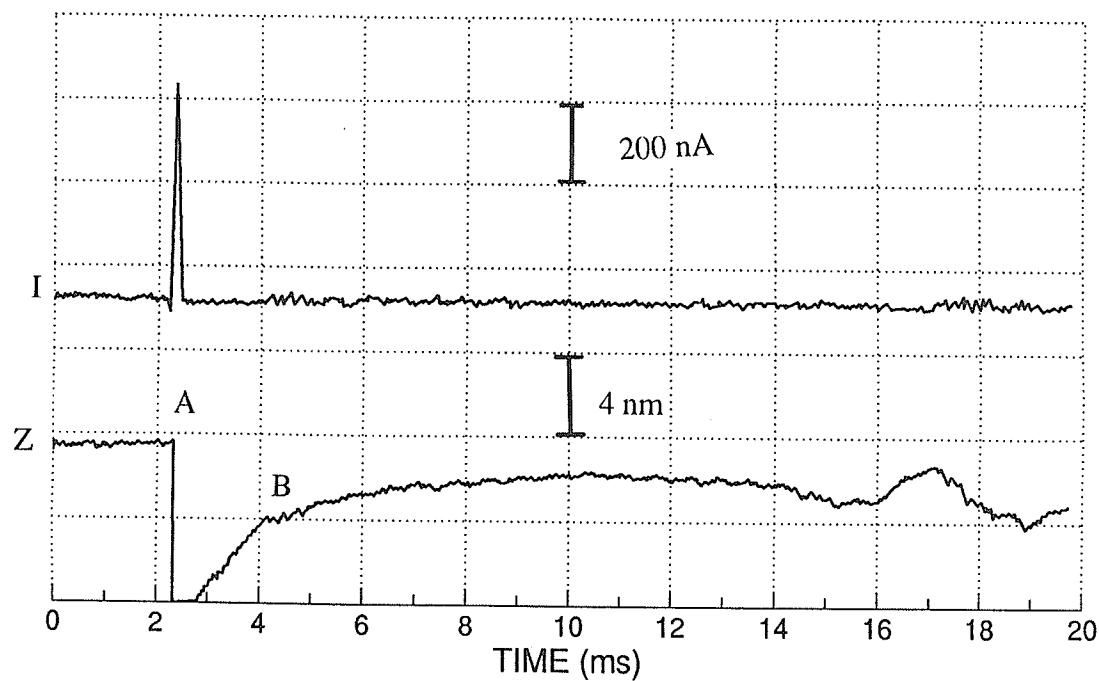


Fig. 3(c) Vertical piezoelectric drive voltage Z and tunneling current I for forming a crater or a hole. The scope trace shows that the tip withdraws from the surface because of the material transfer from the surface to the tip. At point A the voltage pulse is applied resulting in a current pulse and a retraction of the piezo. During the period from A to B the tip contacts the surface, material is transferred and then the tip moves to its new equilibrium B

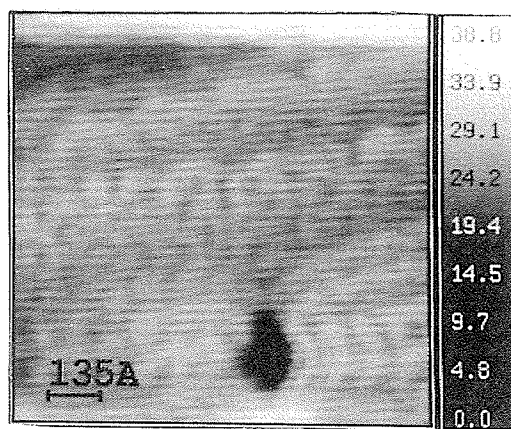
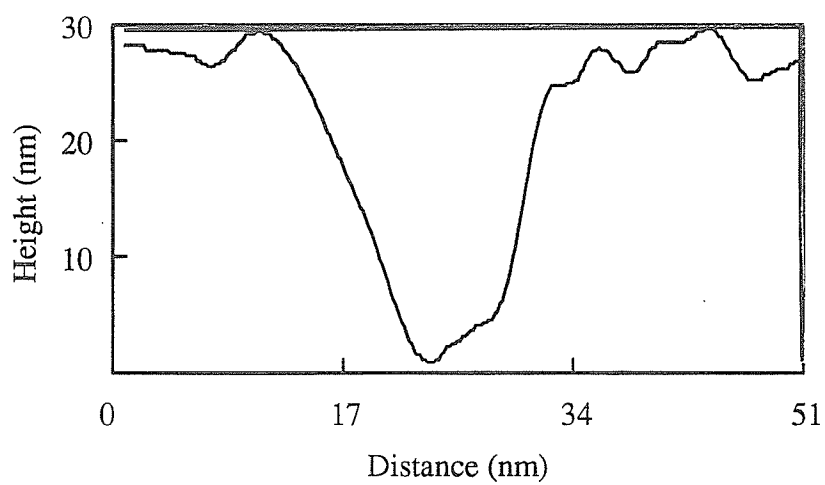


Figure 4(a). A hole formed after pulsing



(b) The profile of the hole

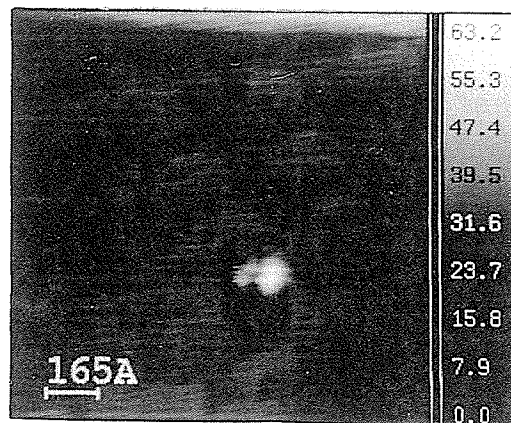


Figure 5. A hillock accompanied with holes

1.5.3 THRESHOLD VOLTAGE AND GAP SEPARATION

Recently Mamin proposed that the transfer mechanism is field evaporation of tip atoms enhanced by the close proximity of the substrate. The threshold value they obtained for gold tip on gold substrate is about 3.5V. That the threshold voltage is dependent on separation is evidence that emission occurs when the applied field reaches a certain critical value.

In our experiment instead of gold tips tungsten tips were used to image the gold surface. Voltage pulse amplitude versus the probability of forming a feature is shown

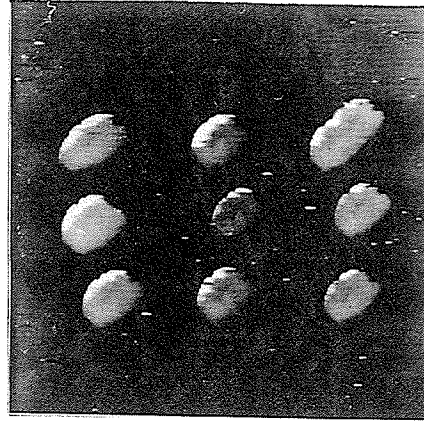


Figure6. An array of nine mounds written on gold substrate by a gold tip in air.

in Fig. 9. We observed the similar linear correspondence. (Fig. 8) Because of different tip materials used and the threshold dependence on tip our threshold value range varied from 3.2V to 4.8V when the gap resistance change from $1 \times 10^8 \Omega$ to $5 \times 10^9 \Omega$. The linear dependence is obvious. The thresholds for both polarities were similar.

1.5.4 THRESHOLDS FOR DIFFERENT MATERIALS

There are still some results in our experiments which cannot be explained by a field evaporation mechanism. As we know that the critical value of the evaporation field for tungsten is higher than that of gold. (see 1.6.2.2 Tab.1) First we thought that the reason why there were more craters formed in our experiments was that material transfer

from gold to tungsten was easier. To explore that we made tips by electrochemical etching of Ni wire, the threshold of the evaporation field of which is lower than that of gold. The possibility to form a crater or a hole was still about 45%. These results imply that the difference in evaporation field between the two materials did not play an important role in the field evaporation process.

To further explore this difference material tips were made by electrochemical etching. We measured the pulse voltage threshold for those tips. The threshold measured were 3.8V, 3.4V, 4.0V and 3.2V for tips made by W, Pt-Ir, Mo, and Ni respectively (Fig. 9–12). Compared with the values of field evaporation the results were not supportive of a field evaporation process. (Tab.1)

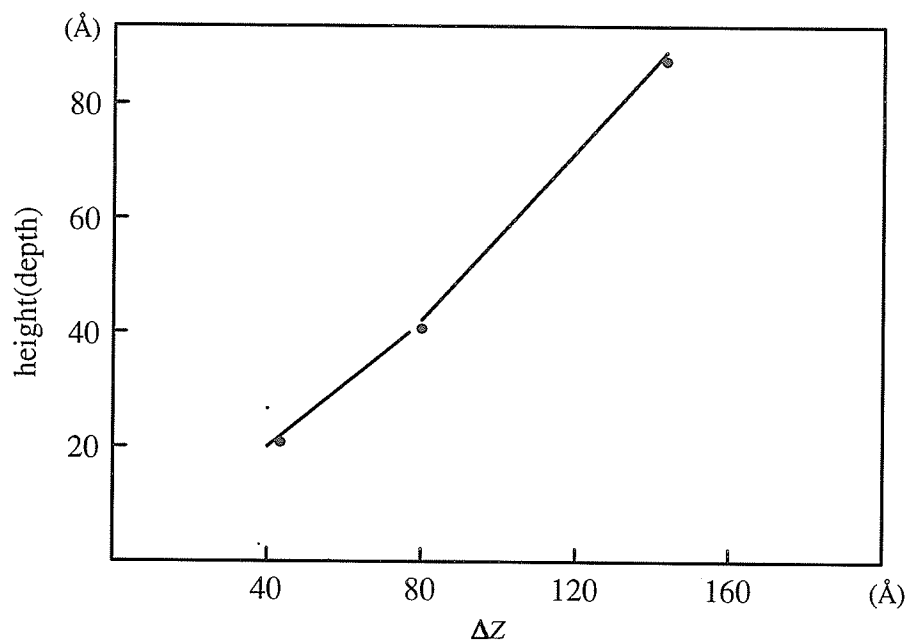


Figure 7. The height or depth of features as a function of piezoelectric drive displacement

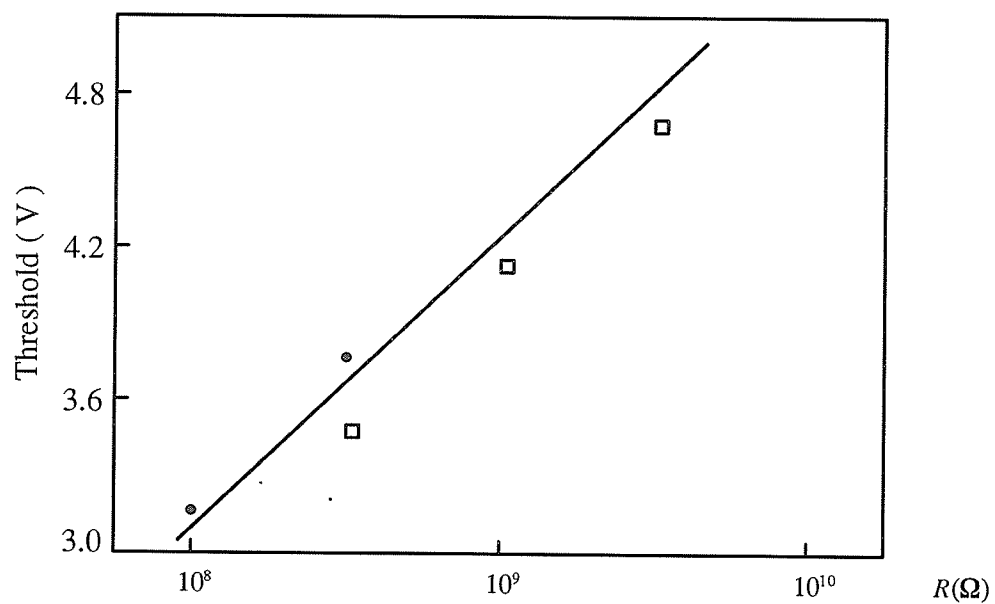


Figure 8. Voltage threshold as a function of tunneling gap impedance.

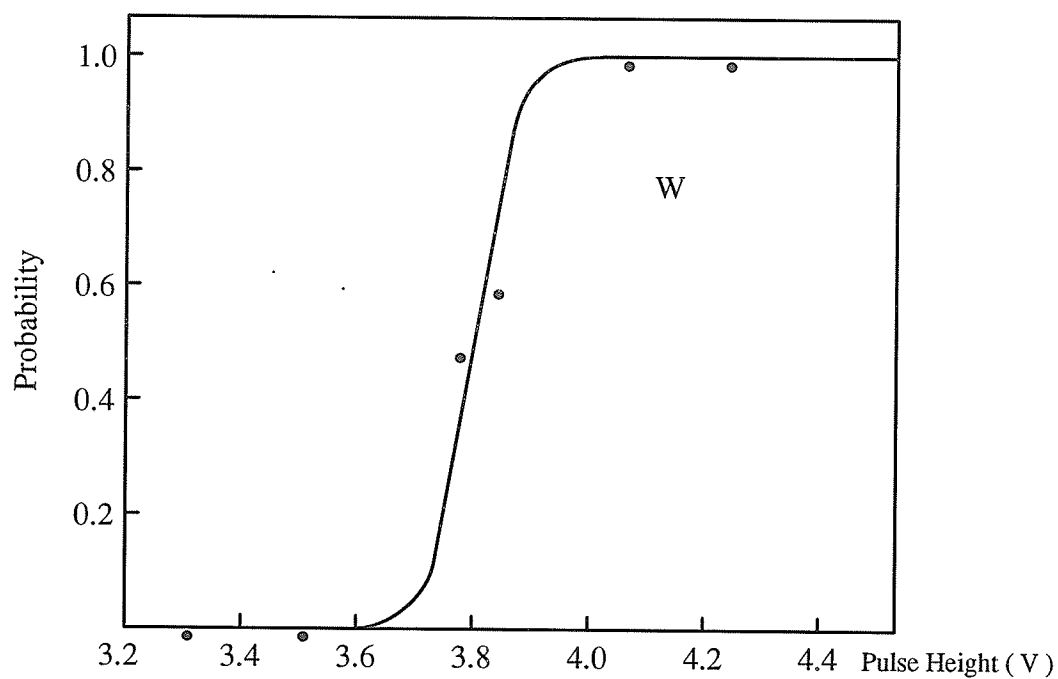


Fig.9 Probability of feature formation as a function of pulse voltage for W tips

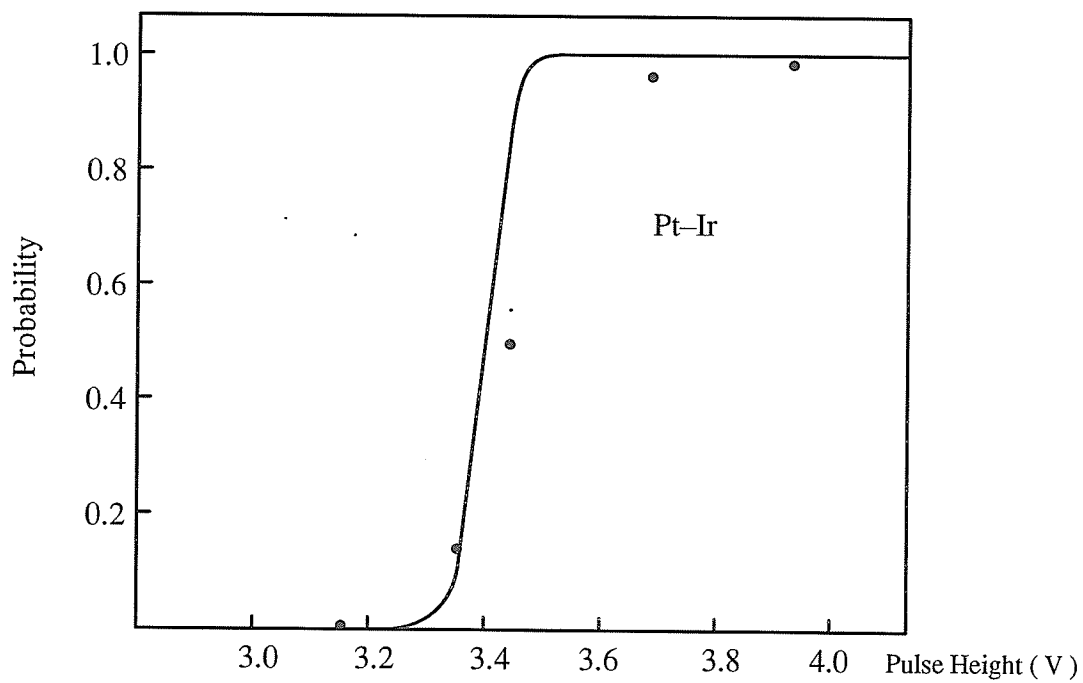


Fig.10 Probability of feature formation as a function of pulse voltage for Pt-Ir tips

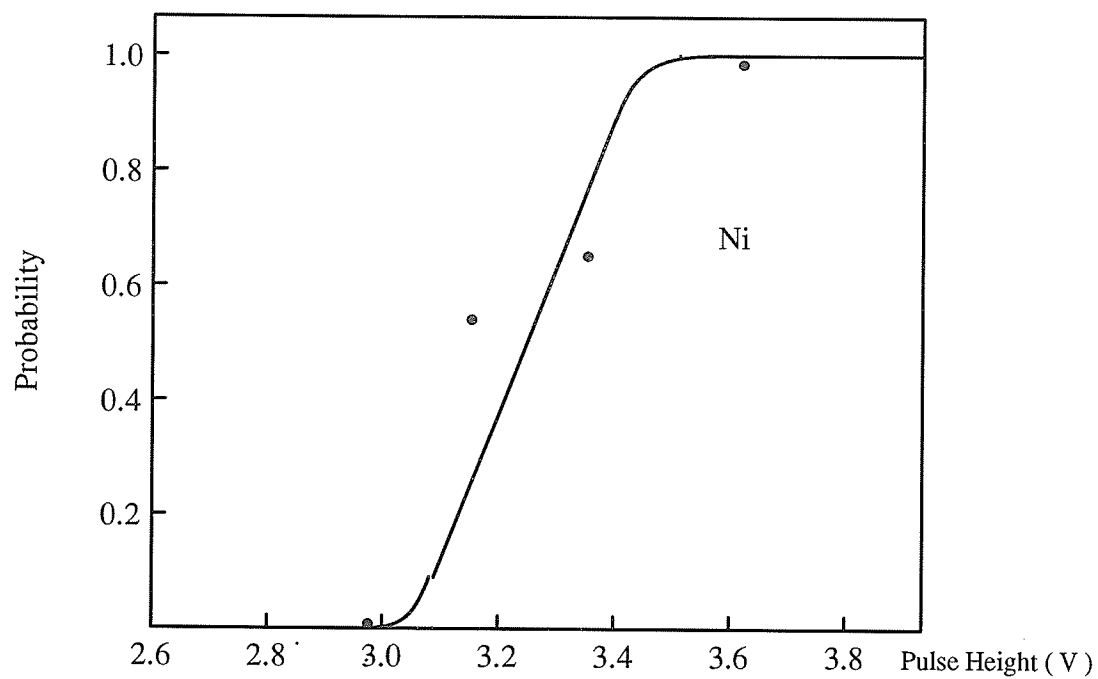


FIG. 11 Probability of feature formation as a function of pulse voltage for Ni tips

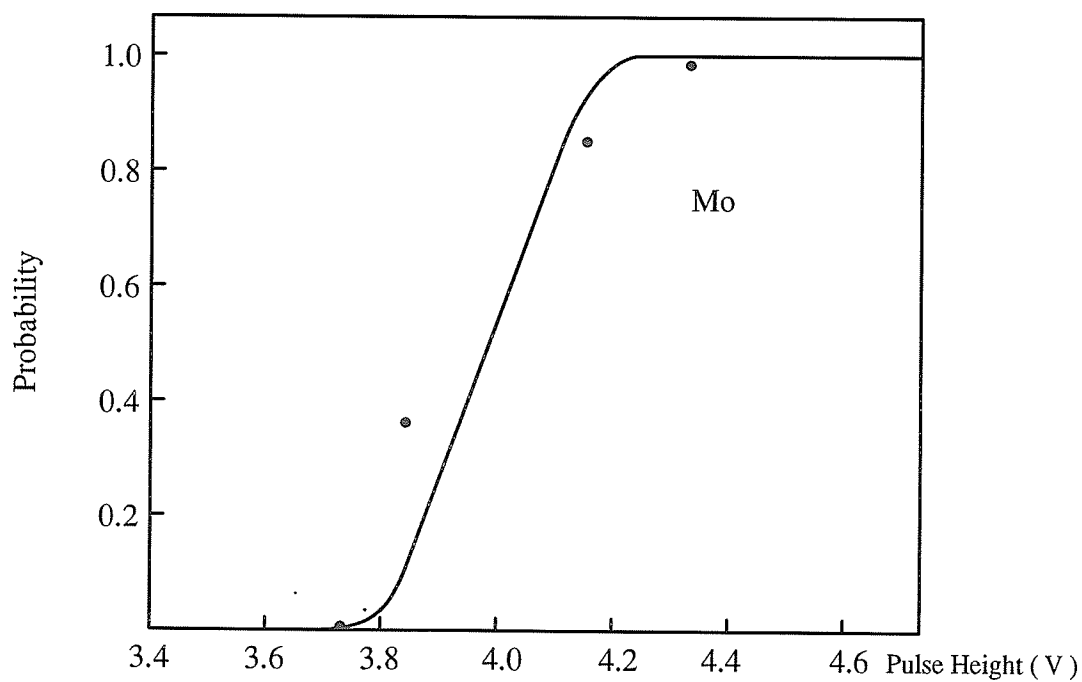


FIG.12 Probability of feature formation as a function of pulse voltage for Mo tips.

1.6 DISCUSSION

A few mechanisms were used to explain the surface modification. Thermal melting, field evaporation and mechanical contact are possible mechanisms for our situations. In the following sections detailed theoretical consideration will be shown. The conclusions will be obtained according to our experiment results.

1.6.1 THERMAL TREATMENT

1.6.1.1 DIRECT CURRENT ENERGY DISSIPATION

Metallic glasses were used by Staufer et. al. [24–26,41] as substrates in their experiments. The high local current density in the STM can raise the temperature in a very small volume near the surface of the metallic glass. An increase in temperature and electric field can lead either to enhanced diffusion of one component or to local crystallization of the glassy state or even to local melting of the surface. Under the influence of the high electric field between the sample and the tip the fluid forms a meniscus similar to a cone. The nanometer-scale structure is then created upon cooling. A current oscillation was observed as it reached at a value of about 300nA.[25] They attributed that to the local melting under the high current.

They also studied the size dependence of the written nanometer scale structures on the applied sample bias voltage.[26] Nanometer-scale structures were visible written with sample bias voltage of 1.0V, 0.9V, 0.8V, 0.7V. Evidently the size of the cones can be significantly decreased by reducing the sample bias voltage for writing.

Obviously the process is related to the energy flux through the gap between the tip and the substrate. The highest energy flux in an STM will occur in the constriction formed by the gap. This region is defined by the tip apex and the sample surface.

When a potential V is applied between the two electrodes the tunneling electrons will gain a kinetic energy eV . Assume that the electrons tunnel from the metal tip. The power generated is ultimately converted into the irregular heat motion[42]. Here we estimate the increase in temperature at the position of the adsorbed molecule.

We assume that the hot electrons which tunnel into metal from the metal of the tip, dissipate their energy according to the formula:

$$P \sim \exp(-r/\lambda) \quad (1)$$

where $P = V_{bias} I_{tunnel}$

r : distance from the entrance point of the current

λ : electron mean free path

The resulting temperature increase is easily calculated by solving the heat diffusion equation:

$$C \frac{\partial T}{\partial t} - \kappa \nabla^2 T = q \quad (2)$$

with C : heat capacity per volume,

T : temperature,

t : time, starting with the 'irradiation' by the electrons,

κ : thermal conductivity,

q : power density.

If we assume that (1) the electrons enter the sample at a point shaped region, (2) the whole electrical power P is transferred into heat at the sample, (3) radiation losses can be neglected and (4) the energy dissipation of the electrons can be described within the concept of the inelastic mean free path λ , meaning that half of the electrons have lost all their excessive energy by a single collision within a distance λ from the entrance point, then q becomes:

$$q = \frac{V_{bias} I_{tunnel}}{4\pi\lambda^3} e^{-\frac{r}{\lambda}} \quad (3)$$

where r is the distance from the entrance point of the current. The temperature increase is then calculated to be

$$\Delta T = \frac{V_{bias} I_{tunnel}}{4\pi\kappa\lambda} \left(2 \frac{\lambda}{r} \left[1 - e^{-\frac{r}{\lambda}} \right] - e^{-\frac{r}{\lambda}} \right) \quad (4)$$

1.6.1.2 ASSISTED TUNNELING PROCESS

A hot electron in a metal, i.e. an electron with an energy ΔE above the Fermi energy, will decelerate by emission of phonons or by excitation of electron hole pairs. For $\Delta E \sim 0.1\text{eV}$ only phonon–emission is relevant and the mean free path due to phonon emission can be estimated to be $\lambda \sim 10 - 100\text{\AA}$ for most metals. Phonons and electron–hole–pair assisted tunneling at low voltage will lead to energy dissipation within a short distance of the interface region [6]. This is in contrast to the dissipation of energy associated with the direct current which occurs inside the crystals forming the interface at distances of the electron mean free path, typically several hundred angstroms. On these grounds one could expect a temperature rise at the surface region, due to assisted tunneling processes, at least comparable to the one created by the direct current.

For bias voltage where $eV_{\text{bias}} \ll \hbar\omega_p$, Flores[44] found the following relation between the power losses of the direct current to the one occurring by assistance through electron–hole–pair formation:

$$\frac{P_{e-h}}{P_{\text{direct}}} = \frac{V_{\text{bias}}^2 \ln(2\kappa_F d)}{4\pi\omega_p \kappa_F \Phi_0} \quad (5)$$

where ω_p : plasmon frequency,

Φ_0 : work function of the tip,

d : separation between the sample and the tip,

κ_F : Fermi wave vector.

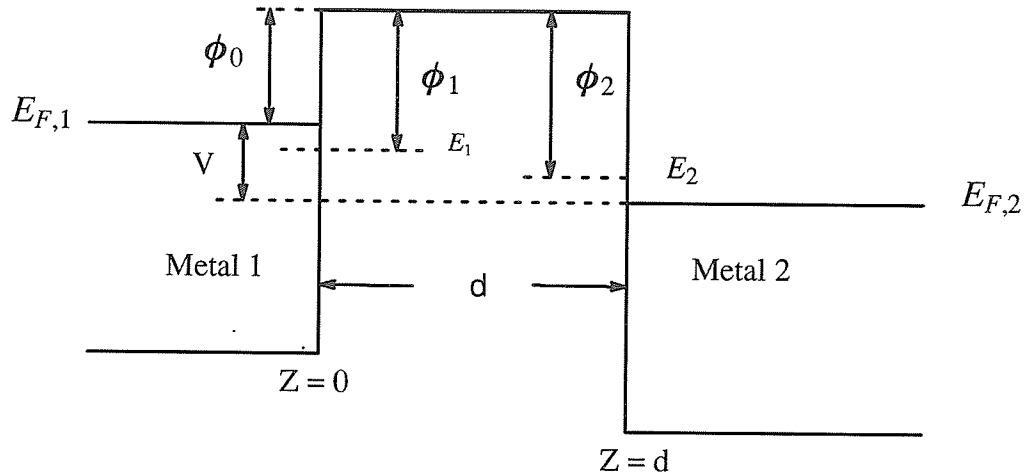


Fig. 13. Model used to calculate the assisted tunnelin process. V is the applied voltage. An electron tunnels from level E_1 to level E_2 .

The energy dissipated by phonons is negligible. e-h pairs can, however, be important in that respect, producing an important increase in the surface temperature. It is also possible that surface plasmon modes characterized by eigenfrequency $\omega_Q \sim \omega_P (Qd/2)^{1/2}$ may be excited in the tip-sample region. An estimate of the probability of such an excitation indicates that it is appreciably smaller than the corresponding probability of an electron-hole excitation.

The pairs excited at the surface can decay into other pairs at a very quick rate (the mean collision time for a pair of 1 eV is around $10^{-15}s$). During these processes the pairs do not have the time to flow away from the interface since the time needed for this process is $10^{-14}s$; so the pairs can be thermalized, creating a region of local thermal equilibrium. Notice in this respect that the requirement of charge neutrality implies that the separation of e-h pairs would be strongly inhibited, resulting in a highly localized

deposition of energy to e-h pair cascades. In a second step, this energy is taken away from the interface [43]. Assuming that a steady state is reached at the interface, and by balancing the energy dissipated in regions [44] of radius r ($r \sim 5\text{\AA}$), with the heat flux; this yields the following increase in temperature:

$$\Delta T \sim \frac{P_{e-h}}{2\pi r \kappa_s} \quad (6)$$

where κ_s is the thermal conductivity at the surface, which might be different from the value of κ for the bulk. It is important to note that the small contact region reduces the bulk thermal conductivity κ by a factor of r / λ , λ being the bulk mean free path for electrons [45]. Using either of these expressions for the analysis of a normal STM experiment, almost no temperature increase will be expected. This means, on the other hand, that if we are looking for a resist which can be modified by a local thermal treatment, we must select a material having a very small λ and κ such as, for example, a thin amorphous metal layer.

For crystalline materials λ is in the range of 10nm and for κ , especially for gold, is about 3W/cmK. Therefore using a bias of 3V and a current of 100nA, for $r \sim 1\text{nm}$. We obtain $\Delta T < 1\text{K}$. It is clear from this analysis that the temperature rise caused by the field-emitted electron in the experiments is not sufficient to melt the substrate. However, in metallic glasses λ is about a hundred times small than in crystalline or polycrystalline metals [46]. κ is in the range of 10^{-2}W/cmK . As the small contact region reduces the bulk thermal conductivity κ by a factor of r/λ , the temperature in amorphous

metals increases hundreds of time, even thousands of times higher than in the crystalline metal cases.

The above discussion indicates that the temperature increase of Au substrates in our experiments is not enough to melt the material to form the features so that the process of feature formation in our situation is not the melting of materials.

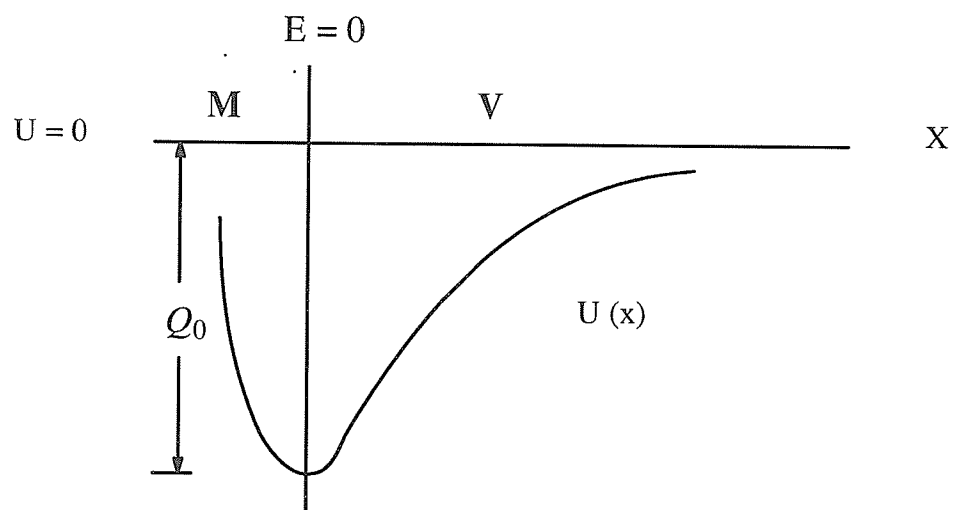
1.6.2 FIELD EVAPORATION

1.6.2.1 BASIC MECHANISM

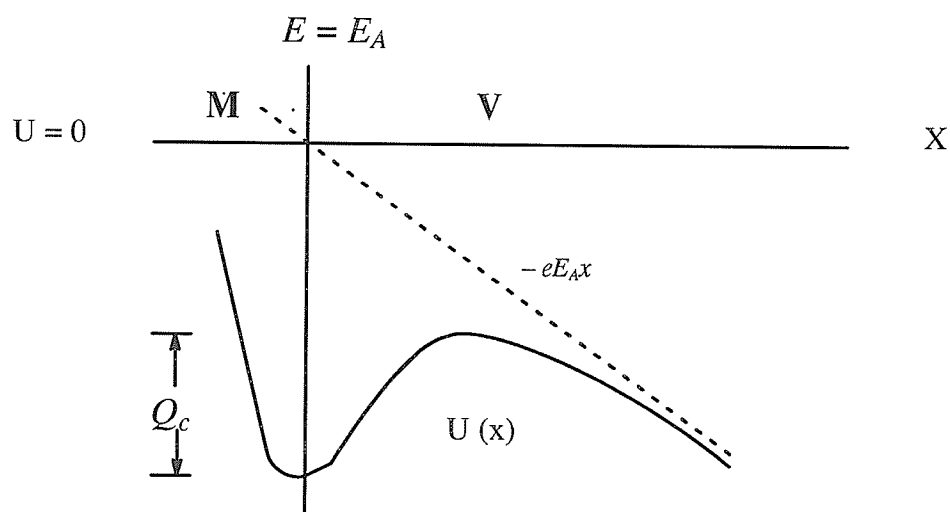
When an electric field of the order of several volts per angstrom is applied to crystal surface, the surface atoms begins to evaporate in the form of ions, even at cryogenic temperatures. This is generally called field desorption when the surface atoms are adatoms and field evaporation when the surface atoms are lattice atoms.

Muller [46] viewed field evaporation as the escape of a metal ion, of charge n , over a barrier resulting from the superposition of the image potential energy $U_0(x)$, which attracts the ion to surface and the potential $U_1(x)$, created by the applied field F .

$$U_0 = \frac{-(ne)^2}{4x} \tag{7}$$



(a)



(b)

Fig.14 Simplified energy diagrams for an ion at a metal-vacuum interface.

(a) Single metal-vacuum interface with no applied field.

(b) Single interface with applied field E_A

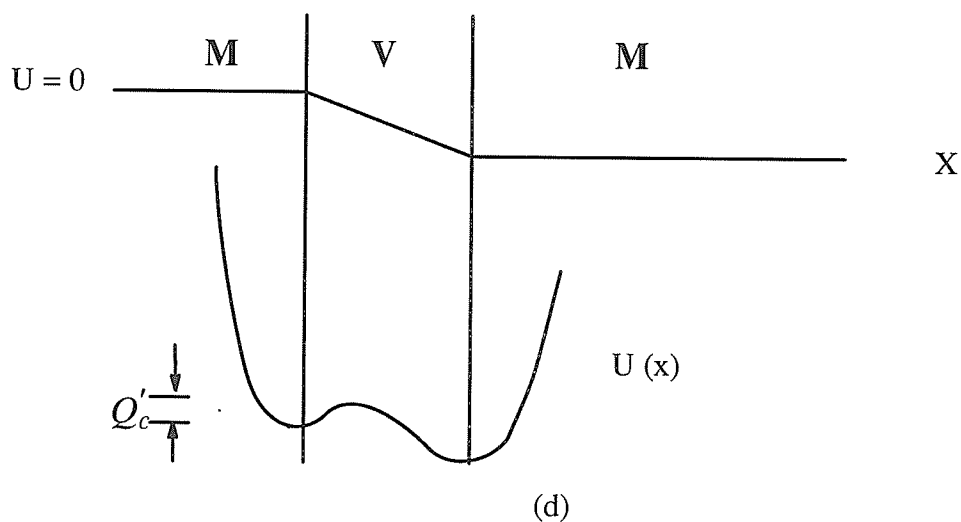
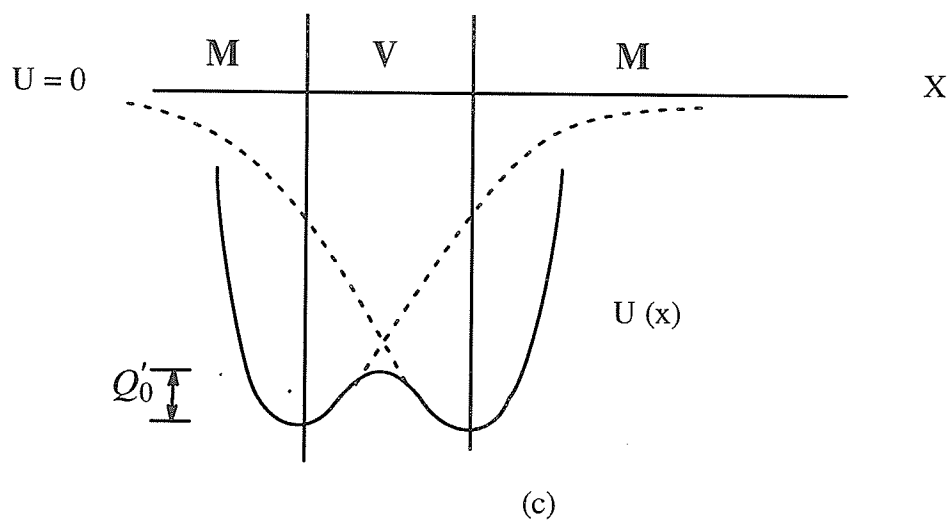


FIG. 14(c) Metal–vacuum–metal structure with two like metals and no applied field

The barrier height is significantly reduced.

(d) Same structure with an applied field.

$$U_1 = -neFx \quad (8)$$

where x is the distance from the surface.

Figure 14.(a) and (b) shows schematically how the application of an electric field can make it energetically favorable for an ion to be emitted from the metal. Figure shows the binding energy Q_0 , the energy to remove an ion from the metal in the absence of an electric field. Application of an electric field lowers the energy outside the metal and creates a potential energy barrier, known as the 'Schottky saddle' [48] over which the ion may escape. One can obtain an expression for Q_e the height of the barrier, by considering the simplest possible model in which the potential energy of an ion outside the metal is given solely by the superposition of the applied potential and the image potential to the metal. For this case, the potential $U(x)$ is given outside the metal by [47,49,450]

$$U(x) = \frac{-(ne)^2}{4x} - neFx \quad \text{for } x > 0 \quad (9)$$

The barrier height is then easily found to be

$$Q_e = Q_0 - (ne)^2 F^{\frac{3}{2}} \quad (10)$$

This is the well known expression derived by Muller. It is also obtained by Gomer for the case of direct ionic evaporation.

For a positive ion

$$Q_0 = \Lambda + \sum_n I_n - n\phi \quad (11)$$

where Λ is the heat of evaporation of a neutral atom, $\sum_n I_n$ is the total ionization potential, and ϕ is the electronic work function. For a negative ion

$$Q_0 = \Lambda + n\phi - \sum_n A_n \quad (12)$$

where $\sum_n A_n$ is the total electron affinity. [46] Q_0 is typically on the order of 5–10 eV.

For the case of gold, $\Lambda = 3.8$ eV, $\phi = 4.3$ eV, $I_1 = 9.22$ eV and $A_1 = 2.3$ eV, so that $Q_0 = 8.7$ eV for a singly charged positive ion and $Q_0 = 5.8$ eV for a singly charged negative ion [51–53]. Thermally activated evaporation occurs when Q_e is of the order of a few times $k_B T$. This simple model then predicts threshold field of $2-7$ V/Å for $Q_0 = 5-10$ eV. These values are of the same order of magnitude as observed in the field ion microscope (FIM). In gold, emission of singly and doubly charged positive ions is observed at fields of about 3.5 V/Å. [54]

1.6.2.2 CLOSE PROXIMITY

As the typical separation should be a few angstroms the threshold fields that we have inferred from our measurements are substantially lower than these values. The above treatment as well as the field ion microscope measurements all refer to isolated tips, however. When two surfaces are placed in close proximity, the barrier for evapora-

tion may be lowered as the atomic potentials begin to overlap, as suggested by Fig. 14(c) and (d). The image potential due to the second surface also contributes to this lowering. This effect is analogous to the lowering of the effective barrier height for electron tunneling calculated by Lang for two surfaces in close proximity. [55] To estimate the effect of the second electrode, we consider a model analogous to that given above. We treat the one dimensional problem and use classical image potentials. We also add a potential to account for the additional chemical binding of an ion to the metal. For electrodes located at $x = 0$ and $x = d$, the image potential can be written approximately as

$$U_{im}(x) = -\frac{e^2}{d} \left[(\ln 2 - 1) + \left[\frac{x - \frac{d}{2}}{d} \right]^2 + \frac{d^2}{d^2 - 4 \left(x - \frac{d}{2} \right)^2} \right], \quad 0 < x < d, \quad (13)$$

as discussed by Binnig et. al. [56] The nonabrupt nature of the electrode edge as well as screening effects can be accounted for by defining d to be the distance between the image planes, which may be offset slightly from the electrode surface. [10,19] We take the ion binding energy to the surface to be of the form

$$U_{be}(x) = Q_0 e^{-\kappa x}, \quad \kappa = 1 \text{ \AA}^{-1}, \quad x > 0. \quad (14)$$

This analysis is chosen for simplicity, but it is justified by the fact that the exchange correlation potential has this form, with $\kappa \sim 1 \text{ \AA}^{-1}$ [54], and because it is consistent with previously calculated metal-metal binding energies, again for $\kappa \sim 1 \text{ \AA}^{-1}$. [57]

In this simple model, the total potential $U(x)$ felt by an ion in the gap is given by

$$U(x) = U_{im}(x) - Q_0(e^{-\kappa x} + e^{-\kappa(d-x)}) - neE_A x, \quad 0 < x < d. \quad (15)$$

for $d = 5\text{\AA}$ we find that Q'_0 , the height of the barrier for $E_A = 0$, is given by $Q'_0 = Q_0 - U(x = d/2) = 0.85Q_0 - 2eV$. Thus the barrier is significantly reduced. The magnitude of the change is model and gap dependent, but the effect is always some reduction in barrier height. This model predicts critical field in the range of $1 - 3\text{V/\AA}$ for $Q_0 = 5 - 10eV$, or about a factor of 2 less than expected for the case of the isolated tip. This simple picture does not fully explain the low threshold fields that we have observed. Neither does it attempt realistically to take into account the exchange, correlation, and screening effects which must be considered at smaller distances.[47,55]

The tunneling impedance increases exponentially with the separation, so that the horizontal scale in Fig.8 represents the tip surface separation. This linear dependence of threshold voltage on separation is therefore evidence that emission occurs when the applied field reaches a certain critical value. It is difficult to assign a distance scale to the horizontal axis, since the conversion requires knowledge of the tunneling barrier height. Mamin also explained why voltage pulses most often produced pits on the gold sample surface by a tungsten tip (instead of the mounds created when they used gold tips) in their experiments. They believed that the pits were formed by local field evaporation of the gold substrate. Because the threshold for field evaporation is significantly lower in gold than in most refractory materials (Tab.1) a strong field is more likely to pull atoms out of the gold substrate surface than out of the tungsten tip. One would expect some of the gold removed from the substrate to be transferred to the tip. With

repeated pulses the gold should at some point be evaporated off the tip back onto the surface, resulting in an occasional mound.

Metal	Field $V \text{ \AA}^{-1}$	Metal	Field $V \text{ \AA}^{-1}$
W	10.2	Fe	4.6
Ir	8.1	Si	4.4
Nb	7.8	Ni	3.8
Mo	6.6	Ge	3.4
Pt	6.3	Cu	3.2
Au	4.7		

Tab. 1 Field evaporation at $T=0K$

In our experiments by using tungsten tips 66.7% features were craters and 30.5% of them were mounds. Firstly we attributed the difference between the results to the different tip materials. Instead of the gold tips used by Mamin we used tungsten tips in our experiments. A higher critical evaporation field is needed to evaporate from the tungsten tip. To explore that we made tips by electrochemical etching Ni wire, the threshold of the evaporation field for which is lower than that of gold. But the possibility of forming a crater or a hole was still about 45%. These results imply that the difference in evaporation field between the two materials did not play an important role in the field evaporation process.

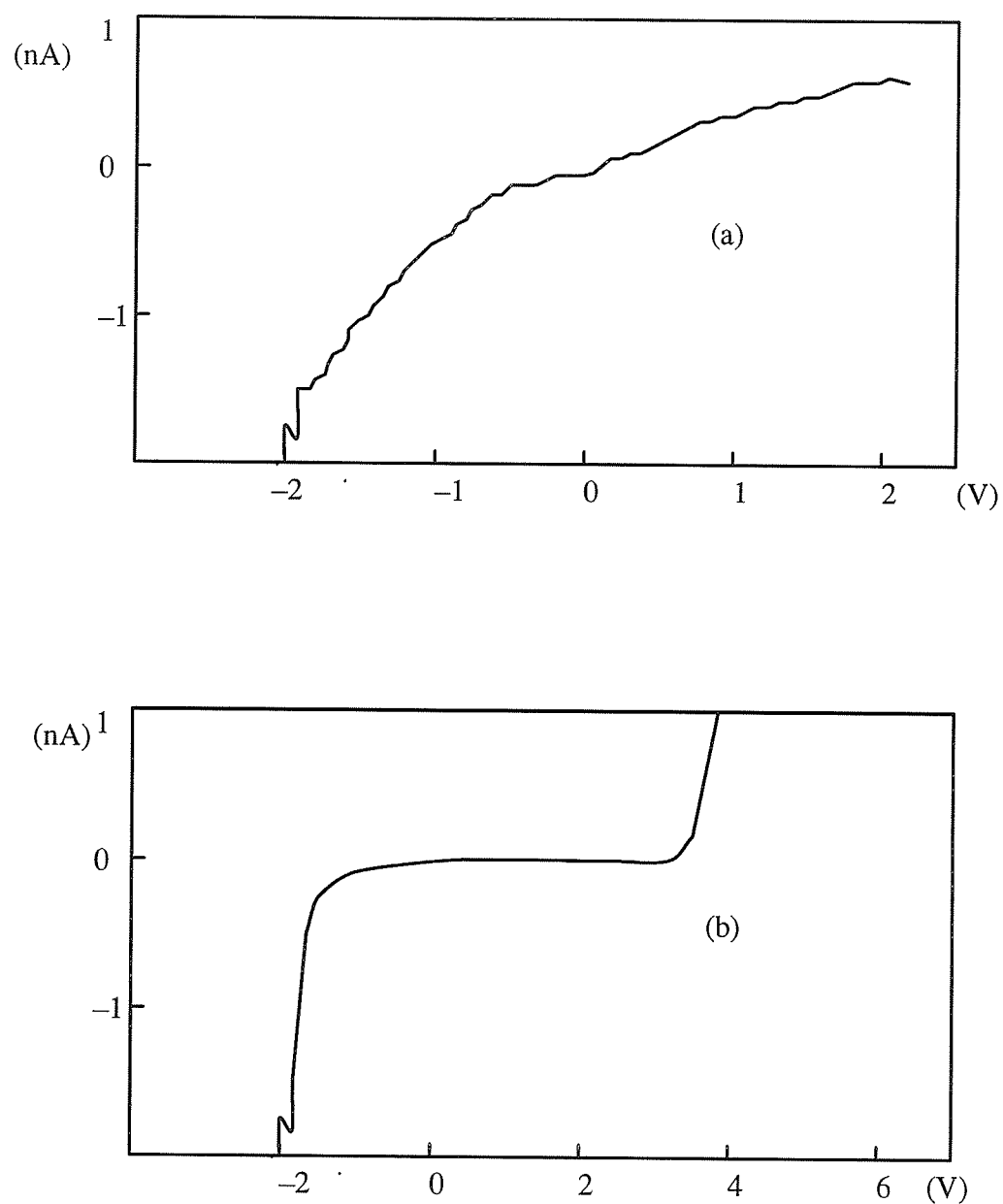


FIG.15 Tunneling current vs voltage (I - V) at constant tip sample separation, corresponding to a constant tunnel current $I=1\text{ nA}$ and tunnel voltage $V=-1\text{ V}$ and -2 V . Curve(a) is for a freshly cleaned tip; curve(b), after several hours exposure. (from [64])

To further explore this different material tips were made by electrochemical etching. We measured the pulse voltage threshold as 3.8V, 3.4V 4.0V and 3.2V for tips made by W, Pt-Ir, Mo and Ni respectively (Fig. 9–12). Compared with the values of field evaporation (Tab.1) the results were not supportive of a field evaporation process.

1.6.3 MECHANICAL MACHINING

Scanning Tunneling Microscopy (STM) involves the interaction of a single cluster (tip) separated by a sufficiently thin vacuum gap to permit electron tunneling to or from a surface. The tunneling regime and point contact are separated by a variation in gap spacing of a few angstroms only.

The effect of deliberate tip surface contact in STM has been reported by Van Kempen and Van de Walle [58] who sought to evaluate tip structure from large indentations induced by contact. Preliminary observations of ‘touching’ the surface with the tip have been reported by Abraham et. al. [59] Interestingly, they produced both protrusions and indentations on Au surfaces about 300 – 400Å across, or smaller structures with distortions extending up to 700Å away from the structure. Soler et. al. [60] first proposed nondestructive tip contact on graphite surfaces to explain the enhancement of the amplitude of atomic corrugation observed in STM pictures. Nondestructive contact imaging forms a basis of atomic force microscopy and repulsive forces have been demonstrated to exist even during apparently normal STM imaging. [61] From these initial results it has become clear that the separation of contact and tunneling is not always

clearcut, and to this end models have been proposed to incorporate both mechanisms to act simultaneously under special conditions. [62,63]

Gimzewski et. al. [64] have studied local surface modifications induced by point contact of a tunnel tip with metallic surfaces. An STM mounted in a ultrahigh vacuum chamber was used with sample transfer and preparation chamber. The sample used were thick ($1000\text{\AA}$) Ag films deposited on a Si (111) wafer by evaporation in UHV.

First it was the transition from the tunneling regime to point contact for a clean metallic tip and surface. The criteria for cleanliness are that the measured value of ϕ is sufficiently high (3.5–5 eV) and that the I–V characteristics are typical for a metal. Fig. 15.(a) shows such a characteristic. Topographies showed a pronounced protrusion at the contact point, localized to dimensions of 30 – 100 $\text{\AA}$ full width at half maximum widths and heights of 20 $\text{\AA}$ for $\Delta Z = 30\text{\AA}$.

For contaminated tip with I–V characteristics similar to Fig. 15.(b), deliberate contact with the surface produced a distinctly different type of surface modification. The resulting nanometer scale structure appears as an indentation rather than a protrusion. Close inspection of the surface directly around the indentation creeds that material is pushed outwards locally from the indentation point.

They believed that for individual clean metal–metal nanometer scale contacts, cohesive bonding between tip and sample occur. Such a result is expected theoretically [65] and found experimentally [66] for microscopic contact. Upon subsequent tip retraction, the contact is in tensile stress, forming a neck of material which breaks, forming a localized protrusion. In contrast, for a contaminated tip such adhesive bonding is much weaker. Consequently, the tip plastically (and elastically) deforms the surface and,

upon retraction, the surface forces are insufficient to pull material from the surface resulting in the indentation observed.

The features we formed were similar to those Gimzewski got by mechanical contact methods. It is also interesting that most of our concave features were not holes but craters, which were formed with collar flanges and depletion of material visible in the area surrounding the mounds. (Fig. 6) This is only explained by the mechanical contact mechanism. The pit was formed as the tip touched the surface and then pulled material out of the substrate during the tip withdrawal from the surface and caused such a distortion.

The results help us to believe that the mechanical contact between the tip and the surface of substrate formed the feature but how can the tip contact happen during the electric pulse.

We suggest that the electrostatic forces on the tip and substrate may result in tip surface contact and the formation of the features observed above. The tip and sample system could be approximated as a parallel plate capacitor C between which there is an electric field F . The applied field generates a static tension σ_N normal to the surface of the specimen given by

$$\sigma_N = \frac{dE}{dx} \quad (16)$$

where E is the electric energy stored by the capacitor. As we know

$$E = \frac{1}{2} C V^2 \quad (17)$$

$$C = \frac{\epsilon_0 \epsilon_r A}{x} \quad (18)$$

where V, the voltage applied on the tip; ϵ_0 , the dielectric constant of vacuum; ϵ_r , the dielectric constant of gap material and A, x, the dimensions of the capacitor. Also we have the relation between potential V and field F

$$V = F x \quad (19)$$

Substitute equation (2), (3) and (4) into (1) and we obtain

$$\sigma = 45\epsilon_r F^2 \quad \text{kg / mm}^2 \quad (1\text{kg/mm}^2 = 9.8 \times 10^{-6}\text{Pa}) \quad (20)$$

where field F is in volts per angstrom. The above result is the same as that of Brandon's. [67] Considering the curved tip shape the value should be even bigger.

Based on the bias and the pulse voltages we used the fields usually lie between 0.3 and 1.0 V/Å so that in vacuum the stress normal to surface is of the order of 4 to 50 kg/ mm² (4×10^{-5} to $5 \times 10^{-4}\text{Pa}$). The presence of H_2O ($\epsilon_r = 80$) on the surface would increase the stress to 320 to 3600 kg/ mm² [20] (3×10^{-3} to $3.6 \times 10^{-2}\text{Pa}$). Most body-centered cubic materials deform plastically at shear stress well below 100 kg/ mm² ($1 \times 10^{-3}\text{Pa}$), even at low temperature. Gold may be particularly susceptible to this as its properties are known to change dramatically when particle sizes shrink to the dimensions of STM tips. For example golds melting temperature drops from 1300K to 500K as particle size shrinks to 1nm.

For a hemispherical tip superimposed on a cylindrical shank the tensile stress in the shank is approximately equal to σ_N , so that the maximum shear stress in the shank, τ , is given by

$$\tau \cong \frac{\sigma_N}{2} \quad (21)$$

These shear stresses are very large and appreciable plastic deformation may occur in the shank. Because of the large stress and small mass of deformed piece the deformation is estimated to occur in picosecond time periods, much shorter than the nanosecond pulse duration.

Albrecht[20] had found the writing process to work more efficiently in air or water vapor. In their experiments after verifying that the tip was capable of reliably forming holes in air, the chamber in which the STM was mounted was pumped down to rough vacuum. The writing process degraded at pressures below 50 Torr and ceased below 10 Torr. When the chamber was vented with water (room temperature vapor pressure of 20 Torr), however, the writing process was as efficient as it is in the air.

Based on above consideration we propose that when the pulse is applied mechanical contact between the tip and substrate is initiated by the increase in electrostatic force associated with the voltage pulse. After pulsing two things may happen; the tip withdraws leaving some residue that forms a hillock or some material is torn from the substrate forming a hole depending on the contamination situations of the tip.

The previous linear correspondence between the voltage threshold and gap resistance can be explained by the mechanism. As the tip withdraws from the surface by setting different bias voltage and current the threshold voltage will be forced to increase in order to provide a field high enough for deformation.

One attractive feature of this mechanism is its lack of polarity dependence. Since the force is proportional to the field squared it is the same for either polarity of

voltage. As mentioned before our thresholds were basically independent of pulse polarity.

As shown in equation (20) the tension σ_N is proportional to the dielectric constant of the gap material ϵ_r . The bigger the constant the higher stress is generated. A material with a very high ϵ_r is water ($\epsilon_r = 80$). Water is well known to adsorb on surfaces and STM tips. Further more it has been found to be important in surface modification of graphite.[68] It has also been reported by Mamin that the gold writing process works more efficiently in air than in vacuum.

In our experiments where tungsten would be contacting a much more ductile gold surface we would expect the surface to deform more easily. Indeed, two thirds of the features were holes and craters. However, with repeated contacts the gold should at some point be transferred back to the substrate from the tip and hillocks would be formed. This probability in our experiments is about 30%.

It is interesting that most of our concave features were not holes but craters, which were formed with collar flanges and depletion of material visible in the area surrounding the mounds. (Fig. 3(a)) This is explained by the mechanical contact mechanism. The pit was formed as the tip touched the surface and then pulled material out of the substrate during the tip withdrawal from the surface and caused such a distortion. With the same idea we also could understand the formation of such a feature like a hole accompanied by a hillock.

1.7 SURFACE SELF-DIFFUSION

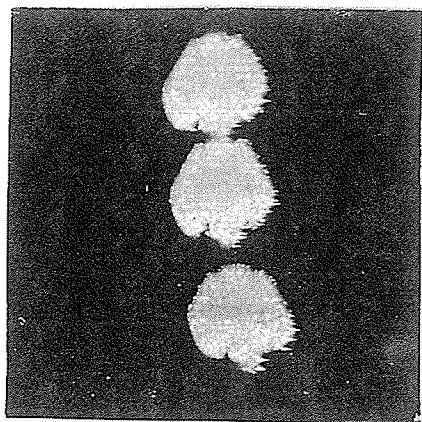
The stability of the written features is crucial for any sort of lithography. One characteristic of lithography on gold is that the features formed are distorted by surface self-diffusion. A number of capillarity-driven morphological change phenomena, such as grain-boundary grooving,[69] smoothing of surface corrugations,[70] sintering of particles,[71] and blunting of field emitter tips[71] have been seen. On surface modification the work of Abraham et. al.,[15] Schneir et. al.,[17] Jaklevic[16] and Emch[21] all showed diffusion and distortion of the written features on a time scale of minutes or hours. Unlike those measurements, Mamin et. al.[72] observed the same amounts for periods of weeks and observed virtually no diffusion. Generally, after features formed, whenever by pulsing or touching the samples, depressions tend to fill up and mounds of atoms tend to smooth out. These observations must be interpreted in terms of a surface diffusion phenomena. Especially the present surface is composed largely of (111) terrace regions whose diffusion sites have low coordination and therefore very rapid diffusion across these region is expected.

We have observed, using time-lapse topography, that for room temperature surface details change with time. The sequence of four topographic images in Figure 16 provides direct visual information about this process. The time per frame is 2.5 min. Both sample and tip were made by gold. In the first frame three mounds were formed after three pulses. The mounds were about $500\text{\AA}$ across. Steps were observed along the three mounds. As the mounds diffusing isotopically the area of each mound expanded and the height decreased. At last the second mound touched the third mound after 6 min(Fig.16(c)). The original space between those two mounds was $200\text{\AA}$. We also observed much faster surface diffusion. A big mound (hundreds across in diameter) could disappear in less than one minute, leaving clusters scattered around the site. But

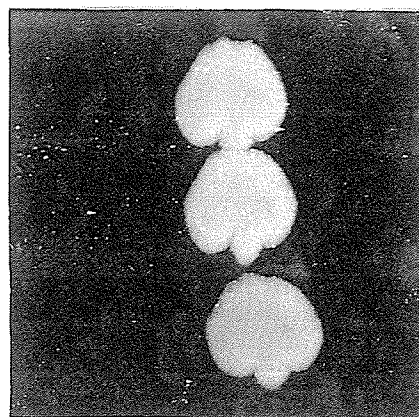
we also wrote some features relatively stable and no obvious change happened during our observed periods. Even on the same observed gold ball diffusion constants were different at different spots. Mamin[72] attributed such a big discrepancies to differing sample conditions, such as substrate stress and surface contamination. We thought it was reasonable but failed to prove it. Gold balls were annealed at 300°C in high vacuum but the obvious diffusion effect still could be observed.

From Fig.16 we could observe that as the area expanded the surface of those mounds became rougher and rougher. Also there were clusters scattered around the mounds. Jaklevic and Elie wondered what the fate of those missing atoms from the features was. Our experiments proved that atoms splashed out of the mounds and moved to remote regions of the sample.

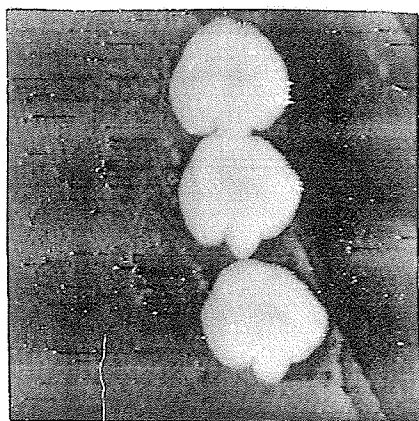
From those experiments we see that the changing topography of a metal surface resulting from diffusion can be monitored with STM. Faster scanning rates are possible with improved STM design and adjusting the temperature will allow individual atoms or groups of atoms to be slowed or frozen in place. Microscopic data would allow for a comprehensive theoretical description of diffusion on a macroscopic scale.



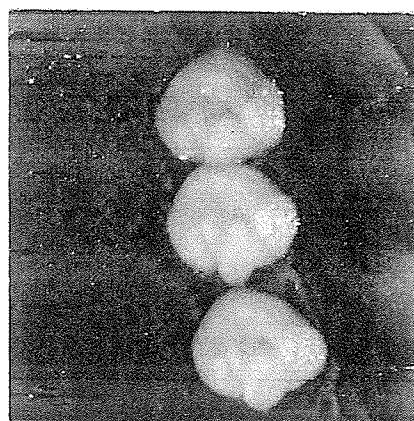
(a)



(b)



(c)



(d)

Figure 16. A series of time-lapse STM topographic images of Au(111) at room temperature in air after 3 pulses. The time per frame is 2.5 min.

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CHAPTER 2

MORPHOLOGIES OF GOLD

2.1 INTRODUCTION

The scanning tunneling microscope probes conductive samples in real space and yields a three-dimensional image of the surface topography, provided that the apparent tunneling barrier height is constant over the surface. Normally the STM is used on 'perfect' surfaces of single crystals or flat thin films to study atomic structures or surface reconstruction at the atomic level. Since the STM has a high lateral and vertical resolution for both periodic and nonperiodic surfaces, it has the potential to reveal three-di-

mensional images of the morphology of polycrystalline surfaces, where steps, facets, grain boundaries, and dislocation can be imaged. The field of film growth, in particular, can benefit from these possibilities.

The metal surface roughness has an important influence on the physical properties of metal films as soon as the film thickness and surface roughness are of the same order of magnitude. Nevertheless, the evaluation of surface roughness is up to now unsatisfactorily solved. For roughness larger than 10nm, transmission electron microscopy (TEM) images of surface replicas were commonly employed. [1,2,3] Below this range only indirect methods were available in the past.

The electron microscopy techniques have several limitations for surface three-dimensional studies: the transmission electron microscopy (TEM) is not surface sensitive, but it offers a high lateral resolution and has the advantage of parallel detection via either photographic plates or video systems. The replica TEM technique yields information on the surface topography, but it suffers from experimental difficulties in the replication process. Scanning electron microscopy (SEM) offers a high lateral resolution, but only limited height information can be obtained. Scanning tunneling microscope is a good tool for studying a three-dimensional image of the surface topography.

An important element of the preparation of samples for microscopy is the selection of a suitable substrate material. For STM studies, the most desirable characteristic

of a substrate is that it be atomically flat so that any deposited species can be easily distinguished. In addition, since the deposition of organic species and films typically takes place in air, the substrate surface should also be relatively inert. Mica is one of the favorite materials for epitaxial deposition studies and consequently some work concerning the oriented growth of noble metals on this material already exists. [4,5,6]

The surface of epitaxially grown Au on mica is interesting for several reasons. First of all, it is relatively easy to prepare to other single crystal metal surfaces studied by STM.[7] It is therefore ideal for studies involving metal to metal tunneling or inter-metallic tip-sample interactions.

Secondly, the Au(111) surface is atomically flat and is relatively inert in air. In addition, it remains hydrophilic for several minutes after exposure to air. This is in contrast to graphite, which has so far been the substrate of choice for organic molecule imaging by STM, which is strongly hydrophobic.

Thirdly, Au(111), as a smooth metallic substrate seems to be suitable for STM lithography and surface modification.

Finally, this surface can also be used as a substrate for characterization of metal on metal epitaxy and for the preparation of other atomically smooth metallic surfaces.

The STM is an ideal tool for studying epitaxial growth, which is of wide technological interest, particularly for integrated circuit fabrication. Theoretical models for

nucleation and epitaxial growth[8,9] have been verified by direct imaging techniques such as scanning(SEM), high resolution transmission(HRTEM), and reflection(REM) electron microscopy.[1] The Au(111) on a mica surface, due to the size of its flat terraces and relatively easy preparation, is ideal for demonstrating STM's capability as a high resolution tool for epitaxial growth studies.

2.2 HISTORY

Reichelt and Lutz[10] measured the orientation and crystallinity of Au and Ag deposited on mica as a function of deposition rate and substrate temperature with x-ray diffraction (conventional transmission Laue technique). For a Au deposition rate of $0.5\text{\AA}/\text{sec}$, for example, growth at room temperature renders a polycrystalline film. At 100°C , on the other hand, the film is textured yielding a 12-fold symmetric Laue pattern. As the temperature is raised above 300°C the pattern is observed to be six-fold. With increasing temperature, this twinned six-fold pattern eventually evolves into a three-fold symmetric untwined pattern indicative of single crystal Au(111) growth. In general, the higher the deposition rate, the higher a substrate temperature one needs for single crystal growth.

Surface topography studies with STM for gold on mica were reported by Marchon et. al.[11] and Hallmark et. al. [12] A smoothly rolling hill structure with hole sizes

in the range of 10nm lateral extension and a few nanometer in height were observed for films grown at room temperature [13]. After annealing in air at 250°C , this topography changed to an atomically flat one with some scattered bumps and trenches attributed to defect structures in the mica substrates or residual grain boundaries in gold films.

Hallmark et. al. [12] performed STM investigations of (111) epitaxial gold films (film thickness = 250nm) evaporated in 10^{-6} Torr onto cleaved mica substrates maintained at 300°C , i.e. in accord with the prescriptions of Reichelt and Lutz [10]. After Ar sputtering and post-annealing in UHV at 350°C , very smooth surfaces with atomic monolayer steps of about 5nm lateral extension were imaged. Finally, on these steps the hexagonal atomic corrugation of Au(111) was excellently resolved both in air and in UHV.

The STEM investigation of the epitaxial growth of gold on mica by Chidsey and coworkers [14] deals with 50, 120 and 480nm/s thickness films grown by e-gun evaporation in $10^{-6} - 10^{-7}$ Torr and 0.1nm/s on air-cleaved muscovite substrates; the substrate temperatures was 25°C, 150°C, 250°C, 300°C respectively. For temperatures higher than room temperature, they observed large flat crystallites containing holes, dislocations and twins. Good epitaxial orientation was obtained only for a substrate temperature of 250°C . With increasing substrate temperature, the films were even flatter but the quality of epitaxy was poorer. This result appears astonishing and contradicts the previously discussed growth experiments of Reichelt and Lutz[10]. For the relevant temperature

of 250°C , high atomically flat plateaus of some hundred nm lateral extension separated by grooves and depressions (lateral extension: 100nm, depth: 5 to 10nm) were observed.

Emch et. al. [15] prepared the gold films by evaporation onto mica under a vacuum of 5×10^{-7} Torr. About 1000Å of Au was deposited at a rate of less than 1Å/s , while the sample was held at a temperature of 500°C .They used STM to characterize the surface of epitaxial gold on mica in air. They found the surfaces were relatively inert to exposure to air or to water, and have atomically flat terraces periodically interrupted by monolayer steps.

2.3 SAMPLE PREPARATION

Our Au films were grown epitaxially with the use of a W filament evaporator within a vacuum chamber with a base pressure of 2×10^{-7} Torr achieved via a diffusion pump. (Fig. 17) $13 \times 13\text{mm}^2$ mica was freshly cleaved and secured firmly onto an heating stage. The chamber was baked for hours until the pressure was low enough. Subsequently, The chamber bake-out was stopped and the mica was heated to deposition temperature and kept at this temperature for periods of time which ranged between 1 and 24 hours. The temperature of the mica was monitored by a K-type thermal couple placed in contact with the stage but due to the long periods of mica heating it seemed

quite reasonable to assume that the mica and stage achieved equilibrium. Afterwards, the W filament was heated resistively for approximately 30 s. Then the gold was evaporated onto the mica at a rate which varied between 0.1 and 1.5 nm/s culminating in an ultimate thickness between 50 and 200 nm. The pressure during evaporation increased to 2×10^{-6} Torr. After the deposition the substrates were allowed to anneal for hours at deposition temperature. Finally the substrate heater was shut off and the films were allowed to cool with the chamber at a natural rate. Upon reaching room temperature, the chamber was let up to atmospheric pressure.

We had also prepared Au substrate by heating a 0.5mm diameter gold wire with a propane torch, forming a 2mm diameter gold ball at its end. This method was also used by others.[16] The resulting gold ball contains several (111) facets of 100–1000 μm in diameter.

Tunneling images were obtained by scanning of the X and Y piezoelectric elements at rates of 20 and 0.043 Hz, respectively, while maintaining the tip at a constant average distance above the sample, so that the tunneling current was modulated by corrugation of the surface electron density. Tip voltages were typically 50 to 500mV, positive or negative, and the dc level of the tunneling current was maintained at 2nA.

2.4 SAMPLE CHARACTERIZATION

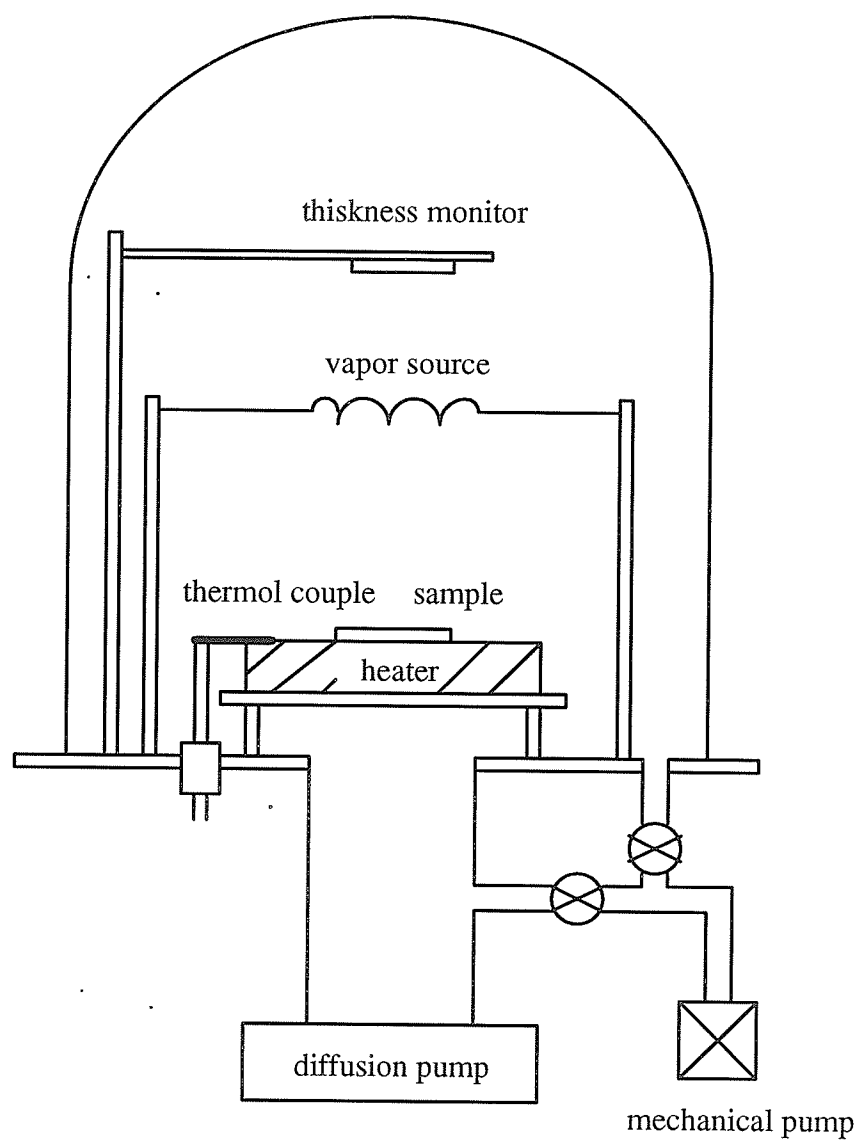


Figure 17 Schematic diagram of the evaporation system

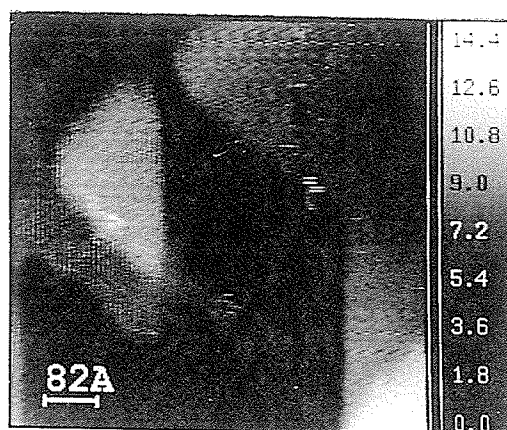
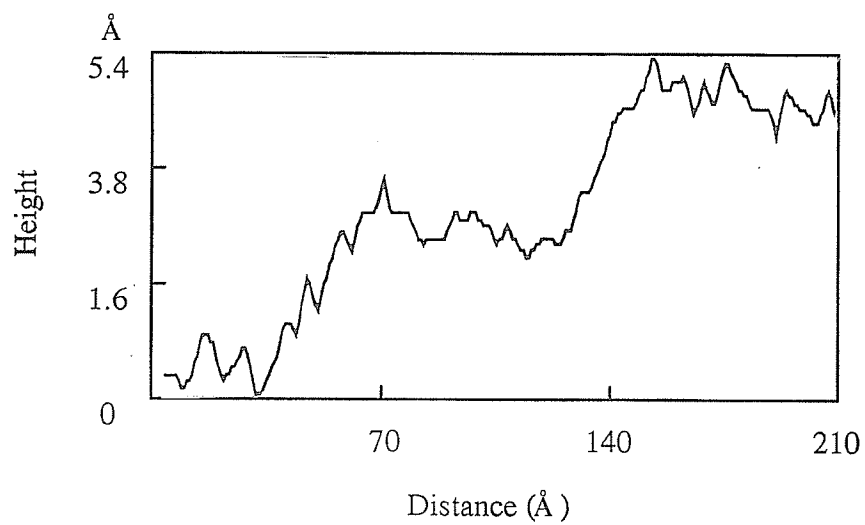


Figure 18(a) An image of the Au(111) surface. Step edges along $\langle 110 \rangle$ directions are observed to be at 120° .



(b) The step height is 2.4Å .

2.4.1 SURFACE ROUGHNESS

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.[17] Figure 18(a) is a typical image of this surface. The surface exhibits atomically flat terraces that extend for several hundred, even thousand angstroms. Step edges along $\langle 110 \rangle$ directions are observed to be at 120° angle to one another which is characteristic of the (111) close-packed plane for the fcc metals, such as, Au. The step height is $2.4\text{\AA}$ consistent with the expected monolayer step on Au(111) (Fig. 18 (b)). Atomically flat terraces are separated by abrupt steps.

2.4.2 ATOMIC CORRUGATIONS

Atomic corrugations of Au(111) facets are too small to observe easily. This difficulty to resolve individual close-packed metal atoms has been attributed to an intrinsic smoothing of electron-density distributions at the surface due to the free electron nature of metals.

Hallmark et. al. [12] first reported their observation of atomic corrugation for a close-packed metal atoms on the surface of a Au(111) thin film. Those novel results are obtained in both air and ultrahigh-vacuum environments and reveal the same highly

ordered, laterally extensive close-packed structure with a corrugation amplitude of $0.3\text{\AA}$ at a tip bias of 30mV and a tunneling current of 3nA .

Later Emch et. al. [15] observed the similar corrugations that correspond to the spacing of Au(111) closed packed atoms. The images were taken at a higher scan speed (horizontal line scan rate at 2kHz) to increase the signal-to-noise ratio. They found that the quality of the imaging was generally much poorer on samples that had been exposed to air for more than a few hours. On dirty surfaces the tunneling was often unstable or the images showed very poor resolution.

During the course of our experiments on mica, we observed some very high formulations on this metallic surface. (Fig. 19) The sample was imaged in the air. The representative tunneling-current image reveals hexagonal close packing over dimensions of 4nm^2 . The observed atomic spacing of $2.8\text{\AA}$, as calibrated against graphite measurements from this instrument, compares well with the known gold interatomic distance of $2.88\text{\AA}$. The tunnel current is 1nA and a tip bias of 100mV . Experiments were designed to exclude the possibility that the observed corrugation might represent an ordered contamination layer. (see 2.8)

2.5 EPITAXY ON Au(111)

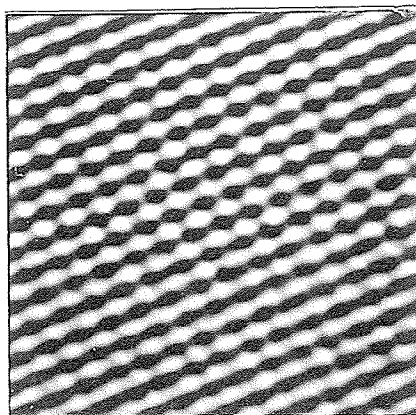


Figure 19 An STM image of a gold lattice

As mentioned in the introduction, the Au(111) surface is ideal for demonstrating the use of the STM as a tool for three dimensional characterization of epitaxial growth. In this section, we will discuss two metals deposited on this surface: Au and Ag. We tried to examine if the structure of thin evaporated metal films depends on a number of parameters, including its temperature during evaporation, before and after evaporation heat-treatment, evaporation rate, vacuum quality, and film thickness.

2.5.1 THE EFFECT OF TEMPERATURE

The substrate temperature during evaporation plays a particularly important role. Therefore a temperature series for both silver and gold was taken.

For the temperature below 200°C Au and Ag films are grainy, practically without any atomically flat regions. Fig. 20(a) shows the image of Au deposited on mica at room temperature. The lateral size of the structures (grains) increases over this temperature range. In the z direction, perpendicular to the film, the peak-to-trough distance remains relatively constant at about $80\text{\AA}$ over the temperature range. These results are in general agreement with Chidsey et. al. [14] these films are not suitable as substrates for STM studies.

We use standard deviation of the Z values σ to indicate the rms surface roughness value, which is defined as:

$$\sigma = \sqrt{\frac{1}{N-1} \left[\sum_i (z_i - \langle z \rangle)^2 \right]}$$

where z_i is a height datum, $\langle z \rangle$ is the average of the height data, and N is the total number of data points (65536 per image). The value calculated for Fig. 20(a) is $72\text{\AA}$.

At the temperature range above 200°C the films are characterized by crystallites with atomically flat tops and lateral dimensions of about $500\text{\AA}$, see Fig. 20(b). (Although our STM technique does not resolve the crystal structure of the films, it is well known

from X-ray diffraction studies [10,14] that Au films on heated mica form (111) crystallites. We assume that to be the case for our films and use the term crystallites to describe the flat island structures.) The valleys and depressions between the crystallites still occupy a significant fraction of the total surface area. The peak-to-trough distance is about $40\text{\AA}$. The crystalline structure was uniformly distributed.

Our best surfaces were obtained at the temperature 450°C . Fig.20(c) shows an example where the surface is flat within $\sim 10\text{\AA}$ over lateral distances of $\sim 1000\text{\AA}$. Steps are observed on the terraces.

Figure 21 is a plot of rms roughness versus the mica temperature for gold deposition. The rms roughness values used for the plots were calculated by averaging the values obtained from several images. It is obvious that the rms roughness decreases as the temperature increases.

The similar images for Ag on mica are shown in Fig. 22. The grain size is bigger when the temperature increases. We got the best silver films at 300°C .

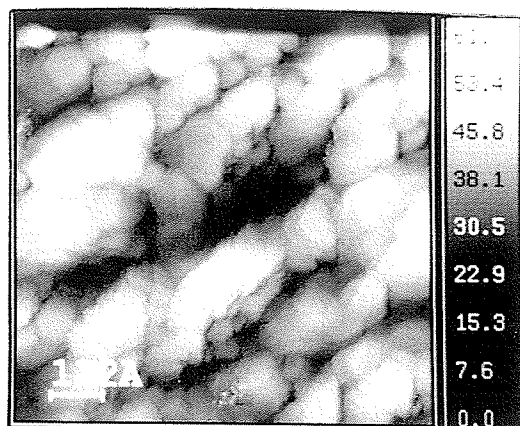


Figure 20(a)

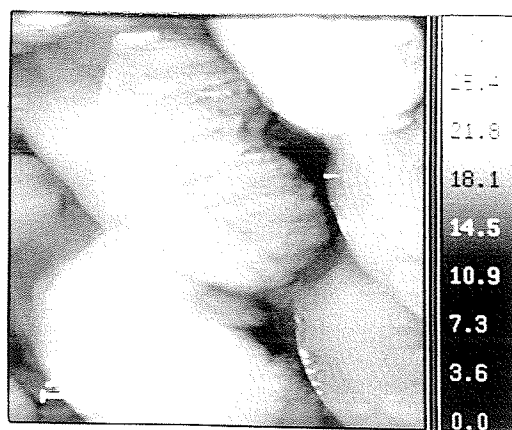


Figure 20(b)



(c)

Figure 20 STM images of Au(111) on mica evaporated at different temperature. (a) at room temperature (b) at 200°C (c) at 450°C

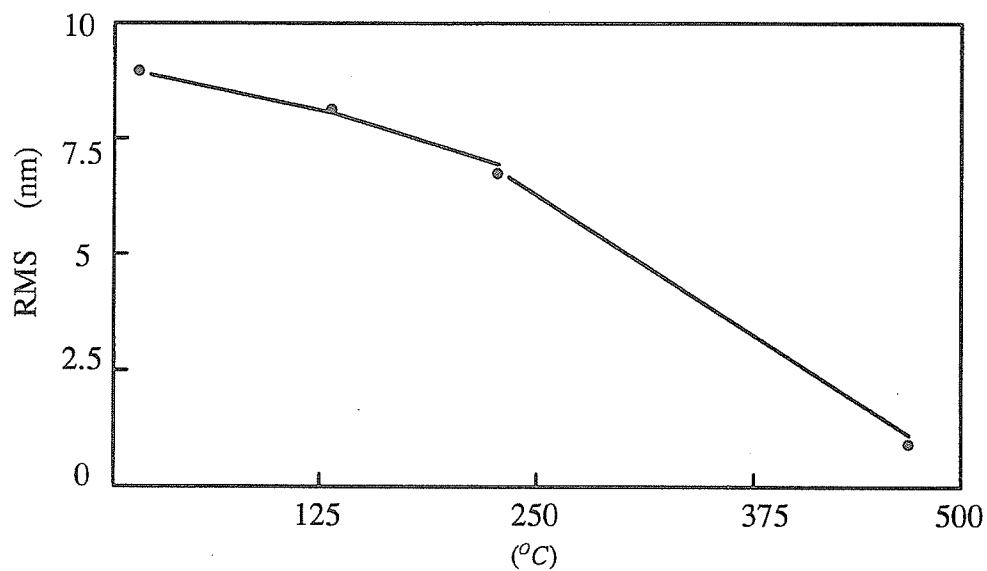


Figure 21 A plot of rms roughness versus the mica temperature for gold deposition
All samples are pre-heated for 24 hours.

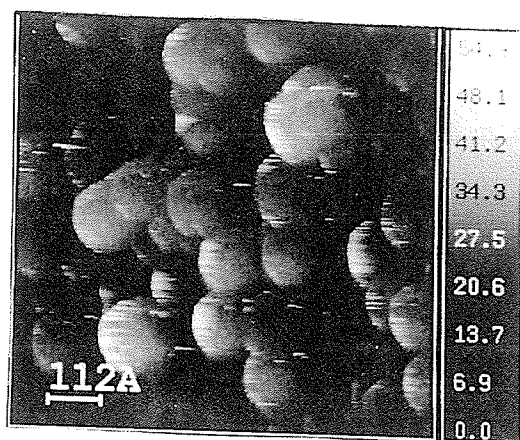


Figure 22(a)

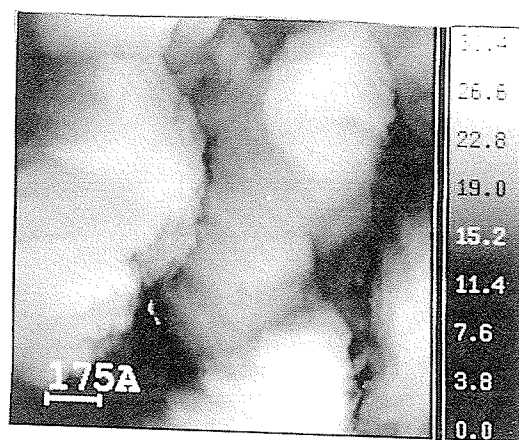
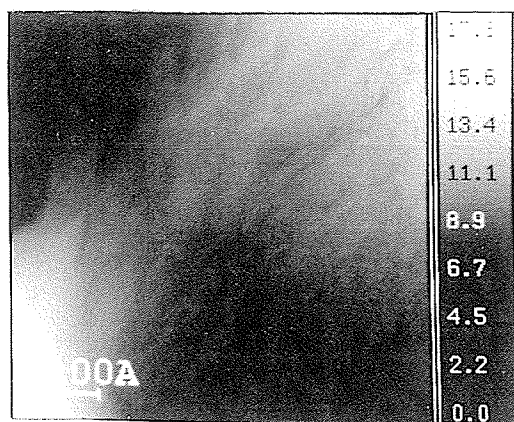


Figure 22(b)



(c)

Figure 22 STM images of Ag(111) on mica evaporated at different temperature. (a) at room temperature (b) at 100°C (c) at 300°C

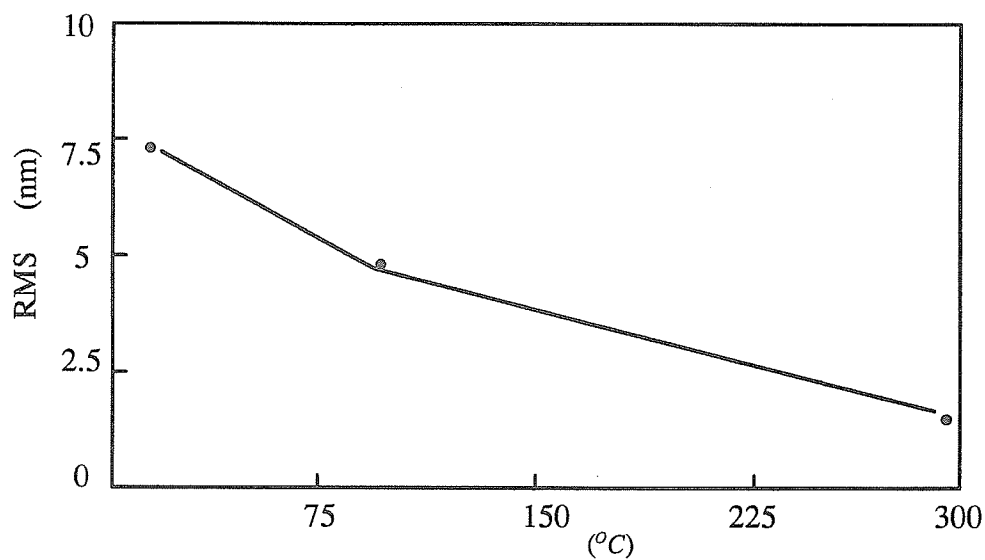


Figure 23 A plot of rms roughness versus the mica temperature for silver deposition. All samples are pre-heated for 24 hours.

2.5.2 THE EFFECT OF HEAT TREATMENT

We noticed that long baking of the cleaved mica, for periods of hours before evaporation resulted in flat Au surfaces. Experiments were undertaken to examine the effect of pre-heating on the morphology of gold films. Before deposition substrates were allowed to pre-heat at temperature 200°C for hours, and then gold films were deposited at the same temperature. Different time periods were used for pre-heating. Fig.24 are the plot of rms roughness versus the pre-heating time at the same temperature. The rms roughness values used for the plot were calculated by averaging the values obtained from several images. The plot indicates a trend that an increase in pre-heating time results in small rms surface roughness. The roughness change was more drastic at the early stages of pre-heating.

On the other hand, Chidsey mentioned that [14] annealing would make films much smoother when the deposition temperature ramping. In their research two experiments were undertaken to examine the effect of annealing on the morphology of gold films. The first sample was deposited near room temperature (30°C rising to 60°C due to radiative heating); the second was deposited during a temperature ramp from about 120 to 225°C in vacuum for periods of time up to three hours. The sample deposited near room temperature became much smoother on annealing. In contrast, the epitaxy of the

sample annealing after deposition during a temperature ramp was essentially unchanged by annealing.

We did the similar experiments on annealing at even longer periods of annealing time but we had not observed obvious annealing effects on the morphology of gold films.

2.6 DECANOL LAYERS ON GOLD

An important concern when the STM is operated in the air environment is the possibility of contamination of the surface and misinterpretation of the images obtained. For gold, the likely contaminants from air are organic adsorbates. We have deliberately prepared gold surfaces with a decanol layer on gold. STM images taken with and without the decanol film are very similar. This result indicates two things. First deliberately added aliphatic organic material on the surface appears not to change the tunneling characteristics very much. Second, the tip appears to be able to easily penetrate such a layer to get within the 5 to 7 Å distance at which nanoampere tunneling currents are calculated to occur[19]. Hallmark et. al. [20] have obtained similar results with both Langmuir–Blodgett films of cadmium arachidate and self-assembled monolayers of octadecyltrichlorosilane on gold (111). Under certain conditions, they were even able to image a periodic lattice ascribable to the gold atoms. We conclude that the presence of organic adsorbates does not have a detrimental effect on the operation of our STM.

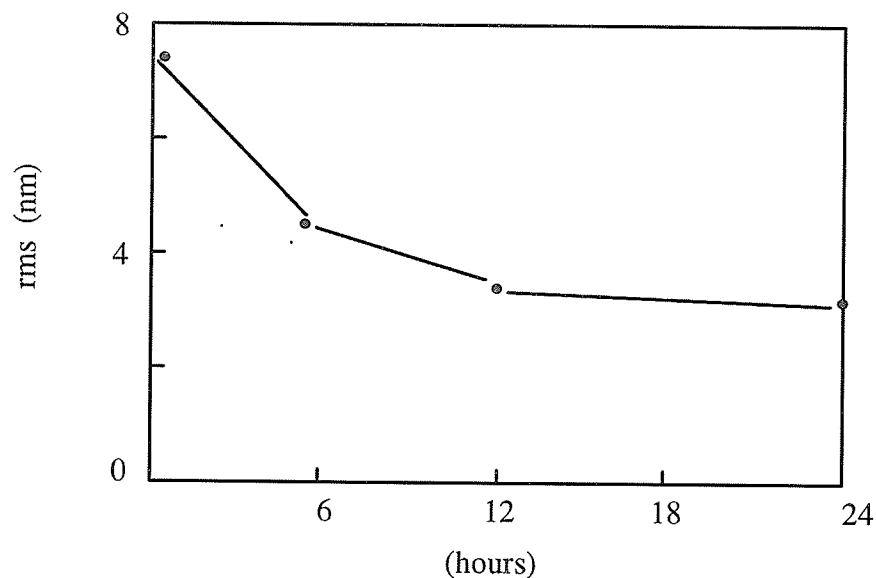


Figure 24 A plot of rms roughness versus pre-heating time
Evaporation temperature at 200°C

2.7 ORIENTATION OF GOLD DEPOSITING ON MICA

The epitaxial orientation relationship found for gold on cleaved mica in the early stages of nucleation is described briefly as follows. Before a sufficient amount of gold has condensed for a diffraction pattern to be observed, the deposits consist of particles of the order $10\text{--}15\text{ \AA}$ in diameter. (Nuclei smaller than this are virtually impossible to distinguish from the background) They generally are single crystals with primarily a (111) orientation (doubly positioned), though some multiply twinned particles are observed. With increasing deposition time the particles grow and the total number in-

creased. The particle morphology is characterized generally by triangular shapes for single particles, and hexagonal shapes for multiply twinned particles. A definite triangular shape is assumed by the single crystal particles when they have grown about 40 Å diameter.

Further development of the gold deposition is characterized by (111) oriented single crystals in both the parallel and 30° rotated alignments (both doubly position) with many multiply twinned particles present. Finally, coalescence phenomena come into play giving rise to a variety of configurations most of which usually contain planer defects. None of the large particles are multiply twinned. The strain energy associated with this structure has increased to the point where further growth cannot take place without transformation to a more stable configuration. Also as a result of a coalescence event, any multiply twinned particle will be transformed into a more stable structure.

Thin film deposits beyond this last stage are dominated by coalescence, recrystallization, and secondary nucleation phenomena(nucleation occurring on fresh substrate exposed by a coalescence event).

Poppa et. al. [21] did detailed investigations on the orientation of epitaxial gold deposited on UHV-cleaved mica substrates in very early and in later stages of deposition.

Very early stages of deposition are characterized by small deposit-partical number densities (about $2 \times 10^{10} \text{cm}^{-2}$), by small particles sizes (of the order of 50Å in

diameter), and by a low value of the condensation coefficient α . From a preliminary estimate, α has a value of approximately 0.1 during early deposition stages at a substrate temperature of 400°C . The corresponding average deposit thickness ranged from zero to about $2\text{\AA}$. In later growth stages α increased and approached unity.

The experimental evidence demonstrates clearly the following two important findings: (a) Small gold nuclei with triangular or hexagonal outlines are found in two basically different epitaxial orientations with respect to the mica substrate, (111) and (211) orientations; and (b) either one of the two types of orientation is found dominating in small regions of the substrate surface the outlines of which are not well defined. The geometrical substrate-overgrowth relationships pertaining to the different epitaxial orientations are schematically illustrated in Figure 25–27. The gold (small circles) is shown in three possible orientations directly on top of close-packed potassium atoms (large dark circles) representative of the cleaved (100) mica surface. Figure 25 and 26 indicate gold (111) parallel to mica (100) and Fig. 27 indicates gold (211) parallel to mica (100) [i.e., gold (111) perpendicular to mica (100)].

In later growth stages the structure of the epitaxial deposit changes. A weak (111) orientation that is rotated by 30° with respect to the substrate develops in addition to the strong parallel (111) orientation, and large numbers of small multiply twinned particles that stem predominantly from parallel (111) oriented parent crystals appear.

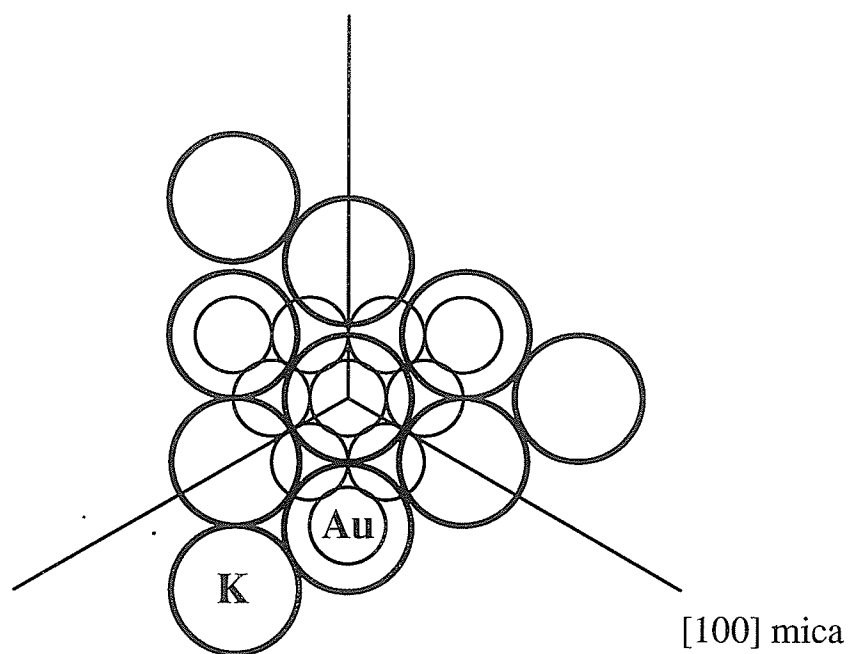


Figure 25 Atomistic arrangements in the mica-gold interface. (111) orientation of Au on mica in 30^0 position.

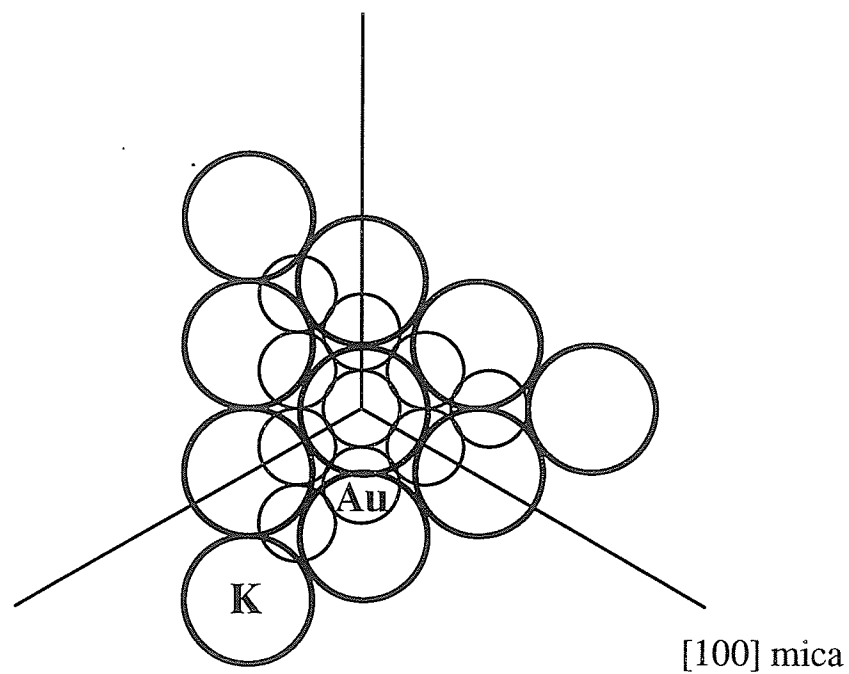


Figure 26 Atomistic arrangements in the mica–gold interface. (111) orientation of Au on mica in parallel position.

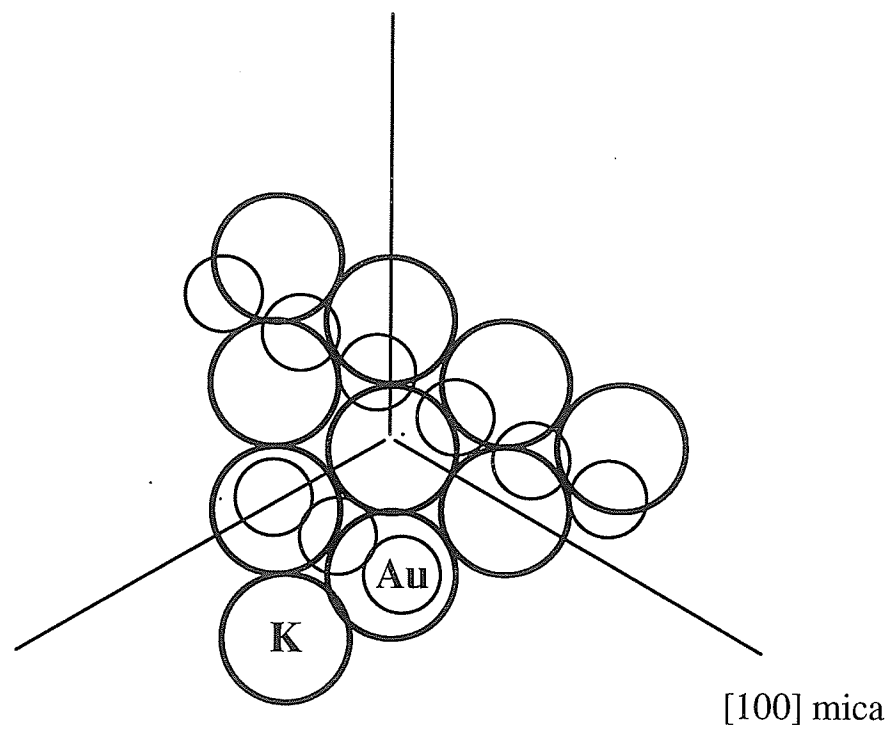


Figure 27 Atomistic arrangements in the mica–gold interface. (211) orientation of Au on mica in parallel position.

2.8 DISCUSSION

As we discussed the general sequence of film growth, individual gold or silver grows as perfect single crystals on substrates like mica so long as they are well separated. Presumably the absence of dislocations is due to the atom-by-atom growth mode and the large energy which would be required to form a dislocation. When two individual nuclei meet, a grain boundary can be formed in the resulting island but, at high enough temperatures, may migrate out of the island leaving just one perfect crystal. Eventually, however, these islands begin to form a network. Substantial misregistry of the coalescing lattices leads to grain boundaries. On the other hand, coalescing islands of similar orientation can form crystalline networks without grain boundaries but often containing holes which have not yet filled in.

With the above ideas, we can now suggest explanations for the surface morphologies we have seen by STM. At low temperatures, we see a topography of rolling hills. We ascribe this morphology to the low mobility of gold atoms on the surface of the growing nuclei and a relatively low probability of the nuclei fusing into fewer, larger islands before the films coalesce. At coalescence, the surface topography is rough, reflecting the shape of the islands from which the film has grown. As the film thickens, the grains grow together to only a limited extent due to the low mobility of gold on gold

at these temperatures. That is, the topography of the grains is nearly unchanged as the film thickens.

At high temperatures, we observe larger, flat-topped grains, with grooves and depressions. The larger grain size presumably reflects in part the fusion of many nuclei early in the deposition to give relatively large islands before the film begins to coalesce. The flat morphology of the tops of the grains clearly reflects the higher mobility of the condensing atoms on the hotter gold surface; large (111) terraces can form. The grooves and depressions probably reflect the topography of the film at coalescence. The grooves clearly occur at the boundaries between grains and would appear to reflect the profile of the grains as they first meet. Because the grains are larger than at lower temperatures, the topography is initially more extreme. On the other hand, due to the large mobility of the condensing gold atoms, the topography fills in more readily as more material is deposited. We, sometimes, see that thicker films show less pronounced grooves than thinner films. The depression apparently occurs where three or more islands meet. These are the last regions to begin to fill in.

We noticed that long baking of the cleaved mica, for periods of hours before evaporation resulted in flat Au surfaces. It appears that long bake-outs of the mica helped to outgas contamination which prevents direct stacking of Au atoms onto the mica surface (Matthews and Grunbaum arrived at a very similar conclusion when doing a study of Au epitaxy on NaCl [22]). The unavailability of a bare mica surface for the

Au atoms to stack upon probably inhibits them from forming a single crystal structure which culminates into large-area flat with hexagonal vacating.

Another possible reason was mentioned by Elliot et. al. [23]. They noticed that potassium atoms are thermally evaporated from both the surface and the bulk of a mica specimen subjected to heat treatment at temperatures in the region of interest for nucleation studies. Their AES analysis showed that the surface is being continually depleted of potassium, the concentration of which is tending to some stationary value. Also the data indicated that the bulk is losing potassium too.

The loss of potassium from the surface as a result of heat-treatment points out that the surface is continually changing, a feature detrimental to nucleation studies. However, the potassium depletion could be minimized as indicated by the above data through adequate pre-heat-treatment.

We noticed that chamber pressure, evaporation rate, and film thickness did not seem to effect the smoothness of the substrate surface a great deal, provided, these variables were fixed within a certain range of values. These results are different to Chidsey's [14].

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