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SCANNING TUNNELING MICROSCOPY

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5. SCANNING TUNNELING MICROSCOPY

5.1 INTRODUCTION

The invention of the scanning tunneling microscope (STM) by Binnig, Rohrer, and Gerber between 1979 and 1982 (Binnig et al., 1982, Binnig and Rohrer, 1987) represented a revolution in the field of surface science comparable only to the introduction of ultrahigh vacuum (UHV), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and other major analytical techniques. STM has already been used to resolve long-standing surface science problems such as the structure of the Si(111) 7x7 surface (Binnig et al., 1983a). It has demonstrated its ability to image surfaces with atomic resolution in air and in liquid environments. STM has virtually no environment limitations, unlike most other surface science techniques that require UHV for their operation. UHV is necessary for STM when reactive surfaces that would degrade rapidly in non-UHV environments are being studied.

STM has apparently unlimited potential in fields beyond the realm of classical surface science. Such fields include the imaging of biological material, atomic-scale electrochemistry, and microengineering.

An ever-expanding number of applications, the continuing development of better instruments, and our increasing understanding—both experimentally and theoretically—of the tunneling phenomenon in real systems make STM a rapidly changing field. Thus this chapter is best regarded as a "status report" of the chemical applications of STM. Several STM review articles are available (Hansma and Tersoff, 1987; Quate, 1986; Behm and Hösler, 1986; Golovchenko, 1986).

This chapter, which focuses on the practical aspects of this new technique, is designed primarily for the newcomer who needs to learn the basic principles of STM and its application to chemisorbed layers and catalyst characterization. Current STM instrumentation can be used to study model catalysts such as single crystals or metal films; however, it is not ideal for studies of industrial catalysts, which are usually made of nonconductive materials such as silica, alumina and other oxides supporting metal particles. Fortunately, Atomic Force Microscopy (AFM), which is a spinoff of STM, facilitates imaging of nonconductive materials such as supported catalysts, zeolites, ceramics, and polymers. The combination of STM and AFM is opening a new and exciting era in the understanding of the structure of surfaces at the atomic level.

5.1.1 Principles of Operation

The scanning tunneling microscope is based on the quantum effect of electrons tunneling through a classically forbidden energy region between two metal or semiconductor solids. In the STM, one of these solids is the sample to be imaged and
the other is the sharp tip of a metal wire, often tungsten, that is brought to within several angstroms. (Other metals and also alloys such as platinum-iridium may be used in place of tungsten.)

The electrons in a solid are confined to the interior by a potential barrier at the surface, the form of which results not only from the attraction of the positively charged nuclei but also from the rearrangement of the remaining electrons. The total potential energy of an electron at the Fermi level as it crosses the surface and moves to an infinite distance corresponds to the work function. In quantum mechanics, the confinement of the electron inside the boundaries of the potential barrier is not perfect, and the amplitude of the wavefunction decays exponentially from the surface. At the short distances between the two electrodes (tip and surface) that are encountered during operation of the STM, this amplitude is still finite. Thus the electron can “tunnel” through the barrier to the opposite electrode.

The tunneling current at low voltages is given by:

\[ I \propto e^{-2s}\kappa \]  

(5.1)

where \( s \) is the separation between the electrodes and \( \kappa \) is the reciprocal of the decay length of the electron wave function. \( \kappa \) is given by:

\[ \kappa = \sqrt{\frac{2m\phi}{h^2}} \]  

(5.2)

where \( \phi \) is the average barrier height. For electrons tunneling into states at energy, \( E \), above the sample Fermi level and for negative tip bias, \( V \), \( \phi \) can be approximated by:

\[ \phi = \frac{1}{2}(\phi_{\text{tip}} + \phi_{\text{sample}}) - (E - eV/2) \]  

(5.3)

where \( \phi_{\text{tip}} \) and \( \phi_{\text{sample}} \) are the work function values of the tip and sample, respectively.

Figure 5.1 illustrates the above concepts. Clearly, the tunnel current will change rapidly with changes in tip-surface distance. For a work function value of 4 eV, for example, \( \kappa^{-1} = 1 \text{ Å} \) and a change in \( s \) of 1 Å changes \( I \) by a factor of approximately ten. Also, the states near the Fermi level of the cathode will contribute most to the tunnel current. A complete formula for the current density, through a one-dimensional square barrier, was derived by Simmons (1963) and corrected later by Payne and Inkson (1985).

The exponential dependence of \( I \) on the distance, \( s \), is responsible for the high resolution of the STM. Laboratory-prepared macroscopic tips always contain irregularities in the form of minitips that are composed of clusters of several atoms.
Figure 5.1. Energy distance diagram of STM tunneling process. Amplitude of wave function of an electron in left electrode (wavy line) decays into vacuum region and couples into levels at an energy $eV_{\text{bias}}$ above the Fermi level $F$ of right electrode.

The minitips closest to the surface will draw all the tunnel current, providing the spatial localization that is required for high-resolution imaging. For small values of the applied bias, equation 5.1 can be simplified to:

$$I \propto V e^{-0.025\phi s}$$  \hspace{1cm} (5.4)

where $\phi$ is in eV and $s$ is in Å.

In a solid, the electronic structure of both the tip and the substrate must be included explicitly in the expression for the tunneling current. The filled density of states for the cathode electrode and the empty density of states for the anode are involved directly in the tunneling process. This fundamental aspect of the operation of the STM determines the images obtained. Tersoff and Hamann (1983) used first-order perturbation theory to calculate the tunneling current as follows:

$$I \propto V \times D_t(E_F) \times e^{2\pi R} \times \rho(r_o;E_F)$$  \hspace{1cm} (5.5)

with

$$\rho(r_o;E_F) \equiv \sum_{\nu} |\Psi_{\nu}(r_o)|^2 \delta(E_{\nu} - E)$$  \hspace{1cm} (5.6)

where $D_t(E_F)$ is the tip density of states and $R$ is the tip radius. The necessary approximations include the assumption of an s-wave tip wave function, which should be
adequate for tip radii of the order of several Å. Equation 5.6 is important because it shows that the tunneling current is determined by the sample density of states, \( \rho(\mathbf{r}_o; E_F) \), at the tip position. Since \( |\Psi(\mathbf{r}_o)|^2 \propto \exp(-2\kappa(R + s)) \), the exponential dependence of \( I \) on \( s \), as in Equation 5.1, is preserved.

Once the tunneling current has been established and stabilized by an electronic feedback control unit (Section 5.2.2), the tip is rastered over the surface in the X and Y directions. At the same time the tip is displaced in the vertical direction (Z) in order to keep the tunneling current constant. These very fine tip displacements are provided by piezoelectric ceramics that expand or contract when a suitable voltage is applied. For the type of piezo ceramics commonly used, changes in length of 10 to 20 Å per V applied are typical. Figure 5.2 shows a schematic of an STM experiment. Typical values for the tunneling current vary from approximately 0.1 to 10 nA, while bias voltages vary from several mV up to ±10 V.

5.1.2 Materials and Environments

From the above discussion, it is clear that both the tip and the substrate must be made of electrically conductive materials. Insulating material cannot be imaged, even at biases where electrons would be injected into empty conduction band states, because these materials contain defects that act as traps. The electrons would remain

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Figure 5.2. Schematic of an STM experiment.
localized in these traps for long periods relative to the time between arrival of electrons. (The time between arrival of electrons for currents on the order of nA is $10^{-10}$ s.) The electrostatic potential created by such a localized charge raises the potential barrier for the next incoming electrons, effectively blocking the tunneling process. The resulting decrease in tunneling current causes the feedback electronic control to bring the tip closer to the surface, which results in a "crash." In principle, it should be possible to image very thin films of insulating materials supported on conductive films if the film is thin enough for rapid discharge into the substrate. Instabilities due to temporary trapping of charges in defects in insulating regions of the sample are one cause of poor imaging in dirty substrates. Such instabilities can also lead to poor imaging when the tip itself is contaminated with insulating oxides.

In theory, STM can operate in virtually any nonconductive environment. At one atmosphere, for example, the average distance between gas-phase molecules is 40 Å, which is larger than the typical distance of 10 Å between the tip and the sample. For practical purposes, the electrons tunnel through a vacuum at this pressure. Even in liquid environments, only about three molecules are interposed between the tip and the surface in the Z-direction. These molecules need only be "transparent" to the electrons—that is, they should have no electronic states at the bias voltage level. If they have empty levels at this energy, effects due to injection of electrons into antibonding states might result in the rupture or modification of the surface and molecule. The following sections detail numerous examples of images taken in air with atomic resolution.

One range of pressures where STM imaging requires special precautions is the pressure range where gases are easily ionized to produce discharge plasmas (between 0.001 and 1 torr). The risk of exciting a plasma discharge because of the relatively high voltages used to polarize the piezos is high in this range and can result in damage to the electronic supply, particularly to the current preamplifier used for tunneling current detection.

The ability to operate in liquid solutions is particularly valuable in electrochemical, biological, and some catalytic applications. In addition to the problems mentioned above, the areas of the tip that do not participate in the tunneling process must be insulated from the solution. This insulation is required to avoid Faraday leakage currents (caused by ionic conduction) contributing to the total current flowing between tip and surface. Such a contribution could possibly overwhelm the current due to tunneling. Fortunately, the tunneling current is highly localized in a microscopic region at the apex of the tip, while the ionic leakage current is contributed by all the areas of the tip that are in contact with the solution. As a result, except for a microscopic region near the apex, the contribution of ionic leakage can be minimized by shielding the body of the tip (Sonnenfeld and Hansma, 1986).
5.2 STM INSTRUMENTATION

For convenience, this review of the practical aspects of STM instrumentation is divided into five parts. Section 5.2.1 is devoted to the mechanical head, which comprises the piezoelectric ceramics (hereafter referred to as piezos), tip, and sample support. Section 5.2.2 discusses the electronic control unit, which contains the feedback loop and the X and Y scan supplies. Sections 5.2.3 and 5.2.4 discuss the approach of the tip to the surface and vibration isolation, respectively. All these aspects of the STM are well-understood, and new developments should involve sturdier head design, improved thermal compensation, faster electronic controls, and more powerful computers. Kuk and Silverman (1989) have reviewed STM instrumentation in depth. Section 5.2.5 discusses building or purchasing an STM instrument.

5.2.1 The Piezoelectric Scanner, Tripods, and Tubes

The delicate tip or sample displacements necessary for the STM are made possible by the frictionless mechanical motion caused by the deformation of the unit cells of piezoceramics. This unit cell deformation occurs in response to applied electric fields. Piezoelectric ceramics are fabricated as plates, tubes, or other shapes. They can be stacked to form bimorphs, for example. Manufacturers provide the piezoelectric constants that enable the user to calculate the change in length of a ceramic under a given applied voltage and a given load.

In the STM, the piezos are usually operated in the static mode and with virtually no load. Therefore the calculated extension usually agrees well with the measured extension. By imaging materials with a known lattice parameter, such as graphite, the length-to-voltage relationship can be calibrated precisely. This relationship usually agrees with that calculated from the manufacturer's data to within ±10%.

The most important piezo problems facing the STM user are hysteresis, nonlinearity, and creep (Figure 5.3). The piezo may not necessarily return to its original length after a closed cyclic change in the applied voltage (hysteresis). The difference in length can be sizable, up to 20% of the maximum length change. The change in length can also depend on the previous polarization history of the piezo. Creep is observed as a slow change in length after the polarizing voltage ceases to change. This slow change can sometimes be mistaken for a thermal drift, which is also present in STM images, particularly after the sample is heated and whenever the various components of the STM head differ in temperature. Since thermal expansion coefficients are of the order of \(10^6\), one degree difference in temperature over a 1-cm distance will cause a change in length of 100 Å.

Nonlinearity, hysteresis, and creep are most problematic at high applied voltages. High voltages can also cause other problems, such as dielectric breakdown (particularly at the edges of the ceramic because of deposited contaminants), partial depolarization,
and polarization reversal. Thus there is a maximum field that can be applied in both the polarizing and depolarizing directions.

As important as these problems are, by far the most detrimental problems to the operation of the STM are those related to the excitation of mechanical resonances in the tip and sample support. A well-designed STM head should have mechanical resonance frequencies as high as possible, certainly above several kHz. Since the resonant frequencies of a mechanical apparatus depend on the rigidity and dimensions of its components, a small and compact head is recommended.

The trend towards compactness has favored the use of single-tube ceramics to execute the XYZ motion of the tip or sample (Binnig and Smith, 1986). The outside wall of the single-tube scanner is one electrode that is divided into four sectors. Voltages applied to opposite sectors relative to the inside electrode deform the tube in the X, Y, and Z directions (Figure 5.4). The tripod arrangement of three piezo bars, one for each motion along a coordinate axis, was used by Binnig et al. in their pioneering work. This configuration is still being used successfully in many STM designs. The mechanical connection of the three bars, however, makes the design less rigid than the single tube.
5.2.2 Electronic Control

The heart of the STM electronic control unit is the feedback loop. This loop maintains the tunneling current at a constant value while the tip scans the surface plane. To accomplish this, the difference between the actual value of the tunneling current and the desired value (the setpoint) is amplified, integrated, and fed to the Z-piezo. With the proper gain, the value of this voltage will cause the piezo to extend or contract, thus maintaining the tip-surface distance that produces the desired tunneling current. As discussed above, this distance is not necessarily constant, since the local density of states near the Fermi level can change from point to point on the surface.

During operation, the time constant and gain of the feedback control circuit should be adjusted such that frequencies near the mechanical resonances of the piezo head scanner and sample support are effectively damped. For example, if the first mechanical resonance occurs at 3 kHz, the time constant should be set at or above 3 ms to ensure effective damping of the amplitude at 3 kHz. A response time of 3 ms allows the correct speed of the tip as it scans the surface to be determined easily. In a 50 Å scan, for example, the time per line should be not smaller than 0.2 s if the tip has to follow the topography of atoms separated by 2 Å. If the total number of lines per image is 256, for example, the acquisition time is approximately 50 s.
The electronic control unit can also contain the ramp generators for the X and Y piezos, offset voltages for a fixed tip deflection, and inputs for modulation voltages that might be applied to the piezos or to the bias voltage. These modulation techniques provide spectroscopic information on the surface composition, as well as increasing the signal-to-noise ratio. Another desirable feature is the ability to track and hold the feedback loop—that is, to open the loop for a short period of time—in order to perform spectroscopic measurements of the current versus bias voltage at a fixed tip-to-surface distance.

Interfacing the electronic control to a computer is not a convenience but a necessity. It allows fast acquisition and display of data and facilitates determination of the large number of data points that constitute the image. A typical image can contain 256 x 256 data points, which requires approximately 130 KBytes of memory space. The computer can not only read and store the data points but can generate the scan ramps for XY as well, and, with a fast processor, perform the feedback control action. This is an area of rapid evolution in STM design.

5.2.3 Approach of Tip to Surface

An essential function of the STM instrument is the approach of the tip to the surface from a distance of millimeters or centimeters to a distance of less than a micron. This motion must be smooth enough to avoid "crashing" the tip. It is in the design of this function that most STMs differ. The design of Gerber et al. (1986) uses a walker made of a piezoelectric slab with three feet that clamp electrostatically. The crawling motion achieved by the sequential clamping of the feet, the extension or contraction of the piezo, and the unclamping of the feet led to the name "louse". Other workers have used reduction levers and differential springs to demultiply the translation of fine micrometer screws (Demuth et al., 1986; Park and Quate, 1987; Salmeron et al., 1987a,b). Still others have used inertial translators that apply impulsive forces to the sample support, causing it to slide on a smooth surface. The impulsive force is produced by magnetic forces occurring between coils and permanent magnets (Elrod, 1985), or by the rapid extension of a piezoelectric support (Pohl, 1987a,b; Lyding et al., 1988b).

Each method has its advantages and disadvantages, depending on the application. In closed environments, such as a vacuum chamber or gas reaction cell, electrically controlled devices that avoid the use of gears and feed-throughs in the chamber are preferred. Most electronic controls combine the circuitry needed to effect the approach of the tip to the surface with a stop control to terminate the approach when a tunneling current is detected. During the approach operation, the feedback circuit is active, protecting the tip from crashing by fast withdrawal and by compensating for the unavoidable unevenness of the coarser approach.
5.2.4 Vibration Isolation

An important aspect of the STM instrument is the vibration isolation system. In order to measure tip displacements with a precision of tenths of an angstrom, the external vibrations must be damped to less than this amount, particularly at frequencies within the bandwidth of the feedback control and at the mechanical resonance frequencies. Fortunately, even a simple elastometer suspension of the STM head produces a large attenuation of the external vibrations. For systems that have to operate within a vacuum, the whole chamber should be isolated from building vibrations and sound. This is particularly true for standard commercial UHV systems that are built with thin walls. While thin walls do not pose a problem for most surface science instruments, the special sensitivity of the STM to vibrations makes this type of chamber too prone to excitation of vibrational modes by sound.

Many vibrational problems are readily dealt with using well-known solutions and commercially available devices. The degree of isolation needed for each system depends essentially on the rigidity of the head design and on the noise level of the laboratory space. External noise that is not completely damped can be observed and distinguished from other types of noise. The frequency of an undamped external vibration that does not coincide with a particular mechanical resonance mode produces a noisy feedback output (Z-piezo voltage signal), since the feedback circuit compensates for the effect of the vibration on the gap. In this case, the tunneling current will be constant and stable if the gain is set high enough and/or if the time constant is low enough. Regardless of the setting of the gain and time constant, the feedback loop cannot compensate for an unstable gap resistance such as that caused by a dirty tip or surface or by excited mechanical resonant modes. Both tunneling current and Z-piezo voltage will be noisy and unstable.

5.2.5 Setting Up an STM Laboratory

A remarkable feature of the STM is the simplicity of its design. It is not difficult to build an STM in any laboratory that has access to modest mechanical and electronic shops. Piezoelectric elements that are ready to use (cut to shape and polarized) are available from several manufacturers at reasonable cost (Channel Industries, EBL, and EDO, for example). Figure 5.5 is a schematic design of a stable STM used at the Lawrence Berkeley Laboratory. This model has two concentric piezo tubes. Figure 5.5b shows the microscope mounted in an 8-inch flange for UHV operation. The outer cylindrical tube is used to translate the sample holder inertially from a macroscopic distance to within tunneling range. This is done by slow contraction, followed by rapid extension, such that inertia causes the sample holder to slide over the quartz tube. The sample holder is supported by sapphire balls. The inner piezo tube supports the tip. The tip is held by spring action, which allows for easy replacement without breaking the vacuum. The metal film that provides the outer electrode of these tubes is divided into four quadrants to provide X and Y deflection.
Figure 5.5. Schematic of double-tube microscope head for UHV studies at the Lawrence Berkeley Laboratory (a) and STM head mounted on an 8-inch UHV flange, showing suspension by viton-O rings (b).
(Figure 5.4). The inner tube is used to scan the tip, while the outer tube is used to offset the sample.

Commercial versions of the STM can be purchased from several manufacturers. Digital Instruments Inc. (Santa Barbara) produces an STM for operation in air and in liquid environments. McAllister Technical Services (Berkeley), RHK Technology (Michigan), VG Microscopes Ltd., (East Grinstead, England), W.A. Technology (Cambridge, England), and Park Scientific Instruments (Palo Alto, CA), for example, are producing STMs for operation in ultrahigh vacuum.

5.3 STM IMAGING

5.3.1 Tips—Their Structure and Preparation

If the microscope is to resolve the structure of the surfaces on a scale of angstroms, the tip itself must be prepared with atomic sharpness. Field ion emission (FIM) studies have provided much data on the atomic structure of tips. Fink (1986) has used field evaporation followed by deposition of atoms from the vapor phase to prepare tungsten tips that terminate in a single atom. Kuk and Silverman (1986) have used FIM before and after the STM scan to determine the geometry of the tip. To obtain the best resolution possible, it is also advantageous to know the tip structure in order to understand the correlation between geometric and electronic effects. In most practical situations, however, the structure of the tip cannot be determined. Fortunately, the fact that most observed structures on metal surfaces are reproducible over a wide range of bias voltages and using different tip materials and preparations indicates that the tip structure is not important in many applications. It is important, however, that the tip be stable during image acquisition.

Since tips naturally end in asperities or atomic clusters, and since the tunneling current depends exponentially on the distance from the tip to the surface, the atom or group of atoms closest to the surface will draw all the tunneling current. With this in mind, many researchers use simple mechanical methods, which include grinding and cutting metal wires with pliers or other tools, to prepare tips. Tips prepared from 60%-40% platinum-rhodium alloys cut with pliers produce good results eighty percent of the time. Tips made of noble metals are particularly good in nonvacuum environments, where formation of thick oxide layers must be avoided. Other materials used include platinum-iridium alloys, tungsten, and gold-coated tungsten. Many tip preparation techniques use electrochemical etching methods to produce sharp tips with radii of a few hundred Å at the apex, (Figure 5.6). Sharp tips are particularly important when imaging highly corrugated surfaces on the scale of 1,000 Å and below.

UHV operation gives an extra degree of freedom in tip preparation. Contaminant and oxide layers can sometimes be removed by operating the tip as an
Figure 5.6. Scanning electron micrographs of two tungsten tips prepared by electrochemical etching of 0.020-inch wires. Tip radii are 1000 to a few hundred Å.
electron field emitter or as an ion emitter under positive polarization. Some researchers have modified the tip structure by purposely crashing the tip on the surface. As yet, however, there are no reliable guidelines for tip cleaning, and the methods used vary tremendously. In many cases—after a severe "crash" with the surface, for example—the tip cannot be restored easily to a stable operating condition. Instead, it must be replaced. Thus many designs incorporate tip exchange mechanisms. Certainly, tip preparation in the field of STM is currently more an art than a science.

A special case is tip preparation for studies of solid-liquid interfaces. To avoid Faraday leakage currents due to ions in the solution, the tip must often be protected by insulating it with a sheath of glass or plastic. Since only the last few microns of the metal needle are exposed, the leakage current is reduced to less than a few nanoamperes. This residual current is comparable to a background that is independent of tip-to-surface distance and can therefore be compensated for. Protected needles of various metals can be purchased from manufacturers such as Frederick Haer & Co. and Digital Instruments. Recently, Heben et al. (1988) have succeeded in producing tips where only a few nanometers of metal are exposed.

5.3.2 STM Imaging Modes

The STM can be operated in several modes, each of which provides different types of information. These modes are the topographic or constant current mode, the current or constant height mode, the barrier height (or $\partial I/\partial z$) mode, and other modulation modes. Also, images can be acquired simultaneously at various voltages, which is the basis of spectroscopic imaging—scanning tunneling spectroscopy and vibrational spectroscopy.

5.3.2.1 Topographic Mode (Figure 5.7a)

The topographic mode is the most widely used mode of operation. The image obtained in this mode is a graphic representation of the height of the tip above the surface, where this height corresponds to a fixed value of the tunneling current for a given bias voltage. Thus the term "topographic" is applied loosely. As discussed earlier, it is the density of states at the Fermi level of the sample for negative bias, or the empty density of states of the sample at an energy $eV$ above the Fermi level ($V$ being the applied voltage), that is mapped by the tip. The density of states of the tip around the Fermi level is important in determining the value of the tunneling current, but this value remains constant within a given image. Because the density of states of most metals varies smoothly with energy (peaks have widths of a few eV), and because imaging bias voltages are often $\sim 2$ eV and below, the correspondence between surface topography and contours of equal density of states should be close. This is not so for semiconductor surfaces, where surface states in the band gap produce sharp peaks in the density of states close to the Fermi level. These states are also highly localized around bonds between the atoms (filled) and in antibonding orbitals (empty) that form lobes outside the bond (Stroscio et al., 1988).
Figure 5.7. Three imaging modes of STM operation: topographic mode, where tunneling current is kept constant (a); current mode, where tip to surface distance is kept constant (b); and barrier height mode, where tip to surface distance is modulated at high frequency while changes in amplitude of tunneling current are measured (c).

5.3.2.2 Current Mode (Figure 5.7b)
The current mode is used often for flat surfaces such as graphite (Bryant et al., 1986). In this mode, the time constant of the feedback circuit is set higher than the value required to move between neighboring atoms. In this way the average value of the current and of tip-to-surface distance is kept constant, while the instantaneous value of the tunneling current changes with the periodicity of the surface lattice. In fact, the tunneling current is a direct measure of the tunneling probability and can be used to generate an image. Because of the fast scanning speeds used, images can be acquired in one second or less. The disadvantage of the method is the need for flat surfaces. Any irregularities larger than the gap distance will cause the tip to crash.
5.3.2.3 **Barrier Height Mode (Figure 5.7c)**

Modulation methods are commonly used in physical measurements to enhance signal-to-noise ratio and to obtain derivative spectra, as in Auger Spectroscopy. A sinusoidal signal is superimposed on one of the parameters that controls the output of the measurement. The output then contains a signal at the modulation frequency whose amplitude is proportional to the derivative of the output with respect to the modulated parameter. In STM, a modulation of the tip-surface distance will produce a component in the tunneling current at the modulation frequency whose amplitude is proportional to the tunneling barrier height, \( \phi \) (Binnig et al., 1983b):

\[
\frac{\partial I}{\partial z} \propto I \times \phi^{1/2}
\]

Since the barrier height is closely related to the work function value, this mode is often, but improperly, called the "work function" mode. The work function is an average property of the surface at infinite distance, while the barrier height is a local property measured at the short distances used in tunneling. Care must also be taken in interpreting this type of image. First, in an inclined region of the surface, the vertical tip displacement changes the distance to the surface in proportion to the cosine of the angle of inclination of the surface, \( \alpha \). Therefore the above formula must be modified to include \( \cos \alpha \), and a topographical component will always be present. Second, the experimental values of \( \phi \) measured in air and in vacuum are often substantially smaller than the typical values expected for the work function (that is, 4 eV). Values of less than 1 eV (sometimes as low as 0.001 eV) have been found. These low values can be attributed to the collapse of the barrier height when the tip is too close to the surface (Lang 1988). Other possible explanations include deformation of the tip or the surface, perhaps mediated by impurities condensed between tip and surface that would reduce the distance change (Coombs and Pethica, 1986; Mamin et al., 1986). Since these questions remain unanswered, the absolute value of \( \phi \), after the topographic effects are discounted, should be interpreted only qualitatively.

Barrier height mode imaging distinguishes between areas of different chemical composition over the surface. At Lawrence Berkeley Laboratory, this method has been used both to enhance signal-to-noise ratio and to identify surface features as arising from substrate reliefs or from changes in composition. The example in Figure 5.8 illustrates surface characterization for TiO\(_2\) deposits on palladium. The deposits were prepared under UHV, and characterization with surface Auger and photoelectron spectroscopies indicated that one monolayer of TiO\(_x\) was present (\( x \approx 2 \)). Upon exposure to air, the two-dimensional oxide layer collapsed into small three-dimensional clusters of TiO\(_2\) (as determined by subsequent examination in UHV). These clusters were imaged by STM, using both the topographic and work function methods. Figure 5.8 shows that the \( \phi^{1/2} \) image is flat (constant value of \( \phi \)), except in the central portion, indicating that the material in this flat region has uniform composition. Thus the reliefs observed in the topographic image are due to palladium irregularities in the
Figure 5.8. Barrier height image (a) and corresponding topographic image (b) of a Pd foil with a monolayer equivalent of TiO$_2$ islands. Islands are visible as areas of different barrier height. Pd areas appear as flat regions. In topographic image, titania islands cannot be distinguished from Pd irregularities. Area scanned is 1500x1500 Å.
regions of constant $\phi$. Only the structures in the center of the topographic image can be assigned to the oxide islands.

5.3.2.4 Scanning Tunneling Spectroscopy Modes

Electron spectroscopy is a truly unique feature of the STM. No other technique can image the density of states locally at the atomic scale. As the bias voltage of the sample is scanned from negative to positive values, a current formed by electrons tunneling first from filled states and then into empty states of the sample is detected at a fixed tip-to-surface distance. Feenstra et al. (1987a) have shown that the ratio of the dynamic to static conductivity, $V/I(dI/dV)$ is proportional to the density of states (Figure 5.9). If the bias voltage is changed at each point (or pixel) in the course of image acquisition, such that electrons are extracted or injected into well-defined orbitals of the surface atoms, an image can be obtained for each bias voltage. A collection of such images offers different views of the surface electronic structure. Feenstra et al. (1987b) have used this method to map the atomic location of the filled (bonding) and empty (antibonding) orbitals of the surface states of GaAs (Figure 5.10).

Hamers et al. (1986) introduced the current imaging tunneling spectroscopy (CITS) method. In this mode of operation, the feedback loop is interrupted briefly in order to measure the tunneling current at various voltages. The tip height is kept constant while the feedback loop is interrupted. (The interruption time should be as short as possible in order to minimize drifts.) After the feedback loop is restored, the height is measured topographically in the normal way. Repeating this sequence at high frequency (2 kHz, for example) maintains a constant sample-tip separation during the current-voltage measurements. Thus both topography and spectroscopy are obtained simultaneously.

5.3.2.5 Vibrational Spectroscopy

Although at a very early stage of development, vibrational spectroscopy can be performed in principle with the STM. When the energy of the tunneling electron is scanned (as in the spectroscopic measurements described above), resonant scattering occurs when the energy of the tunneling electron equals that of the vibrational mode of an adsorbate. The corresponding change in tunneling probability is reflected as a small change in the I-V characteristic, in much the same way as in inelastic tunneling spectroscopy of metal-oxide-metal sandwiches (Hansma, 1982). This change is evidenced as a peak in the plot of $d^2I/dV^2$ against $V$. The energy scale for vibrational spectroscopy is in the range of tens of millielectronvolts, while the energy scales for electron spectroscopies are in the range of eV. Low temperatures are needed to keep the tip over an adsorbate molecule during the measurement. Low temperatures immobilize the adsorbate, improve thermal stability, and sharpen the Fermi distribution to below $k_B T$ ($=25$ meV at room temperature). This new aspect of STM is being explored (Smith et al., 1987; Eigler, 1987).
5.4 STM OF INERT MATERIALS

This section reviews the use of STM to study adsorbates on inert substrates such as graphite and gold.

5.4.1 Graphite

Because of its ease of preparation, atomic flatness, good electrical conductivity, and chemical inertness, graphite is one of the most widely used substrates for STM. It has been studied in air (Binnig et al., 1986a, Park and Quate, 1986), liquid (Sonnenfeld...
Figure 5.10. Combined color images of constant density of states for occupied (red) and unoccupied (blue) orbitals of GaAs(110) surface. Occupied orbitals correspond to Ga; empty orbitals correspond to As.

Reference: Feenstra et al., 1987b
and vacuum environments (Mamin et al., 1986), both as a substrate for deposition of adsorbates and as a test and calibration of the instrument. The layered, nearly two-dimensional structure of graphite also gives rise to anomalous effects in STM imaging. These effects have produced heated debate and numerous publications in recent years.

5.4.1.1 STM Imaging of Graphite

The anomalous effects in STM imaging of graphite are the giant corrugations, the asymmetry of alternate carbon atoms, and the variable appearance of the atomic unit cell.

Giant corrugations are observed as much larger vertical displacements of the tip over the unit cell than would be expected from a charge-density corrugation observed several angstroms from the surface. Helium scattering experiments (Boato et al., 1978), for example, showed a corrugation of a few tenths of an angstrom, whereas experimental values of the corrugation for graphite range from 0.5 Å to tens of angstroms. Tersoff (1986) attributed these large corrugations to electronic effects. Other authors have attributed the anomalous corrugations to the elastic deformation of graphite as the tip moves over the surface. The increase of the corrugation amplitude as the tip is brought closer to the surface supports this explanation (Soler et al., 1986; Mamin et al., 1986; Morita et al., 1987). Because of this deformation, the true change of the tip-to-surface distance is only a small fraction of the total tip displacement. Some authors have proposed that the deformation occurs on the scale of single atoms (Soler et al., 1986). Others imply that the deformation encompasses many surface atoms (Pethica, 1986). If the deformation encompasses many surface atoms, the high lateral resolution could be preserved by the periodic registry of two layers of graphite, one bound to the tip and the other being scanned. Mamin et al. (1986) showed that contamination layers between the tip and the surface play a major role in surface deformation. These authors measured corrugations of 0.9 Å when graphite was imaged in UHV with clean tips and clean surfaces.

The appearance of the unit cell of graphite, which is known from X-ray crystallography to contain two nonequivalent carbon atoms that form a honeycomb arrangement, is also peculiar. One of the most commonly obtained images shows a hexagonal structure, with a lattice parameter of 2.46 Å (Figure 5.11a). This arrangement corresponds to graphite planes with alternate carbon atoms missing. In some cases, the triangles formed by the centers of surface atoms are alternately high and low. These observations prompted several theoretical studies of the electronic structure of graphite, particularly the local density of states at the Fermi level for the two nonequivalent atoms of the cell. One of the two nonequivalent atoms has a neighboring second layer atom (A sites) while the other does not (B sites). It is the small interaction between the first and second layer atoms in A sites that modifies the
Figure 5.11. Current mode image of graphite: (a) half the atoms and (b) honeycomb lattice.
charge density distribution in these two sites, making the B sites more prominent than the A sites (Batra et al., 1987).

The third peculiarity observed in graphite is the variation in the appearance of the surface unit cell in different experiments. Although the above images with alternate atoms missing are the most commonly observed, honeycomb lattices (Figure 5.11b), elongated atoms, and zigzag chains are also observed. Mizes et al. (1987) explained these observations by assuming that several minitips are tunneling simultaneously. The easy deformation of the graphite substrate would help to bring secondary tips into tunnel range. By adding one, two, or three images with different phases and amplitudes, Mizes et al. generated all the reported images of graphite.

5.4.1.2 Graphite as a Substrate

Because of its flatness and chemical inertness, graphite is used extensively as a substrate to support a variety of deposits. Such deposits can be clusters or large organic and inorganic molecules that can adhere to the surface. Ganz et al. (1988) studied gold, silver, and aluminum clusters by evaporation in UHV. The clusters formed at coverages of ~0.1% of a monolayer consisted of monomers, dimers, and two-dimensional islands. The islands showed a coexistence of phases with an ordered but incommensurate interior and disordered edges. Images of the edges of gold islands showed that some atoms formed a buckled chain arrangement, with the entire island rotated four degrees relative to the substrate. Grain boundaries between two different regions in silver islands were also observed. Interestingly, these studies show that the rectangular and honeycomb unit cells formed by the metal adatoms are out of registry with the graphite lattice.

The above discussion shows that the STM is an excellent tool in the study of deposited clusters. Such studies are important in catalysis, since they provide a way to model metal clusters and provide information on the structure of the clusters. The use of graphite as a substrate provides both an atomically flat surface and a reference lattice for precise calibration of the XY-piezo displacements. Such studies, if combined with studies of the effects of chemisorption on the structure of the clusters, could provide a wealth of information on the chemical properties of supported catalysts.

Graphite has also been used as a substrate in the study of semiconductor clusters of PbI₂ and BiI₃ deposited from colloidal suspensions (Sarid et al., 1988), phosphotungstic acid and rhenium carbonyl complexes, and organic molecules such as acetone (Lyding et al., 1988a,b). In the study of acetone, a complete and ordered monolayer of acetone molecules on graphite was formed after continuous exposure for ~24 hours. Recently, Foster et al. (1988) observed di(2-ethylhexyl)phthalate molecules pinned to the graphite surface. A 100-ns, 3.7 V pulse to the tip, which was immersed in the solution containing the molecules, was used. According to these authors, the voltage pulse served to bond the molecule to the surface. The pinned molecule can be
removed from the surface with another pulse as the tip passes over the adsorbed molecule. Foster and Frommer (1988) also imaged the interface between a solution of smectic and nematic liquid crystals and graphite. Ordered arrays of the organic molecules were observed with nearly atomic resolution. Smith et al. (1987) observed sorbic acid on graphite at liquid helium temperatures. Vibrational measurements were also made.

Other materials that have layered structures like graphite can be prepared in similar ways. These materials exhibit a similar chemical inertness (Salmeron et al., 1982) that makes them attractive for operation in air or liquids. Among such materials used in STM are MoS$_2$ (Weimer et al., 1988), NbSe$_{23}$ (Bando et al., 1988), WS$_2$, TaSe$_2$, and TaS$_2$. Most studies have focused on the observation of charge density waves (CDW) (Coleman et al., 1985; Slough et al., 1986; Thomson et al., 1988), although in recent studies these materials are used as substrates for deposition of metals (Uozumi, 1988) and polymers (Dovek et al., 1988).

5.4.2 Gold

One of the most widely used metal substrates is gold, primarily because of its chemical inertness, which makes it ideal for use in air and in cases where minimum chemical interaction between deposit and support is desired. Also, gold can be prepared in an atomically flat form by depositing thin films on substrates such as mica.

Gold is important in its own right because each of its three low Miller index surfaces—(100), (110), and (111)—reconstruct to geometries that depart from the ideal bulk termination (Van Hove et al., 1981). Thus gold surfaces were the first to be studied by STM. The (111) surface of gold has the peculiarity of being the only face-centered cubic (fcc) surface of compact orientation that is known to reconstruct. Atomic resolution of the (111) surface has recently been achieved by several authors (Hallmark et al., 1987; Emch et al., 1989; Wöll et al., 1988). All observed large periodicities that were attributed to the 22x3 reconstruction. Wöll et al. (1988) resolved the atomic structure of this surface over large regions, which enabled the site occupation of the gold atoms in the two regions of the unit cell to be determined. In one region the atoms occupy their normal fcc position; in the other they occupy hexagonal close packed (hcp) positions.

Salmeron et al. (1987a,b) observed faceting of stepped gold surfaces in single crystals of (334) orientation prepared in UHV and studied in air with the STM. Segregation of iron impurities to the surface after heating caused this stepped surface to facet into large (111) facets and two other smaller facets with a different orientation.

Because of their ease of preparation and importance as an inert support, gold films on mica have been studied extensively. Marchon et al. (1987), Chidsey et al. (1988), and Emch et al. (1989) observed large (several hundred Å) atomically flat areas
in such films. In some cases, these areas form after annealing the films to between 250 and 300 °C. Monatomic-height steps and dislocations were also observed. Jaklevic and Elie (1988) studied the diffusion of gold on Au(111) from defect structures created by touching the surface with the STM tip.

Many authors have used gold films as substrates for the deposition of molecules such as polyoctadecylacrylate (Emch et al., 1989) and phthalocyanine (Lippel and Wilson, 1988). Gold has also been used in the form of very thin coatings (~50 Å) to provide conductivity to insulating substrates. Jaklevic et al. (1988) have used this approach to image silica, sodium chloride, and even polymers.

## 5.5 STM OF CHEMISORPTION

This section reviews STM studies of strongly interacting systems; that is, systems involving chemisorption. Most of the work done to date involves semiconductor substrates and metal adsorbates. This is partly because the development and first applications of STM occurred in laboratories that had a strong research interest in semiconductors. Nonmetallic adsorbates on semiconductors have also been studied recently, particularly the surface reactions between silicon and ammonia.

Recently, metal substrates have received attention. Because of the need to use conductive samples, however, metals deposited on oxide supports cannot be studied directly with current STMs. Such studies will have to await further development of the atomic force microscope (Section 5.6). Thus the following discussion is confined to the area of model catalyst systems, usually single crystals. These systems can be characterized in UHV using a variety of surface science techniques.

### 5.5.1 Metals on Semiconductors

A variety of metal/silicon overlayer systems, including silver, palladium, aluminum, indium, gallium, and copper, have been studied with the STM. The metal is usually deposited by evaporation and then annealed.

Silver deposited on Si(111) was first studied by Wilson and Chiang (1987a) and Van Loenen et al. (1987). In agreement with previous LEED studies, the structure formed is the $\sqrt{3} \times \sqrt{3}$. As with clean semiconductor surfaces, these studies also show that the surface corrugation due to the adsorbed metal atoms is dominated by electronic effects. The atomic features appear either as bumps, with a corrugation of 2 Å at a negative sample bias of -1 V, or as shallow holes (0.2 Å deep) at biases greater than -1.8 V. In the former case, tunneling occurs from the occupied orbitals into the tip at 1 eV below the Fermi level. In the latter case, the silver structure has strong surface-state contributions (Demuth et al., 1988). Wilson and Chiang (1987b) studied the structure formed by silver at coverages that allowed simultaneous observation of the $7 \times 7$ substrate and the three silver overlayer islands. The registry of the two lattices suggests that the structure is a honeycomb arrangement of silver atoms.
on the threefold sites of the Si(111) surface. The registry method, which uses the change in lattice across the island boundary to the bare substrate, is the only way to determine the site of the adatoms, since the STM image provides information only on the outermost surface layer.

At one-third monolayer coverage, a different $\sqrt{3} \times \sqrt{3}$ structure is formed by aluminum on the same Si(111) substrate. Hamers and Demuth (1988) studied this surface with the STM. They found that substitutional defects, in which silicon replaces aluminum adatoms in the overlayer, are present, together with vacancies. The different electronic structure at these defects (as observed by CITS) causes a depression in the topography at a sample bias of +2 V and a protrusion at a sample bias of -2 V. (V/I)dI/dV curves for the defect sites at -0.4 eV indicate the presence of a state associated with the isolated silicon substitutional defects. This is another example of the dramatic contribution of the electronic structure to the observed corrugation profiles in semiconductor surfaces.

Köhler et al. (1988) studied the initial stages of Pd silicide formation. These authors found that initial nucleation at room temperature occurs almost exclusively in the faulted half-unit cell of the 7x7 Si(111) structure. This initial compound formation seems to involve only the outermost silicon layer.

Park et al. (1988) studied indium and gallium on Si(111). They found that, at low densities, indium atoms replace silicon in the original 7x7 adatom positions. At higher coverages of these metals, a sequence of reconstructions was observed.

Wilson et al. (1988) studied the surface structure formed by evaporating Cu on Si(111). They found that the surface breaks up into 5x5 subunits packed at spacings varying from 5 to 7 lattice constants. Demuth et al. (1989) concluded that at least three electronically and structurally independent local phases coexist and arrange to form a quasiperiodically ordered structure.

The wealth of both electronic and topographic information on the structure of metals on silicon revealed by these examples is a great help in our understanding of the reactions of silicide formation. These examples also illustrate STM’s unique ability to determine the atomically localized nature of many of the properties of these interfaces.

5.5.2 Nonmetallic Adsorbates

The first chemisorption study that utilized STM was a study of oxygen atoms on Ni(110) by Baró et al. (1984). A 2x1 structure consistent with the "sawtooth" model, with oxygen atoms sitting in long bridge positions, was observed. As with metals on semiconductors, the correlation between observed topography and atom position requires careful consideration. Does an oxygen atom appear as a bump or as a
depression? Since the electronic density of states at the bias voltage determines the tunneling current, the question cannot be answered without understanding the electronic structure of the surface. Lang (1986 and 1987) has shown that both situations can occur for chemisorbed atoms, depending on bias voltage and tip distance. Doyen et al. (1988) calculated the corrugation due to oxygen adatoms on Ni(100). At small surface-tip separations (below 6 Å), they found a negative corrugation. At larger distances, they found a positive corrugation with maxima at the oxygen atom positions.

Hösl er et al. (1986) studied the adsorption of carbon monoxide and ethylene on Pt(100). While there were no features that could be identified as carbon monoxide molecules, the effect of carbon monoxide adsorption was shown dramatically by the formation of terraces of platinum atoms that resulted from the removal of the 5x20 reconstruction. The difference in the surface density of platinum atoms in the 1x1 and 5x20 surfaces gives rise to the accumulation of the excess atoms into terraces. These authors also observed the buildup of carbon due to the thermal decomposition of ethylene, proceeding from the steps, which supports the enhanced activity of these step sites in surface reactions.

Another catalytically interesting chemisorbed system is carbon on platinum. Ogletree et al. (1988) studied the structure of the carbon monolayer formed on Pt(111) after high-temperature treatment (≥1000°C) of the sample in UHV. The graphitic nature of the carbon layer is demonstrated by the images obtained (Figure 15.12).

Molecular adsorbates were first imaged by Ohtani et al. (1988) using benzene coadsorbed with carbon monoxide on Rh(111). A study of both the 3x3 and the c(2√3 x 4)rect (Chiang et al. 1988) structures corroborated previous site determination by LEED (Lin et al., 1987; Van Hove et al., 1986). The structure is shown in Figure 5.13a. The best resolution was obtained at low bias voltages and tunneling into empty orbitals of the substrate. Under these conditions, the benzene ring was resolved and imaged as a threefold symmetric donut-shape, (Figure 5.13b). The carbon monoxide molecules, imaged under the same conditions on the c(2√3 x 4)rect structure, appeared as bumps ~0.2 Å high as compared with the 0.6 Å bumps of the benzene molecule. Since the lowest empty antibonding levels of benzene and carbon monoxide (e_2a and 2π*) are several eV above the Fermi level, the authors propose that tunneling into low-lying molecular orbitals with strong metallic character occurs.

Another chemisorption system studied at LBL by Marchon et al. (1988a) is the sulfur on Mo(001) system, an important model catalyst for studies of hydrodesulfurization catalysis. Sulfur forms a variety of structures on the (001) surface of this metal (Salmeron et al., 1983). The structure corresponding to saturation coverage (one sulfur atom per molybdenium surface atom) forms an ordered arrangement with 1x2 (and 2x1) periodicities. The surface was prepared in UHV and characterized by Auger spectroscopy and LEED. This surface is remarkably stable upon exposure to air, as
shown by subsequent examination in UHV. The STM revealed the atomic structure of the sulfur adatoms, which form 1x2 unit cells that have an extra sulfur atom in the center of the unit cell. The corrugation was observed to be \( \sim 0.3 \, \text{Å} \). Images were also obtained in the barrier height mode to enhance the signal-to-noise ratio (Figure 5.14). Both the topographic height and the barrier height were found to be the same, within experimental error, for all the sulfur atoms (Figure 5.15a). This result led the authors to discard the model proposed by Clarke (1981), in which sulfur atoms occupy bridge and fourfold hollow sites. Figure 5.15b shows a model that is consistent with the present results. In addition to the perfect ordered areas shown in Figure 5.14, many defects were observed (Marchon et al., 1988b). These defects include domain boundaries, steps, and substrate low-angle, grain boundaries. The passivating effect of sulfur is short lived. After several hours or days, depending on the perfection of the sulfur overlayer, oxide spots that progressively cover the surface develop. Figure 5.16 shows an image of an oxidized area.

Figure 5.12. Current mode image of 15x15 Å area of carbon monolayer on Pt(111) produced in UHV after heating crystal to 1000 °C at 10\(^{-10}\) torr.
Figure 5.13. Diagram of 3x3 $C_6H_6 + 2CO$ structure, as determined by LEED (a) and corresponding STM image (b).

Reference: Lin et al., 1987; Ohtani et al., 1988
Figure 5.14. 35x45 Å barrier-height image of 1x2 saturation monolayer of sulfur on Mo(100). Surface layer was prepared in UHV and imaged in air.

Reference: Marchon et al., 1988a

Marchon et al. (1988c) also studied sulfur chemisorption on Re(0001), which shows a similar passivation effect at saturation sulfur coverages. Figure 5.17, shows a large scan of 0.5x0.5 μ on this surface. The surface exhibits numerous steps of mono- and multiple atomic height. Such defects are difficult to see using any other technique. These results are important in that they show that it is possible to image adsorbate atoms at high pressures. The next step should be the study of chemical reactions under the high pressure of controlled gas environments. This would open the way to in situ studies of important catalytic systems for which there is no way currently to obtain atomic-level information on the surface structure and processes.
Figure 5.15. a: Line scan profiles along (1) [100] and (2) [120] directions (barrier height mode), (3) [010] direction (topographic image), and (4) [120] direction. b: Models of sulfur overlayer with sulfur (black dots) occupying fourfold and twofold sites (1) and in equivalent sites forming a zigzag chain (2).

The reaction of ammonia with Si(111) and (100) [Hamers et al. (1987) and Wolkow and Avouris (1988)] also deserves mention. These authors have followed the chemisorption process by examining the changes, atom by atom, in the electronic structure of the silicon substrate. On the Si(111) 7x7 structure, the most reactive atoms are the so-called rest atoms in the first layer. (These atoms have occupied, dangling
bonds.) The next most active are the corner atoms, followed by the center adatoms. Figures 5.18a and 5.18b depict these sites and show the electronic spectra obtained by tunnel spectroscopy (Figure 5.18c). On the surface exposed to ammonia, a dramatic change in the electronic structure is observed on these sites (Figure 5.18d). Particularly obvious is the disappearance of the peak due to the occupied dangling bonds of the rest atoms. These results suggest that it should be possible to monitor the charge transfer between surface sites and the changes in these interactions induced by the surface reaction. This type of study could effect a tremendous advance in our understanding of surface reactions and of the role of the various types of sites. This is particularly true for surface defects, which have often been invoked as the sites responsible for the activity of many catalysts.

5.6 ATOMIC FORCE MICROSCOPE

The atomic force microscope (AFM), invented by Binnig et al. (1986b), operates by sensing the minute forces acting between tip and surface as a result of either attractive or repulsive interactions. Attractive interactions include Van der Waals, dipolar, electrostatic, or magnetic forces. Repulsive interactions arise from the overlap of the outer electronic orbitals of the atoms at the tip and at the surface.
Figure 5.17. 0.5x0.5 μ image of Re(0001) passivated by a saturation monolayer of sulfur in air. Mono and multiple atomic height steps are visible.
Figure 5.18. Unit cell model of 7x7 surface of Si(111): (a) top view; (b) side view; (c) V/I(dI/dV) curves of local density of states, with tip sitting on top of rest atoms (curve A), corner adatoms (curve B), and center adatoms (curve C); and (d) after reaction with ammonia.

Reference: Wolkow and Avouris, 1988
Since these forces are a function of distance, they can be used to produce an image in much the same way as the tunneling current is used in the STM.

Because the attractive forces are long-range compared to the repulsive forces, these forces must be integrated over all the atoms in the tip and in the sample (Adamson, 1976). Considering Van der Waals potential energies, which vary with the interatomic distance $z$ as $z^{-6}$, a full integration over the half space of the sample changes the $z$ dependence to $z^{-3}$. A further integration over the atoms of the tip (which can be approximated by a sphere, a cylinder, or a cone), gives:

$$V(z) = -\frac{Hr}{6z}$$

(5.8)

where $r$ is the tip radius and $H$ is the Hamaker constant, which is of the order of $10^{-20}$ Joules. For a tip in the radius of 12 Å at a distance of 5 Å, $V = 4 \times 10^{-21}$ J and the force $F(z)$, which is the derivative of $V(z)$, is $10^{-11}$ N. Also of interest is the magnitude of the force constant, which is the derivative of $F(z)$. This force constant is of the order of 0.1 N/m.

Because of its long range, imaging in the attractive force regime will have a limited resolution of several nanometers. On the other hand, the repulsive regime that dominates at short distances can be limited to one atom and can therefore produce atomically resolved images. Figure 5.19 illustrates these concepts. Since the repulsive regime is equivalent to atomic contact of the tip with the surface, chemical bonding may occur at the very short distances of operation (that is, at about the ionic or Van der Waals radii of atoms). In the repulsive mode, the forces, which are limited by the hardness of the material in the tip and surface, can be much higher than those in the attractive mode. In the transition from the attractive regime to the repulsive regime—that is, as the tip is moved closer to the surface—there is an unstable position at which the tip is displaced suddenly to the surface. As shown in Figure 5.20, this occurs when the curvature of the attractive potential $V''(z)$, equals the force constant of the cantilever spring, $k$.

Several methods have been developed to measure the forces in the AFM. All use tiny cantilevers that support the tip and that bend under the forces acting between tip and surface. From the above discussion, the deflection of the cantilever due to these minute forces will be very small. For example, a cantilever with a spring constant of 10 N/m will bend 0.1 Å under a force of $10^{10}$ N. The various AFM designs differ in how these deflections are measured. In their original work, Binnig et al. (1986b) used the tunneling current flowing between the back of the metalized cantilever and a fixed STM tip. This method was used by several other authors, including Albrecht and Quate (1988); Marti et al. (1987); and Heinzelmann et al. (1987). The method is inconvenient, however, in that it uses two locally sensitive
probes—the STM and the AFM tips—acting in series. Also, all the difficulties that are typical of the STM operation—drift and erratic changes of tip structure, for example—are greatly magnified. For this reason, methods that used nonlocal probes to measure the cantilever position were soon developed. Some of these methods use optical interferometry in which the back of the cantilever comprises one end of the optical cavity. Since, for visible light, the wavelength is \( \sim 6000 \, \text{Å} \), deflections of 1 Å modify the cavity by \( \sim 0.1\% \). With a stable laser, this modification produces measurable changes of intensity (Erlandsson et al., 1988). Alexander et al. (1989) used an optical lever to detect cantilever deflections. In this method, the changes in tip height due to the atomic forces are measured by reflecting a laser beam from a small mirror mounted on the back of the cantilever. The changes in the position of the reflected spot are measured by a position-sensitive detector photodiode pair.
A source of noise is the excitation of vibrations in the cantilever. The magnitude of the thermally excited vibration can be obtained from the equipartition theorem (McClelland et al., 1987):

\[
\frac{1}{2} k \delta^2 = k_B T
\]  

(5.9)

where:
- \(d\) = Maximum vibration amplitude
- \(T\) = Temperature
- \(k_B\) = Boltzmann constant

When \(k\) is 10 N/m, \(\delta\) is approximately 0.3 Å. Also, for cantilevers made of metal wires with diameters on the order of tens of microns and with lengths on the order of millimeters the resonance frequency is of the order of 10 to 20 kHz. This is above the band pass of the feedback circuit for a reasonably fast image acquisition time. Other
sources of noise include shot noise from the laser, light intensity fluctuations due to back reflection into the laser cavity, air turbulence, and building and acoustic vibrations.

Clearly, the AFM is on a rising curve in instrument development, and many new approaches to the detection of the cantilever deflection are being explored. Even so, the demonstrated capabilities of ATM, particularly in the imaging of insulating materials, make this type of microscope invaluable in surface science in general and in catalysis in particular. The AFM will facilitate the study of the surface topography of oxide supports, the external surfaces of zeolites, plastics and polymers, and biological materials. None of these materials is studied easily with the STM because of insufficient electrical conductivity. As with the STM, the AFM can operate at atmospheric and higher pressures and in liquids (Marti et al., 1987).

5.7 FUTURE DIRECTIONS OF STM AND AFM

The last three years have seen a dramatic growth in the field of STM and AFM. In the six years from its introduction in the open literature in 1982 to the end of 1988, the STM has revolutionized the field of surface science. Even so, STM and AFM are still in an exploration phase. The development of the spectroscopic modes of operation is a continuing process that has been applied only to a limited number of cases. The reaction of ammonia with silicon surfaces described above, for example, is merely an indication of the type of results that can be obtained. Indeed, the study of surface chemistry and the role of surface defects will benefit enormously from the application of these spectroscopic techniques. The development of the AFM may have an even greater impact than STM on surface chemistry and catalysis.

Another exciting application of STM and AFM is electrochemistry (Drake et al., 1987)—a field that could experience a tremendous change with the capability of imaging surfaces under liquids and following electrode processes with atomic resolution. Biology is also emerging as a new study area for these microscopies. As suitable substrates and fixation techniques are developed, the techniques could be used to help resolve the structure of DNA, RNA, proteins, etc. (Amrein et al., 1988; Beebe et al., 1989). These microscopy techniques should also move tribology from an empirical science to a science where the fundamental interactions and forces between surfaces can be studied at the atomic level. For example, the AFM has been used to study friction between graphite substrates and tungsten tips through measurement of the deflection of the cantilever both perpendicularly and horizontally to the surface (Mate et al., 1987). The STM and AFM can also be used as microtools in the modification of surfaces on scales never before possible (Jaklevic et al., 1988; Marchon et al., 1988d; Gimzewski and Molder, 1987; Becker et al., 1987).

STM and AFM are revolutionizing scientific and technological areas in which surfaces play a direct or indirect role. And this revolution is of such a profound nature that no laboratory involved in microelectronics, electrochemistry, catalysis, metallurgy, or
biochemistry can afford not to take into account these powerful and yet relatively inexpensive microscopies.
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