WRDC-TR-90-2118

②

ACTIVATED-SURFACE CHEMICAL VAPOR DEPOSITION

ALAN GALLAGHER

Joint Institute for Laboratory Astrophysics
Quantum Physics Division
National Institute of Standards and Technology
325 Broadway
Boulder, CO 80303-3328

Approved for public release; distribution is unlimited.

February 25, 1991

Final Technical Report for Period May 1, 1989 - August 31, 1990

AERO PROPULSION AND POWER LABORATORY
WRIGHT RESEARCH DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

This report is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

Alan Garscadden

ALAN GARSCADDEN
Research Physicist
Advanced Plasma Research Group
Power Components Branch
Aerospace Power Division

Lowell D. Massie

LOWELL D. MASSIE, Chief
Power Components Branch
Aerospace Power Division

FOR THE COMMANDER

Michael D. Braydich

MICHAEL D. BRAYDICH, Lt Col, USAF
Deputy Director
Aerospace Power Division
Aero Propulsion & Power Directorate

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified

1b. RESTRICTIVE MARKINGS N/A

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution is unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S) WRDC-TR-90-2118

6a. NAME OF PERFORMING ORGANIZATION National Institute of Standards and Technology

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION Aero Propulsion & Power Laboratory (WL/POOC) Wright Laboratory

6c. ADDRESS *(City, State, and ZIP Code)*
325 Broadway
Boulder, CO 80303-3328

7b. ADDRESS *(City, State, and ZIP Code)*
Wright-Patterson AFB
Dayton, OH 45433-6563

8a. NAME OF FUNDING / SPONSORING ORGANIZATION Air Force Office of Scientific Research

8b. OFFICE SYMBOL *(If applicable)* NP

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER MPIR FY1455-88-N051

8c. ADDRESS *(City, State, and ZIP Code)*
Bolling AFB
Washington, DC 20332

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61102F	2301	S2	04

11. TITLE *(Include Security Classification)*
Activated-Surface Chemical Vapor Deposition

12. PERSONAL AUTHOR(S) Alan Gallagher

13a. TYPE OF REPORT Final

13b TIME COVERED FROM 5/1/89 TO 8/31/90

14. DATE OF REPORT *(Year, Month, Day)* 25 February 1991

15. PAGE COUNT 37

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
20	9	4
9	1	20

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)* Plasma phenomena, microcircuits, surface science, surface measurement and modification, scanning tunneling microscope

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)* The purpose of this study has been to construct and to achieve operation of a high-resolution, ultra high vacuum scanning tunneling microscope (STM) and to use the instrument to reveal the chemistry and physics of surface modification, etching or deposition that can be induced by the STM current. Typical approaches to the operational requirements of the STM are described: (1) The mechanical structure of the STM must allow a large range of 3-dimensional motion, yet be sufficiently rigid and isolated from external vibrations to provide less than 1 angstrom vibration of the tip-sample gap and lateral position. (2) Piezoelectrics used in STMs normally depolarize below 200°C, thus limiting vacuum bakeout temperatures to around 150°C. A turbomolecular pump combined with ion and titanium sublimation pumps is used to reach 10^{-10} torr (UHV). (3) Tungsten tips of a few hundred angstroms radius are produced by suspending a wire in an etching solution with the weight or size of the wire hanging below the neck minimized and the current rapidly terminated after the wire breaks. (4) Various procedures for sample preparation are documented. The details of the in-vacuum procedures are elaborated so that future work on STM-induced surface modifications has a sound basis.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☑ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL Alan Garscadden

22b. TELEPHONE *(Include Area Code)* (513)255-2923

22c. OFFICE SYMBOL WL/POOC

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

FOREWORD

This report describes work conducted by Robert Ostrom, David Tanenbaum, and Alan Gallagher, respectively a postdoctoral and graduate student of the University of Colorado, and a staff physicist of NIST. The work reported was performed during the period of May 1, 1989 to August 31, 1990. Dr. Alan Garscadden was the technical monitor of the program.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

I. INTRODUCTION

The present study has been devised to assist the advance of two technologies. The first is the miniaturization of semiconductor integrated circuits, and the second is the use of electric discharges for many purposes. In both cases, the effect of charged particle bombardment of surfaces is of crucial importance, yet the microscopic physics and chemistry is generally very poorly understood. This is in large part because of the complexity of the problems, particularly when many gas and surface species are involved. There has also historically been a lack of effective tools that can be used to observe the surface with the necessary atomic scale of resolution. Most surface-science tools average over large areas of the surface, whereas charged-particle bombardments normally occur at random, individual sites. Those traditional tools which do achieve atomic-scale resolution utilize high energy electron or ion beams, which rapidly modify the surface under study. The invention of scanning tunneling microscope (STM) by R. Young in 1971 [1], and its advancement to an atomic-resolution tool by Binnig and Rohrig in 1982 [2], has now provided a tool which can measure individual surface features with atomic resolution, using a very low energy electron "beam" that generally does not change the surface being studied. This electron "beam" energy can also be increased "at will," potentially providing an opportunity for controlled surface modification and ultimately for microelectronics miniaturization.

The principal investigator, Alan Gallagher, has worked for 30 years on the physics and chemistry of electron, atom, and ion collisions, for 20 years on the physics of electric discharges, and for 10 years on the plasma chemistry of semiconductor chemical vapor deposition (CVD).

In this work, he has frequently encountered the consequences of plasma-surface interactions, which have often had important consequences for unknown reasons. In his plasma-enhanced CVD work, it has been essential to model surface reactions and to make whatever related measurements are feasible. But as already noted, it has been very difficult to make definitive measurements with traditional surface-science tools. The rapidly advancing field of scanning tunneling microscopy now provides a unique window of opportunity. The physical and chemical surface processes that are induced by charged-particle surface bombardment may now be observable, as well as useful for circuit miniaturization. These atomic-scale surface "collisions" have not been a significant component of surface science up to this time, whereas their gas-phase counterparts dominate plasmas and plasma chemistry. Thus, plasma scientists often have valuable insights and more interest in the relevant surface physics and chemistry. In addition, the plasma-enhanced etching and CVD that is ubiquitous in semiconductor production involve both electric discharge and surface phenomena; an understanding of both is essential. For these reasons the principal investigator has initiated this STM study of the surface modifications and reactions that are induced by charged particle surface bombardment.

This report covers the first 15 months of this new program, starting from an "empty laboratory." Many different apparatus features must be devised, experimental problems must be solved, and observations must be carefully analyzed to obtain meaningful information from such a new research program. Thus, the initial period covered by this report has been largely devoted to developing well-understood and reliable STM images of crystal planes, before charged-particle modification. This is still an ongoing process, in spite of the fact that we have now obtained many images on a variety of surfaces with spatial resolution on a 1 Å scale. We believe that drawing meaningful conclusions from these is much more complex than is often implied in the literature, particularly for observations made in air. The following report thus primarily describes the experimental issues and general characteristics of STM surface measurements. In addition to reporting on our contract, this should provide a more detailed guide to the issues and requirements of STM measurements than is available in the technical literature.

II. GENERAL DESIGN PRINCIPLES AND USE OF THE SCANNING TUNNELING MICROSCOPE

The STM involves a piezoelectrically positioned metal probe, which is raster scanned across a surface [3]. (A common mechanical arrangement is shown diagrammatically in Fig. 1 [4].) During this scan the probe tip is held at a fixed height above the surface by tunneling-current feedback. The tunneling current (i) traverses the small gap between probe and surface, such that the gap is typically ~5 Å. Labeling the scan sweep direction as x, the raster direction as y and z out of the surface, the surface topology is then reflected in the z-piezo voltage necessary to maintain constant current at each x, y position. Another scan mode is to keep z constant and record i(x,y), but this is less frequently used as the tip is already so close to the surface that it will "crash" into the surface if the latter is irregular or if vibrations are too large. Additional information can be obtained from the i(z) relation at each x, y coordinate. In essence, the electron current tunnels through a potential barrier of height φ and width z, so that i(z) reflects the size of φ at each x, y. The φ(x,y) in turn refers to the rate of falloff, with z above the surface, of the sample electron wave function. For a monatomic material, φ is the work

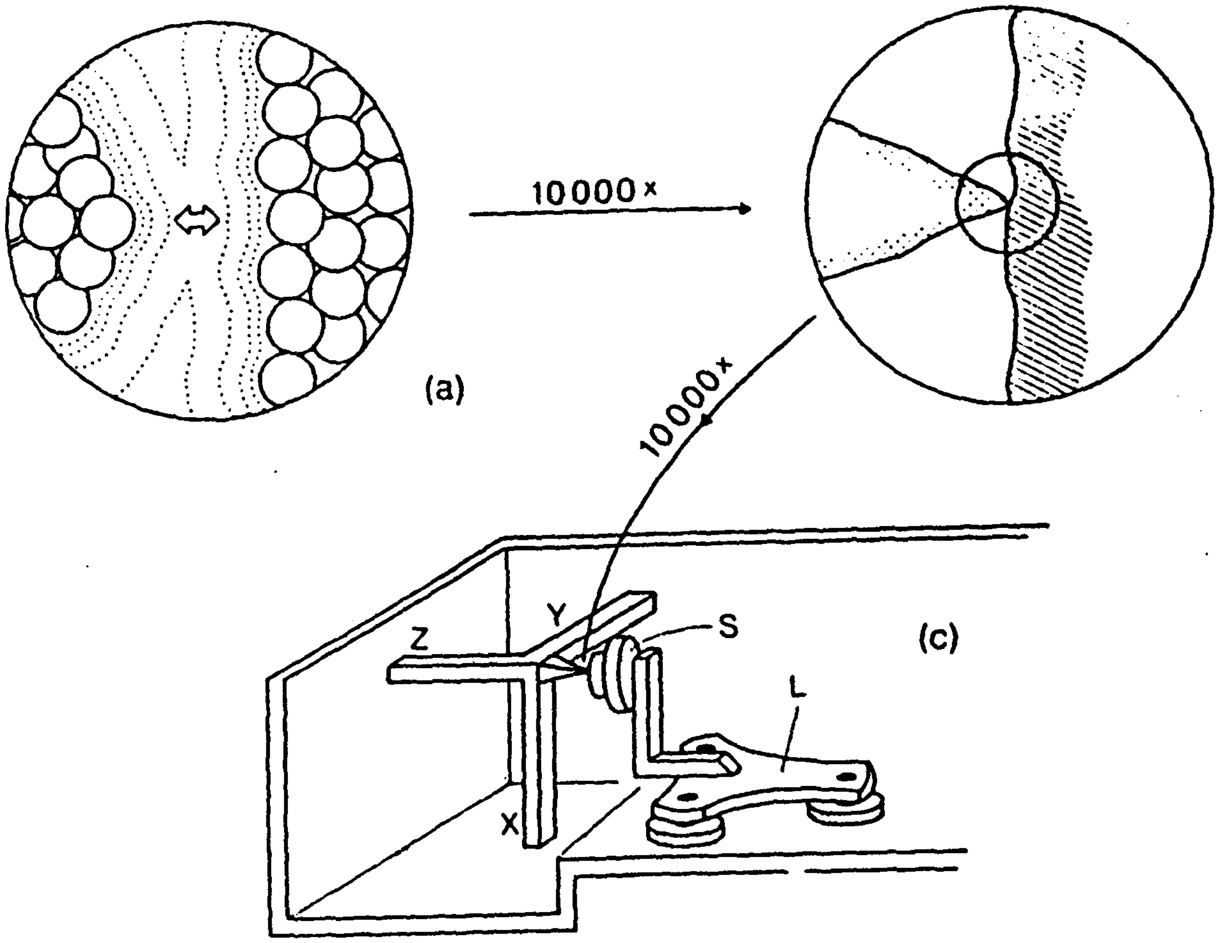


Fig. 1 Diagrammatic representation of a scanning tunneling microscope, taken from Ref. 4. A tripod piezo tip translator is labeled x, y, z, a capacitively clamped "walker" is labeled L, and the sample is labeled S.

function, but for an inhomogeneous material it varies above different surface atoms or sites, thereby providing "chemical" information with atomic resolution.

One of the most amazing characteristics of the STM is its ability to measure surface topology with ~1 Å lateral (x,y) resolution. This achievement is not intuitively obvious, because the probe tip is generally produced by etching tungsten wires to a tip with ~1000 Å radius [5-7]. (The atomic scale tip shape shown in Fig. 1, taken from Ref. 4, is clearly not valid.) A hemisphere of this shape, placed ~5 Å above a flat surface, would produce tunneling over a ~100 Å diameter spot, not 1 Å diameter. The apparent answer to this dilemma is that the surface of the hemisphere is atomically rough. Indeed, it is generally believed that a molecule of the background gas or an atom from the sample occasionally sticks to the tip apex, forming a several Å extension through which the tunneling occurs [3]. This interpretation is supported by the fact that atomic resolution sometimes suddenly comes or goes, and it can sometimes be obtained or changed by briefly raising the probe voltage to induce ionization near the tip. Another surprising fact is that atomic resolution can be obtained while operating an STM in air, and operation is even possible in liquids. Surface science experiments have traditionally utilized ultra high vacuum (UHV), since background gas generally reacts with the surface and also interferes with electron and ion beams. (At 10^{-6} Torr about one molecule/s strikes each surface atom, and the rate in air is ~10^{9}/s.) Clearly, only surfaces stable in air can be used for this, but apparently there are many. Gold, and F-coated Si are examples. The instantaneous probability that a molecule is in the ~10^{-23} cm^{3} volume of the tunneling current is only 10^{-3}, so if they do not adhere to the adjacent surfaces STM measurements are feasible. This is in contrast to almost all other surface science techniques, which require electron or ion beam transmission over macroscopic distances. However, the utilization of air-based STM is much more limited than in vacuum, and interpretations of air-based measurements are often difficult and highly questionable. The aim of the present program, to understand the effects of charged-particle bombardment on etching and deposition reactions, would be extremely difficult in the presence of air. Particularly for reactions of interest in semiconductor production, air is precluded. Thus, we have constructed a UHV system to house our STM and samples.

The purpose of the present effort has been to a construct and achieve high-resolution, UHV operation of a STM, then to use this to study the chemistry and physics of surface modification, etching or deposition that can be induced by the STM current. A large number of STM-induced surface modifications, in air and vacuum, have now been reported from other laboratories [8-14]. Indeed, STM investigations of semi-conductor surfaces must be very carefully operated to avoid inadvertent surface damage, and we have found it quite trivial to induce changes in a variety of surfaces. On the other hand, very poor control and understanding of these changes exists in almost all cases, and the size and shape of the impacted region is not very controllable or understood. Generally at least a 50 Å diameter spot of 10-50 Å height or depth is affected; this corresponds to $> 10^3$ atoms [8-14]. A unique exception to these relatively large spot sizes is a recent report of controlled dragging of individual adsorbed Xe atoms across a cryogenic surface [15]. These various approaches and developments will be discussed further in Sec. IV. Here we will simply note that these rapid advances signify the ultimate importance we expect for this approach to nanolithography. Thus, we believe that the present studies of the chemical and physical causes of these surface modifications will help advance this method of nanotechnology, as well as traditional semiconductor processing.

We will divide this section into components that discuss different design and operating characteristics of a vacuum operated STM. Some of these characteristics, such as vacuum and sample preparation are common to all surface science. Briefly, using an STM to obtain well characterized and understood surface data requires four things: (1) The mechanical STM structure must allow a large range of x,y,z motion, yet be sufficiently rigid and isolated from external vibrations to provide < 1 Å vibration of the tip-sample gap and x,y positions. Typical approaches to these problems, as well as the methods we have adopted, will be described in the following sections.

A. STM Designs

The mechanical design of an STM must provide for both coarse and fine positioning. The coarse positioning is necessary to bring the tip and sample into tunneling range (z motion), and preferably also allows different regions of the sample to be probed (x and y motion). The fine motion is piezoelectrically controlled, and normally provides 1-10 μm of x, y, and z range without much difficulty. Many, widely varying methods are used to obtain the coarse motion, which is often the Achilles heel of the device. The most critical feature of the coarse motion is that the mechanism lowers the stiffness associated with the tip-sample gap, and thereby renders the STM more susceptible to vibration. For a vacuum STM with clean tip and sample, the tunneling current typically doubles for ~1 Å of z motion, and atomic structure typically represents ~1 Å height variation. Thus, one wishes to maintain gap fluctuations well below 1 Å, whereas the mechanical structure is normally 1-10 cm in length. This $\Delta\ell/\ell \leq 10^{-8}$ criterion, while still allowing for large scale positioning, is the critical feature of STM mechanical designs.

A second, related feature is the gap change with temperature; a small temperature drift can seriously interfere with image acquisition.

As shown diagrammatically in Fig. 1, the original device used by Binnig and Rohrig to obtain the first atomic scale STM pictures, as well as many subsequent IBM designs, use an ingenious piezoelectric and capacitance "walker" for x and z motion in a plane [2,4,15]. This achieves a very "stiff" final device. This walker operates by alternately clamping and unclamping one of three "feet" to a metal plate, while piezoelectrically stretching and contracting the spacing between the feet. The clamping action is achieved by placing a thin insulator on the end of each foot and applying a voltage across it. The force ($2\pi\epsilon_0 Q^2$, where Q is the charge) associated with the resulting capacitor produces the clamping action. Unfortunately, no commercially available devices utilize this coarse-control method, doubtless due to IBM patents. At least one commercial device does use an "inchworm" sold by Burleigh Instruments for the z approach, where the "inchworm" is a one-direction "walker" that uses alternate piezoelectric clamping at either end of a tube, with piezoelectric stretching and contracting between clamps. The Gaithersburg group under R. J. Celotta uses a better "inchworm" design [16]. They use inchworms for coarse sample x and z positioning, but only allow them to touch the sample mount during coarse positioning. These "inchworms" push a "hockey puck" across a flat surface, then disengage during sample imaging to isolate from mechanical vibrations and thermal drifts in the inchworms and their mounts.

The coarse z positioning used in our commercial STM (McAllister Inc., Berkeley, CA), which is based on a design by Lyding [17] uses inertial slip to walk the sample. Here the sample holder is a cylinder that slides toward the tip on a pair of rods, and the rods are mounted to a piezoelectric cylinder that provides the stepping motion. This design is shown in Fig. 2. A sawtooth voltage is applied to the outer piezo tube, and the sample follows the rod z motion during each ramp and slides on the rods during each flyback. This design provides a rigid tip-sample structure but no x or y coarse positioning. We have modified our device slightly to also obtain coarse sample rotation, thereby achieving coarse "x" positioning. We apply the sawtooth asymmetrically to different quadrants of the outer piezo tube. This inertially pulls one rod away from the sample, which then rotates on the other rod due to gravity forces.

Many STM designs, commercial and otherwise, utilize screw motion with or without lever reductions for coarse positioning. These devices normally have much greater vibration sensitivity and thermal drifts, and are more suitable for lower resolution use in air and liquids, although some are also currently used in vacuum. I will not discuss them further here, except to note that many laboratories doing vacuum STM work wait days to achieve adequate thermal stability for sample imaging. As another indication of how critical this thermal problem is, if we illuminate our STM through a vacuum window for a few seconds with a flashlight, the tip-sample gap changes by about 100 Å.

Our "McAllister" STM also uses a more rigid form of fine scan control. This method was also first reported by a IBM group, and is now in widespread use. Here a piezo tube electrode is sectioned into quadrants, as indicated in Fig. 2 for the inner piezo. Applying oppositely signed voltage changes to opposite quadrants then bends the tube, achieving transverse motion. x, y and z motion is thus obtained using a single piezo tube, which is mechanically very rigid.

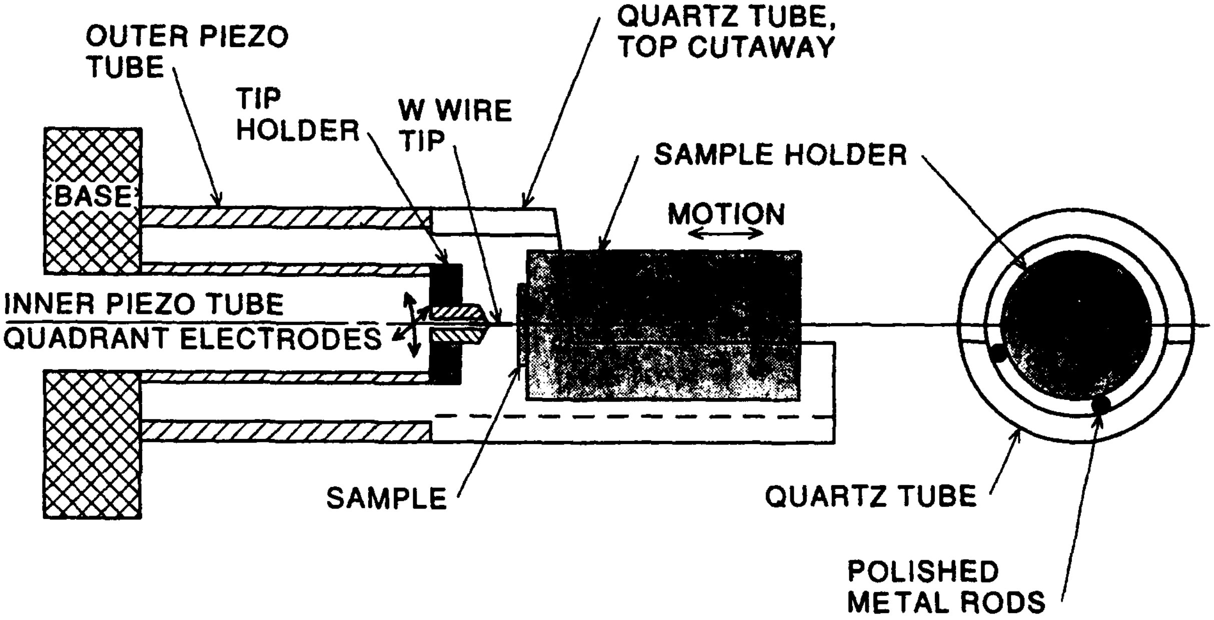


Fig. 2 Cross section and end view of the Lyding two-tube STM design, as adapted by McAllister in the STM we are using. The piezo tubes are ~0.5" and 0.75" diameter.

B. Vacuum Aspects

As already noted, at 10^{-6} Torr approximately one collision per second occurs at each surface atom ($n\bar{v}A_s/4$, where A_s is the surface area associated with one atom, n is the gas density and $\bar{v}$ its mean thermal velocity). Thus, surface studies are normally done at "UHV" pressures $P \leq 10^{-10}$ Torr, allowing ≥ 1 hour sample analysis before background gas can greatly change it. Of course, some surfaces are fairly inert to most residual gases, in which cases this is an excessive requirement. UHV is normally obtained by utilizing all-metal chambers and seals and baking the chambers. The piezoelectrics used in STM's normally depolarize at 170-200°C, limiting bakeout temperatures to ~150°C. Ion, cryo, Ti-sublimation, and turbomolecular pumping are normally used. The most ubiquitous residual gases are H_2O and H_2, sometimes accompanied by significant amounts of CO_2, N_2 and Ar.

We use a turbomolecular pump for initial pumpdown to the 10^{-8} Torr range, and during initial bakeout, then ion plus Ti-sublimation pumping to reach 10^{-10} Torr. The Ti sublimation pump is very effective at pumping H_2, which is our principal residual gas. The ion pump removes the other gases much more efficiently. About 2 days bakeout at 100-150°C, followed by a day of cooling, normally produces a 10^{-10} Torr vacuum. In order to maintain this during sample and tunneling-probe changes, we use the turbomolecular pump to pump down a load-lock chamber. New samples are pumped down to $< 10^{-7}$ Torr in this chamber, typically in a few hours, then transferred through a gate valve to the UHV chamber. We have not yet acquired sufficient long-term STM data to ascertain how rapidly our clean crystal surfaces of Si and GaAs become contaminated in our vacuum.

C. Tunneling Tips

The vacuum tunneling in an STM occurs between sample and the tip of a metal probe. Generally, either Pt or W wires are used for the probe. A very sharp wire tip, on nm scale, is desired. This is sometimes obtained with Pt wires by simply cutting the end off at an angle, using scissors or a razor. It is assumed that the resulting tearing action leaves sharp atomic scale protrusions. The low reactivity of Pt in air makes this a frequent choice. However, it does not achieve reproducible or robust tips, and almost all vacuum STM's utilize etched W probes. Electrochemical etching of W wires to fine tips is a very old art, used for the production of electron microscope field emitters. Etched wires with tip-end radius of curvature $R \approx 2000$ Å are typical in electron microscopes, and were also typical in early STM research. Of course, a smooth tip end of this radius would not yield an atomic resolution (~ 2 Å) picture of the sample. When placed at ~ 5 Å from the sample such a probe would emit electrons over a ~ 200 Å spot. Single-atom resolution using such tips is believed to result from small tip-end protrusions, most often resulting from sample atoms transferred during accidental contact on background-gas molecules that have adsorbed or reacted onto the probe tip. One of the principal values of UHV is thus to allow obtaining an STM image of the sample before this protrusion desorbs or changes shape, and before a new protrusion is added nearby. Since molecules strike every probe-tip atom $\sim 10^9$ times/s in air, obtaining and interpreting air images is much more problematic.

There are many prescriptions and tricks to the art of etching W probe tips. A variety of recent papers describe some of these and reference earlier work [6,7]. Several laboratories now report using W probe tip ends of "a few hundred Å radius," as seen using SEM (scanning electron microscopy) or sometimes from an STM image [14]. We are now producing W probe tips of this radius, based on our adoption and expansion on published techniques. We believe that the size of the tip end is partially fixed by a weight factor which is not discussed in the literature. In order to obtain a sharp wire tip, the wire is always suspended in the etching solution and etched to a narrow neck. As etching proceeds the neck narrows until it can no longer support the weight of the wire end below the neck. It then stretches and breaks. Immediately after breaking, etching continues at the broken tip until the etching current is terminated. To obtain a sharp tip, one must therefore minimize the weight or size of the wire hanging below the neck, and rapidly terminate the current after it falls off. Based on these principles, we now produce robust tips with $R < 300$ Å.

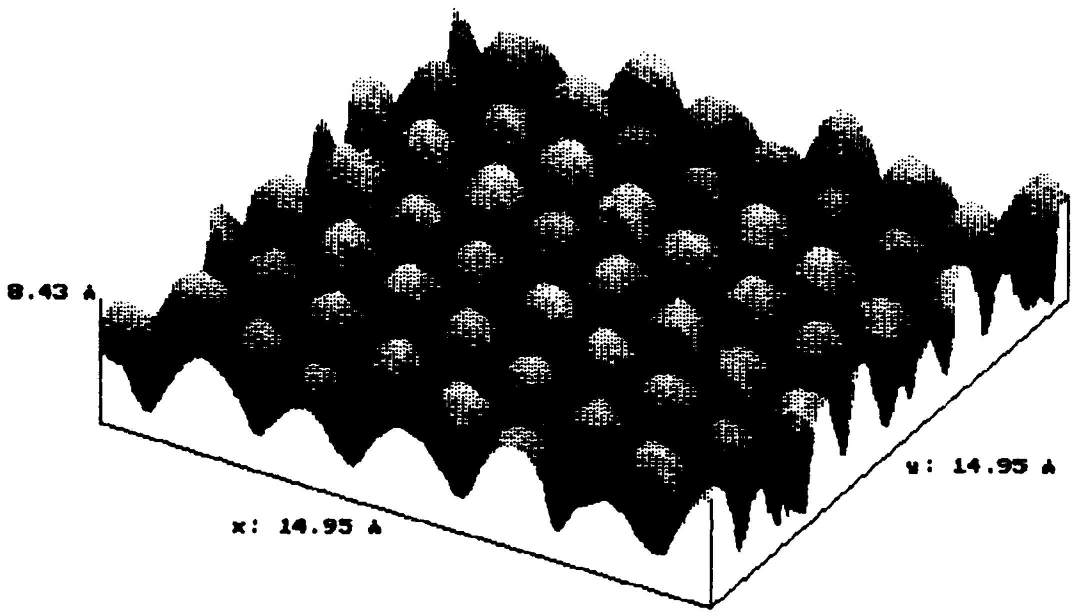
Tungsten tips, produced by etching and handled in air, have oxide layers that must be removed in the vacuum to achieve STM tunneling only though a ~ 5 Å vacuum gap. Tip-sample contact and sample gouging occur if this is not done. On hard samples, such as Si, such initial tip-sample contact may actually clean off the oxide, exposing the W for later scans over new sample regions. However, this may also pile up tungsten oxide and silicates on portions of the probe tip, causing instabilities and other problems. Thus, we utilize a tip cleaning procedure modeled after that used in electron microscopy. We electron bombardment heat the probe wire to > 1500°C in vacuum, driving off the oxide. This tip cleaning procedure is repeated more or less daily, and particularly after a "tip-crash" has occurred and possibly left residues on the tip end.

Some other, very sophisticated tip preparation methods have now appeared, which can produce single-atom end points in a less random fashion [18]. However, these are not used anywhere else that we are aware of due to their complexity. Obtaining single-atom resolution is still an art rather than a controlled feature in most laboratories, and it is not obtained at all times. Multiple emitting points on the probe end, surface adsorption and desorptions, and scraping or "crashing" the tip against the surface often change and confuse images. In essence, this is still a very new field, without well developed procedures or easily reproducible results.

D. Sample Preparation

We have found this to be the most difficult, and poorly documented or understood component of STM research. Since the STM tunneling is most sensitive to the top atomic layer of the sample, any impurities, partial monolayer coverages, or surface damage is crucial. On the other hand, with appropriate sample preparation some laboratories appear capable of obtaining STM images of metals and semiconductors in air or even liquids. We initially tested our apparatus on pyrolytic graphite in air, and obtained standard atomic-scale images. An example is shown in Fig. 3. However, as already noted the causes of these images are not clear, and a frequently voiced suspicion is that graphite layers are being slid over each other with the probe tip pressed into the top layers. All other work in our laboratory has been carried out in UHV, since this is ultimately necessary to study the effects of charged particle surface bombardment.

We initially studied pyrolytic graphite in vacuum, placing the sample into the load lock immediately after peeling off the top layer with tape. We obtained similar images to those in air, but the surface and topology was unstable. Furthermore, i(z) decreased very slowly, indicating severe tip-sample contact. We believe, and have found supporting suggestions in the literature, that sections of graphite layers are gouged out and piled up on regions of the sample and tip,



File	18-g11
Setpoint	2 nA
Bias	9.768 mV

Fig. 3 Our STM image of atoms on a pyrolytic graphite surface, taken in vacuum with 10 mV sample bias and 2 nA tip current.

causing these instabilities. We also found that large (> 100 Å) holes could easily be etched into the graphite by pulsing the sample voltage from a normal 0.1 V to 5 V. A subsequent STM image of one of these is shown in Fig. 4. Similar holes, found in air, are reported in Ref. 19. We believe that the holes are formed in vacuum by sample evaporation. The pyrolytic graphite layers are parallel to the surface, so that heat conduction is very poor perpendicular to the surface. The impact energy of the tunneling electrons is dissipated within < 100 Å, and causes sample vaporization. The initial flatness and cleanliness of pyrolytic graphite, plus the ease of preparing a surface, is excellent. However, due to this extreme sensitivity of graphite to tip contact and current-induced heating, we have not attempted to use this as a substrate for CVD studies.

We were able to find large (> 1000 Å × 1000 Å) atomically flat regions on these pyrolytic graphite samples, so we later vaporized ~500 Å of Pt onto pyrolytic graphite to obtain flat metallic layers for studies of electron induced surface reactivity. However, we were unable to achieve stable, reproducible images on these samples either. We concluded that the probe tip was still occasionally contacting the sample, and whenever this occurred it gouged out sections and piled scraps onto sample and tip. It is noteworthy that this preliminary work was done before the tip oxide removal system and final vibration isolation were installed. Thus, this approach might work in the present, improved setup. However, our current work is concentrated on semiconductors, and described in the following paragraph. We also prepared and studied crystal Ni and W foil samples, but were unable to obtain atomically flat surface polishes; "hills" with typical heights of ~200 Å were ubiquitous.

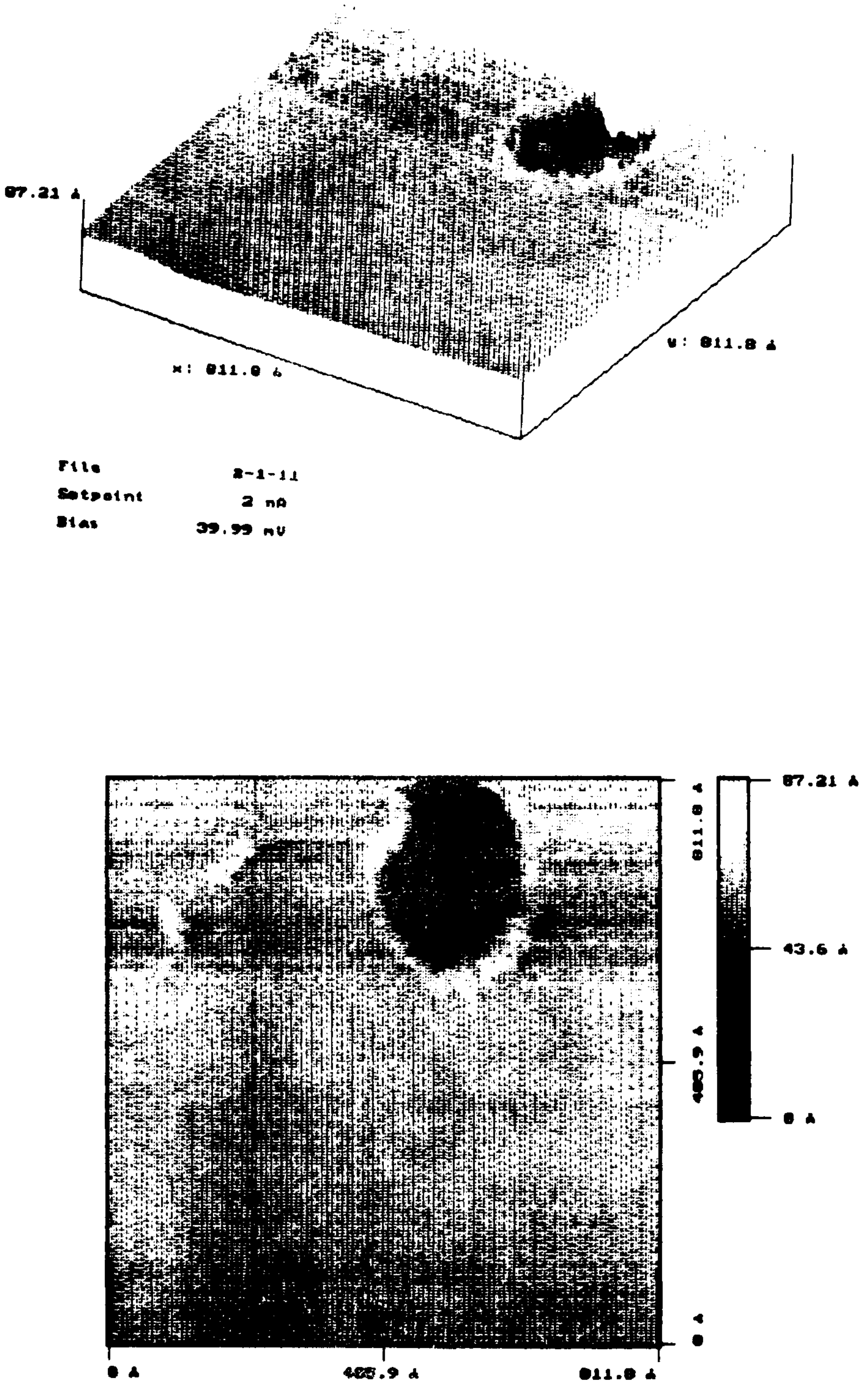
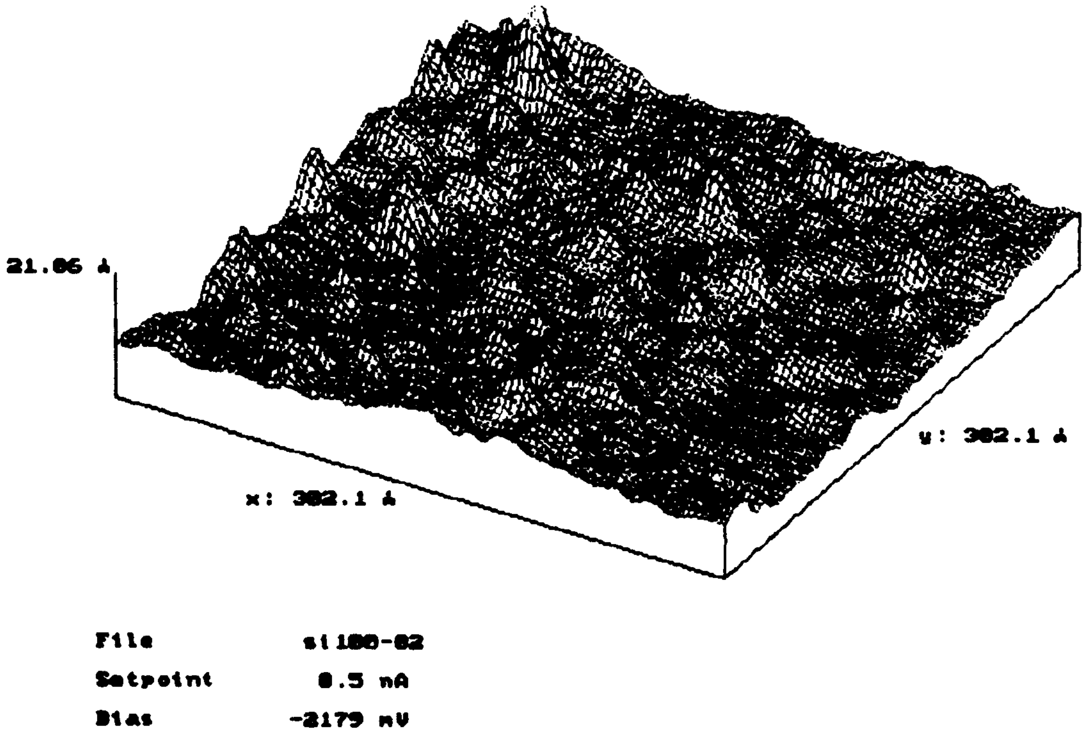


Fig. 4 Vacuum STM image of a pyrolytic graphite surface, after etching a ~300 Å wide hole by pulsing the STM tip to 10 V for 10 ms.

Polished crystal Si wafers are so widely used that they are extremely inexpensive. They are also exceptionally flat as standardly polished, and very hard. Well established cleaning procedures leave either oxide layers or H atoms terminating the surface layer. Thus, crystal Si appears to be an ideal sample for STM investigations, and it is often used. As the fluoride surface is very stable, bare Si is normally produced by a chemical cleaning that leaves oxide layers, then heating the sample in vacuum to drive off the oxide. This vacuum heating, however, must be done with extreme care and in UHV to obtain atomically flat, "reconstructed" regions of the sample [20]. Si evaporation occurs during this sample heating (typically to with 100°C of the 1420°C melting point), and a very rough surface of 50-500 Å scale mountains results if the vacuum exceeds $\sim 10^{-10}$ Torr during sample heating. We have not yet managed to maintain a 10^{-10} Torr vacuum while heating Si wafers to these temperatures, but we can testify to the fact that the Si (100) surface resembles a $\sim$ 10 Å scale mountain range when the vacuum rises to 10^{-7} - 10^{-8} Torr during sample heating. An example STM scan of such a prepared Si surface is shown in Fig. 5. Although we have now produced a more efficient sample heater and better pumping, and should be capable of the correct Si sample preparation, we are now working with cleaved GaAs, as described in the following paragraph.

One way to obtain atomically clean samples is by cleaving a crystal in vacuum. Here a rectangle cut from a crystal wafer is clamped in a holder, with typically half of the rectangle protruding. The protrusion is mechanically broken in the vacuum by a sideways force. If the sample is correctly oriented and broken, most of the surface exposed by the break is a crystal plane and has large (μm to mm) atomically flat regions. We are currently using this method to obtain flat, clean sections of 0.015" thick GaAs (110) wafers. We generally obtain many useful,



File si100-02
Setpoint 0.5 nA
Bias -2179 mV

Fig. 5 STM image of an Si(100) surface annealed in UHV at 700°C for 24 hours and at 1200°C for ~20 s.

essentially atomically flat regions of 3000 Å × 3000 Å size on the exposed surface, where this is our maximum scan range. An example is shown in Fig. 6. The surface shown there appears locally flat, as it is. It appears to have curvature on a larger scale, but this is due to instrumental effects.

A clean W probe tip above a clean metallic surface will readily produce a typical 1 nA tunneling current (i) without tip-sample contact using only 10 mV sample bias. In contrast, a semiconductor forms the equivalent of a MIS (metal insulator semiconductor) junction when the probe tip is nearby. Due to the resulting depletion layer, 1-3 V of tip-sample bias is necessary to achieve $i = 1$ nA above a semiconductor. When this current and voltage drop occurs in a very small region of the sample, damage readily occurs. Thus, care must be exercised to minimize i and V. Based on suggestions from other laboratories, we use $i \approx 0.2$ nA and $V \approx 2$ V, but we do not yet have clearcut proof that this is sufficient to eliminate all GaAs surface changes.

We find that the most clearcut diagnostic of clean sample and tip surfaces is in the measured i(z) relationship. The Fowler-Nordheim equation, or simply elementary equations for electron tunneling through a vacuum gap, predicts that i(z) should vary as $\exp(-z/z_o)$, where z_o is typically 1-2 Å. If many insulating atomic layers intervene then the tip is usually pressed through these into the sample. Due to mechanical compliance and many contact points the actual sample-tip spacing then changes much more slowly than indicated by the z-piezo voltage. i(z) then changes much more slowly with "z" or piezo voltage. This also occurs for semiconductors at $V < 1$ volt, as tip-sample contact again occurs. In essence, whenever actual tip-sample contact occurs this is reflected in a large z_o, sometimes reaching 100 Å. A thin insulating layer on the tip also raises z_o, but only to perhaps 2 or 3 Å. We now demand and standardly achieve

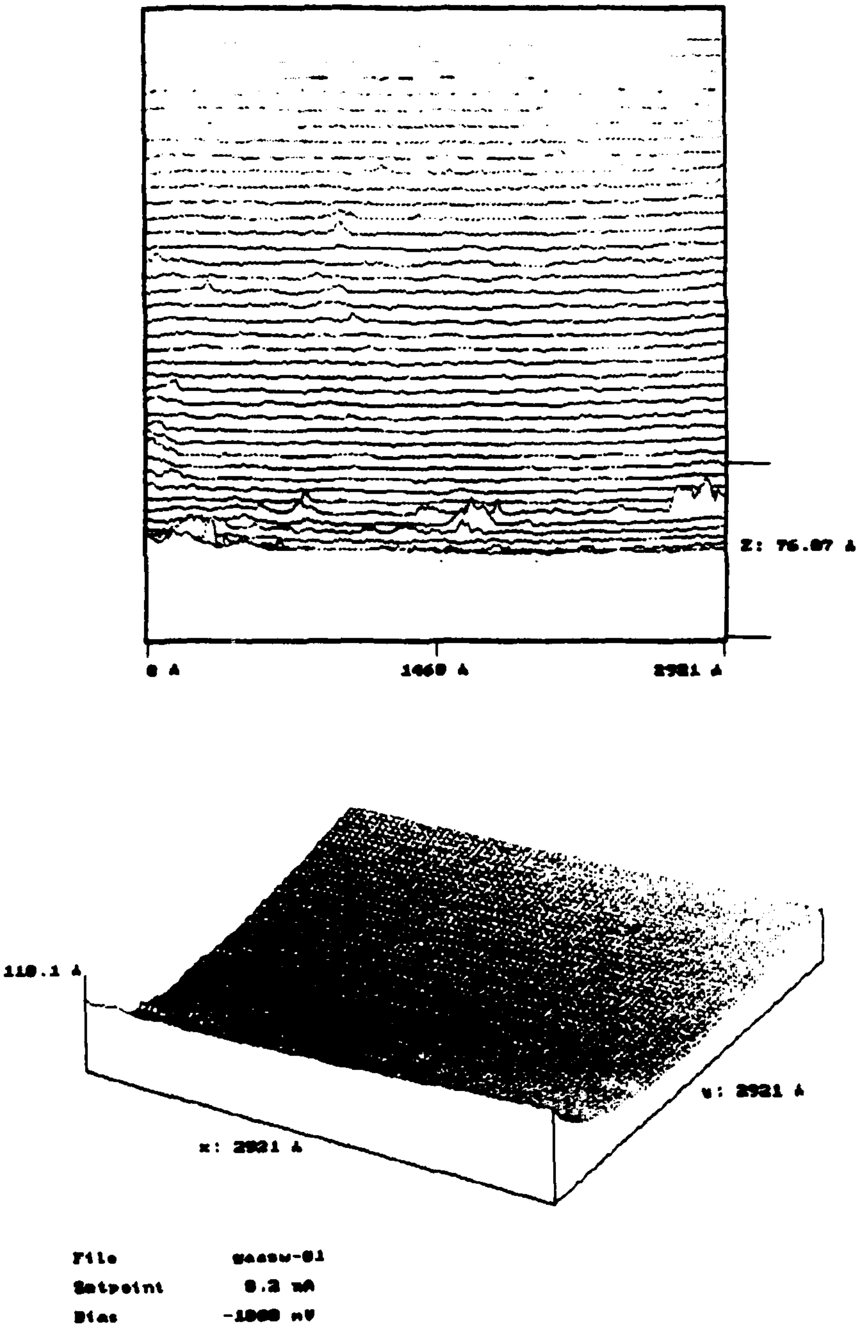


Fig. 6 STM image of a GaAs (110) surface prepared by cleaving in vacuum. The upper figure shows a portion of the individual row scans, and the lower figure is a three-dimensional view of the same 200-line scan. The irregularities in the lower left corner are attributed to a "tip crash" during approach to that region.

z_o = 1-2 Å on GaAs, Si and metallic samples. We also measure i(V,z) and infer from these data that we are typically operating with a probe-sample gap of ~5 Å.

E. Environmental Isolation

As already noted, the requirement of maintaining the tip-substrate gap constant to < 0.3 Å, and the x and y positions to < 2 Å while the supporting structure has dimensions of at least 1 cm, is a $\Delta\ell/\ell < 10^{-8}$ requirement. This requires exceptional vibration isolation, rigid structures, and low thermal drift. Moderate thermal drifts are tolerable, as raster scans typically require ~10 minutes and the linear portion of the drift can be removed during computer image reconstruction. Drifts of 0.1°C/hr are normally quite tolerable. However, heating of samples and tips to hundreds or even > 1000°C is often a required preparation, and these must be fully recooled before inserting into the STM if data are desired in less than a day. We often use a small W-filament lamp inside our UHV chamber to minimize the net STM thermal drift during moderate sample or tip cooling. By adjusting the power to this lamp, typically at a few watts, the < 1% that is absorbed by the STM balances the slow cooling effect and allows scans without running out of range.

I have already discussed STM structural designs; the best of these achieve structural resonances above 10 kHz, but resonances below 100 Hz are not uncommon . Our STM is believed to have no resonances below 1 kHz, although we have not tested this. The most important factor in STM use is to isolate the entire structure from external vibrations. Many vacuum STM's are hung from two sets of three springs, working in series with a copper ring at the junction and magnets attached to the chamber nearby. This provides eddy-current damping of the first stage. The vertical resonant frequency ν_R of any weight hanging from an ideal spring is $(2\pi)^{-1}(g/\ell)^{1/2}$, where ℓ is the length of spring stretch and g is the earth gravitational constant. Spatial constraints of vacuum chambers normally fix ℓ at 3-10 cm, while $g \approx 10^3$ cm s^{-2}. Thus, 1.5-3 Hz is a typical value of ν_R. Vibration frequencies above $\sim 2\nu_R$ are rapidly cut off whereas those at and below the resonance are fully transmitted and even somewhat amplified. Pendulum and wobble modes have lower ν_R. The STM z axis is normally horizontal, minimizing direct coupling to the highest-frequency vertical mode. However, laboratories generally have very large vibrations in the 1-120 Hz region, partly due to building motions and resonances. These can produce very severe STM gap fluctuations. It is common practice to place STM's in the quietest possible locations on solid ground far from pumps, etc. We unfortunately did not have that option readily available, and our laboratory is on a second floor above the mechanical shop. Our STM is hung in vacuum from one set of springs, with $\nu_R \approx 3$ Hz. When we supported the vacuum system from the floor with ~10 Hz air-cushion table supports, this combination gave us several Å of z vibration. We therefore changed to hanging the (~500 lb) vacuum system from 4-foot-long springs, obtaining $\ell \sim 40$ cm, $\nu_R \approx 0.8$ Hz and sometimes less than 0.2 Å gap vibration. A photograph of our hanging apparatus is shown in Fig. 7.

The other major environmental coupling to the STM is magnetic, due to ac fields in laboratories. This, of course, is primarily at 60 Hz and its harmonics, although color monitors and computer cables often generate very large, virtually random magnetic pulses. For this reason good STM designs, including ours, do not contain magnetic materials. Large loops formed by STM hookup wires can also be a problem, particularly for the tunneling current. Due to the need for intra vacuum wire hookup to the spring-hung STM, there is a tendency toward loops

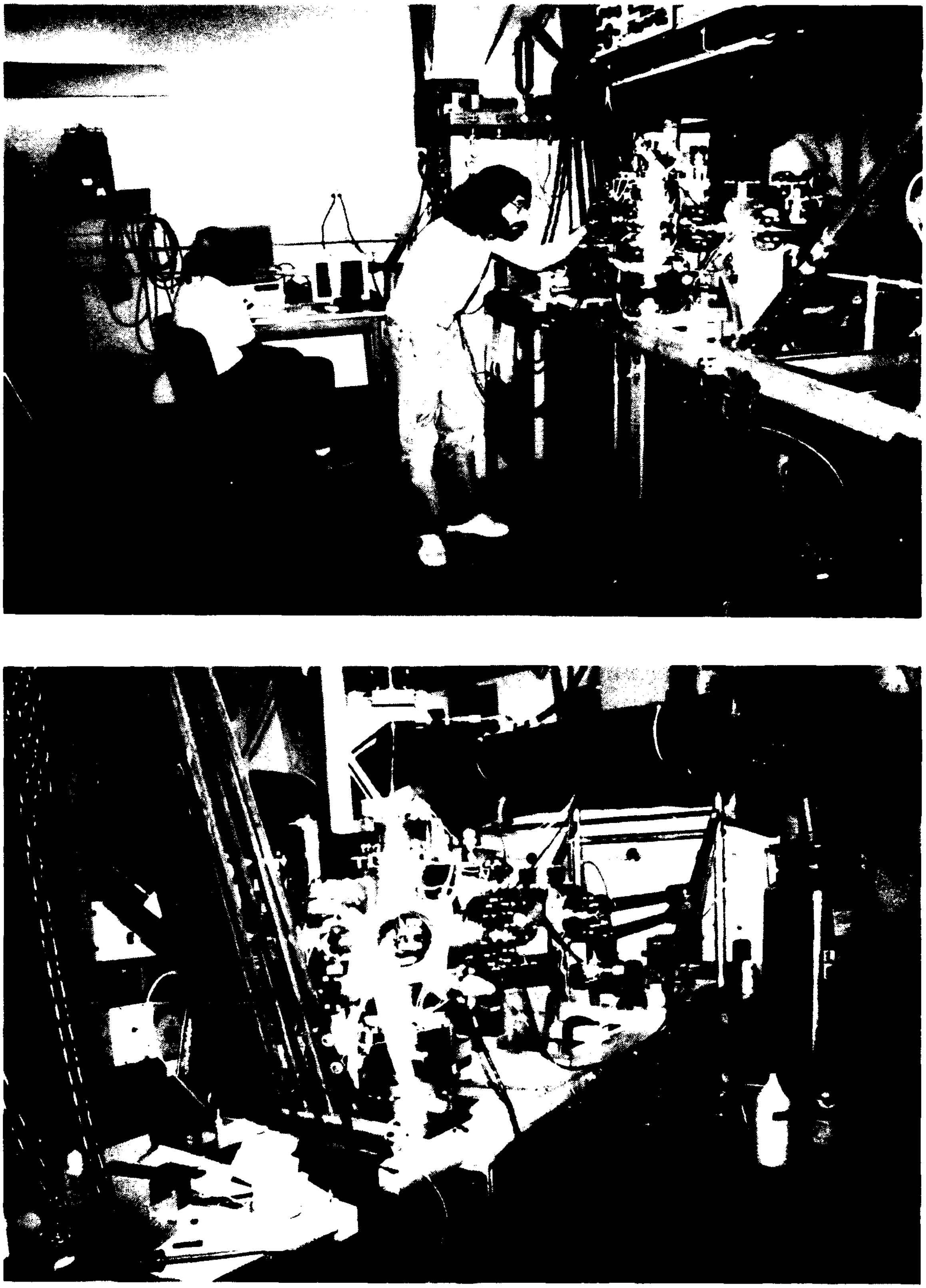


Fig. 7 Two photographs of the apparatus, with Robert Ostrom and David Tanenbaum present.

that generate noise signals from ac magnetic fields. Our STM was designed by a mechanical designer (McAllister), who did not appreciate many electrical issues. We have therefore modified some of his wiring and cursed at others that are not easily amenable to improvement. Another important wiring consideration, also ignored in our STM, is the pickup of piezo voltage changes as the tunneling current signal, due to capacitance coupling.

III. OUR OBSERVATIONS AND RESULTS

A. System Behavior

A "working" STM was delivered to our laboratory in January, 1990. Just before delivery Bob Ostrom spent several days in Berkeley, with McAllister, obtaining an STM atomic image of pyrolytic graphite in air with the instrument. This was achieved at night in a very quiet corner of a building built over a concrete pad on the ground. In addition to all of these vibration quieting factors, as already noted we and most other workers believe that graphite atomic images in air are obtained with the tip pressed into the graphite and sliding planes across each other. This is, of course, much less susceptible to mechanical vibrations than a tip separated from the sample by 5 Å. Later observations in our laboratory demonstrated a typical i(z) half-height falloff distance of z_o on the order of 100 Å in graphite under these conditions, clearly confirming deep sample penetration by the oxide covered W probe tip and very low sensitivity to "gap" changes. In contrast, the vacuum tunneling form a clean W tip, that we are now studying, has $z_o \approx 1$ Å.

By the end of February 1990, we had obtained STM atomic images of pyrolytic graphite in our just-assembled vacuum system, and we had noted the ease with which graphite can be damaged and etched in vacuum by the STM current (Fig. 4). However, this was still done with as-etched or oxide-coated W tips, and with $z_0 > 30$ Å. The pyrolytic graphite surface was nonetheless usually initially flat over large areas, and when we vapor deposited a ~500 Å layer of Pt on top, this yielded a less easily damaged and less contacted surface. We then obtained z_0 values below 10 Å, but neither the graphite nor the Pt covered graphite was stable under repeated STM scanning at low voltages and currents (~0.02 V, 1 nA). In essence, it should have been possible under these conditions to scan the Pt surface with a positive tip-sample gap, but repeated scans indicated that the tip was actually gouging out and piling up Pt and graphite in many different locations. We now understand this problem and have removed the causes, which are (1) oxide on the W probe tip, such that mild contact or scraping is necessary to obtain the "tunneling" current, (2) vibrations that occasionally exceed the capability of the current feedback to prevent tip-sample contact or "crashing." Although we have now fixed these problems we have not returned to metalized pyrolytic graphite samples, as these are much more susceptible to contact damage compared to bare or metalized Si or GaAs.

The 6 months from March to August 1990, have been used to make many apparatus, sample, tip and procedure improvements, as is required to obtain meaningful, reproducible vacuum STM atomic images of semiconductors. Most of these issues and improvements have already been reported in the subsections of Sec. II. Briefly summarizing: (1) We now obtain UHV ($\leq 10^{-10}$ Torr) in a few days after opening the UHV chamber. (2) We can introduce new samples or tips in a few hours through a load lock chamber. (3) We can heat samples and tips in the UHV, by electron bombardment, to annealing or surface-cleaning temperatures. (4) We have achieved vibration isolation that obtains an rms fluctuation of 0.2-0.6 Å in the tip-substrate gap. (5) We reliably obtain $z_0 \approx 1$ Å values, crystal LEED patterns, and i versus z relations that are appropriate for an atomically clean metal or semiconductor sample and a metal probe. (6) We can reach different areas of the sample by sample-holder rotations, and we often obtain atomically flat, 3 μm × 3 μm regions on our cleaned GaAs crystal samples. (7) We can evaporatively metalize the sample surface in the UHV, and are currently using Cr on GaAs. (8) We have gas handling and gases setup for the study. (9) We can study the surface symmetry in the UHV chamber by LEED (low energy electron diffraction) and also cleanliness by using the LEED optics as a RFA (retarding field analyzer) for Auger electron analysis. (10) We can produce state-of-the-art etched W tips, with R ~200 Å.

The STM in our laboratory is the first made and delivered by McAllister Services Inc., based on the Lyding design and full computer control of operation and data manipulation. This was a complete change from McAllister's previous tripod and micrometer device, which did not include computer control of operation. We recognized at the time of the order (June 1989) that this would demand much more improvement and trouble shooting than other, more established commercial STM's. We nonetheless chose the McAllister instrument for three reasons. (1) There are very few commercial STM's made to operate in vacuum, and the basic design characteristics of these were inferior to the Lyding design (e.g. in-vacuum micrometers for coarse sample approach, poor vibration isolation). (2) The McAllister bid was below $100,000, including vacuum chamber, manipulators, computer and software, while no other bid was even close. As the STM was purchased within a highly constrained NIST equipment budget, this was a very important consideration. (3) There is always a learning process associated with a complex new technique and apparatus. If it quickly provides data, then one is generally deceived about the meaning of the results. One either learns while making many measurements plus improving the apparatus, or learns only by making many measurements. Within the ten important advances listed in the previous paragraph only numbers 4 and 6 involve improvements in the equipment that would have been avoided with a more developed instrument.

B. As-Prepared Surfaces

In Figs. 3-6 we have shown some STM images of different surfaces, some with a very high resolution scale that exhibits individual atoms and some on a larger scale to exhibit topology of larger surface areas. In order to measure current-induced surface reactivity modifications we wish to start with an atomically flat region of at least 1000 Å × 1000 Å, representing $> 10^5$ surface atoms. We can now achieve reproducible scans over such sample areas, but with occasional height irregularities or noise of 1-10 Å. Thus, it is still not straightforward for us to detect atomic scale changes, and we are not fully prepared to do so. In this regard, it may be worth noting that, judging from work reported at the recent "STM 90" conference [14], very few laboratories have this capability in vacuum. In essence, reproducible, atomic scale vacuum images covering relatively large areas are still only reported by a few leading laboratories, most of which are in IBM Corporation and have been involved in STM work for 5-10 years. We feel that we are rapidly approaching this state-of-the-art capability, but we are definitely not there yet.

C. Surface Modification

The ultimate purpose of our program is to study modification of surface reactivity, leading to etching or CVD, by charged particle impact. We have spent the period of this contract building up our ability to study this, but we have not yet started deliberate surface-modifications on semiconductors or metals. It is quite easy to inadvertently or deliberately modify surfaces with an STM, and we have certainly done this many times. Most frequently the comparatively hard W wire probe tip gouges material from the sample and piles it up elsewhere on the sample and tip. Probe tips are also easily roughened and even bent by sample contact. However, such contact is neither charged-particle impact nor of practical value. We have briefly studied the ability of the STM current to etch ~100 Å pits in pyrolytic graphite, as shown in Fig. 4. But when one realizes that the probe was doubtless already in direct contact with the sample, this is also not "charged particle impact" with the graphite surface. Rather, it is simply excessive "resistive" heating of a very small graphite region that carried the pulse of current, until graphite evaporation produced a tip-sample gap, terminating the current. Also, no gases were present here, and this etching is not connected to enhanced surface reactivity. We have similarly etched away in damaged slightly smaller regions of our crystal GaAs surfaces, using 5-10 V pulses of current without gases present. Thus, all forms of surface modification studied so far in our STM are not the bombardment-enhanced chemical reactivity of primary interest and value in semiconductor manufacture. This statement also applies to all STM-based surface modifications reported to date [14, 21].

IV. DISCUSSION AND CONCLUSIONS

It appears that the STM is an ideal tool for studies of surface reactions and changes induced by electron and ion bombardment, as it can measure individual surface irregularities with atomic resolution. These chemical processes are fundamental to plasma processing of semiconductors, as well as other plasma uses, yet they are very poorly understood and to our knowledge are not currently studied with the STM. On the other hand the STM is a very new tool of surface science, without clearly developed methodology or agreed upon interpretations. Thus, achieving meaningful, reproducible atomic scale STM images in UHV is a significant research effort. In our laboratory we have just achieved this after 6 months of construction followed by 8 months of apparatus and procedure developments and modifications. Many of the problems and improvements we have worked through are outlined above, for the benefit of others new to the field. It is important to note that most of these issues only apply to in-vacuum STM research. Most STM research is not done in vacuum, and is much easier to perform and more ambiguous to interpret. In contrast, the semiconductor processing and other plasma issues of interest here require not only vacuum, but UHV and very careful surface probing without inducing significant surface damage at the single-atom level.

Controlled surface modification using the STM is now widely discussed as a very promising nanotechnology tool. Dozens of papers and conference proceedings report STM-induced surface modifications [14]. Many of these simply represent micromachining by gouging or tearing a surface with the probe tip [8]. A slight modification on this is to tear off surface atoms at one location and deposit them elsewhere by direct contact [10]. Other approaches are based on pulsing the probe-substrate voltage, typically from 0.02 V on metal samples to values of 3-20 V. A very high current (typically ~ 1 μA) flows during the pulse, changing the local surface shape and often producing a crater as shown for graphite in Fig. 4. Generally, power densities are sufficient to indicate severe sample heating during the pulse. In another approach, a 50-100 Å region of deliberate or accidental (pump oil) resist is cracked below the STM tip [9]. In another approach, done in air, the protective F termination on Si is removed from ~ 100 Å areas so that oxidation proceeds thereafter [13]. In the most microscopic and well-controlled experiment reported so far, Xe atoms adsorbed to a 4°K, Si surface were individually dragged across the surface to desired atomic positions by an STM tip directly above [15]. These experiments support the exciting possibilities inherent in STM controlled nanolithography. However none so far uses or studies the chemical etching and deposition processes of normal semiconductor processing. (The Si-F study might be an exception, unfortunately done in air.) Thus, the present study appears unique not only in utilizing the STM to study surface reactivity changes, but also in planning to use the STM current to modify chemical reactivity over small areas of the surface. Following 6 months of equipment design, purchases and construction, then 8 months of experimental work, we have now achieved STM imaging of atomically clean semiconductor and metal surfaces with atomic resolution, and are in a position to investigate electron-bombardment induced surface reactivity changes. This is months behind our desired schedule, but realistic (we think) in view of the inherent complexities of this very new research field.

REFERENCES

1. R. Young, Phys. Today, 24, 42 (1971). R. D. Young, J. Ward, and F. Scire, Rev. Sci. Instrum. 43, 999 (1972). R. Young, J. Ward, and F. Scire, Rev. Sci. Instrum. 47, 1303 (1976).
2. G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. 49, 57 (1982) and 50, 120 (1983).
3. Paul K. Hansma and Jerry Tersoff, J. Appl. Phys. 61, 2 (1987).
4. G. Binnig and H. Rohrer, Physica 127B, 37 (1984).
5. G. Binnig and H. Rohrer, IBM J. Res. & Dev. 30, 355 (1986).
6. D. K. Biegelsen, F. A. Ponce, and J. C. Tramontana, Appl. Phys. Lett. 54, 1223 (1989).
7. Vu Thien Binh, Journal of Microscopy, 152, 355 (1988).
8. M. A. McCord and R. F. W. Pease, Appl. Phys. Lett. 50, 569 (1987).
9. M. A. McCord and R. R. W. Pease, J. Vac. Sci. Technol. B 4, (1986).
10. E. E. Ehrichs, S. Yoon, and A. L. de Lozanne, Appl. Phys. Lett. 53, 2287 (1988).
11. R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Nature 325, 419 (1987).
12. R. M. Silver, E. E. Ehrichs, and A. L. de Lozanne, Appl. Phys. Lett. 51, 247 (1987).
13. J. A. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, and J. Bennett, Appl. Phys. Lett. 56, xxxx (1990).
14. Proceedings of The Fifth International Conference on Scanning Tunneling Microscopy/Spectroscopy and The First International Conference on Nanometer Scale Science and Technology, July 23-27, 1990.
15. D. M. Eigler and E. K. Schweizer, Nature, 344, 524 (1990).
16. R. J. Celotta (private communication).

17. J. W. Lyding, S. Skala, J. S. Hubacek, R. Brockenbrough, and G. Gammie, Rev. Sci. Instrum. 59, 1897 (1990).

18. H. W. Fink, IBM Jour. Res. Develop. 30, 460 (1986).

19. T. R. Albrecht, M. M. Dovek, M. D. Kirk, C. A. Lang, C. F. Quate, D. P. E. Smith, Appl. Phys. Lett. 55, 1727 (1989).

20. A. Ishizaka and Y. Shiraki, J. Electrochem. Soc. 133, 666 (1986).

21. G. M. Shedd and P. E. Russell, Nanotechnology 1, 67 (1990).

U.S. Government Printing Office 548-076