

Probing the Wave Properties of Electrons and Manipulating Atoms at Surfaces with the Scanning Tunneling Microscope

PHAEDON AVOURIS

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

Received November 5, 1993

The scanning tunneling microscope (STM) was introduced in 1982 as an instrument for the atomic-scale imaging of surfaces and of adsorbed species.¹ Since then, it has been applied successfully to determine the structure of metal and semiconductor surfaces and the sites of chemisorption of atoms and molecules, and also in probing processes such as surface chemistry and crystal growth.^{2,3} In its spectroscopic version, scanning tunneling spectroscopy (STS), it has been used to study the local electronic structure and states of, primarily, semiconductor surfaces.⁴ In surface chemistry it has made possible the correlation between the reactivity of individual sites of semiconductor surfaces and their local electronic structure.⁵

STS has a somewhat limited energy range, about ± 3 eV from the Fermi level of the sample. In the case of semiconductor surfaces whose surface states are mostly of the "dangling-bond" type, i.e., narrow, nonbonding levels close to the Fermi energy, the limited spectral range does not pose a serious problem. Metal surfaces, on the other hand, have broad, featureless spectra, and STS has had little impact on the study of the electronic structure of such surfaces.

As is true with most other probing techniques, there is an interaction between the sample and the probe (STM tip). This interaction is kept at a minimum when the study of the unperturbed properties of the sample is the objective. On the other hand, one can take advantage of the many different physical or chemical mechanisms by which the metal tip and sample can interact, select the appropriate interaction mode, control its magnitude and spatial location, and use it to bring about a desired atomic-scale modification of the sample.^{6,7}

In this Account we discuss and provide examples of two developments that enhance the capabilities and applications of STM and STS. First we show that one can take advantage of the wave character of electrons and the resulting ability to undergo interference in the same way as light waves do, to obtain novel fundamental information about the interaction of the delocalized surface electrons of metals with atomic-scale structures such as steps or adsorbed atoms and molecules. The results presented include the real-space observation of electron standing waves formed by the interference between the incident and the reflected electron wave

by these objects, the visualization of the probability amplitudes of the confined ("particle in a box") states of small metal islands and of the screening charge oscillations surrounding individual adsorbates. We then discuss an experimental approach that allows the breaking of strong covalent chemical bonds in preselected sites of a surface and the manipulation of individual atoms or clusters of atoms. Results are shown involving the manipulation of Si atoms.

Basic Principles

The heart of the STM is a sharp metal tip, which is brought very close to the sample surface, and which can be scanned laterally by piezoelectric transducers. When the gap between the sample and the tip is ≤ 1 nm, electrons can tunnel through the gap. The ability of the STM to image surface topography with atomic resolution is based on the fact that tunneling is a very sensitive, exponential function of the tip-sample distance. As a result, the tunneling current predominantly flows through the tip atom or the few tip atoms that are closest to the sample surface, yielding high lateral and vertical resolution. In the absence of an applied bias the Fermi levels (E_F) of tip and sample are at equilibrium. Upon application of a voltage bias, the Fermi levels are displaced relative to each other in energy and a tunneling current flows. If the sample bias is negative, electrons flow from occupied states of the sample to empty states of the tip, and the situation is reversed for positive sample bias. If the overlap between the tip and sample wave functions is small, one can use first-order perturbation theory to obtain an expression for the tunneling current:

$$I \propto \int_{E_F}^{E_F+eV} \rho_S(r, E) \rho_T(r, E-eV) |M_{ST}|^2 dE \quad (1)$$

In eq 1, $\rho(E, r)$ stands for the local density of states (LDOS), i.e., the density of states at a given point in space (r) and at a given energy (E), and V is the applied

(1) Binnig, G.; Rohrer, H.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57.

(2) Stroscio, J., Kaiser, W. J., Ed. *Scanning Tunneling Microscopy*; Academic Press: New York, 1993.

(3) Güntherodt, H.-J., Wiesendanger, R., Eds. *Scanning Tunneling Microscopy*; Springer-Verlag: Berlin, 1992.

(4) Hamers, R. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 531.

(5) Avouris, Ph. In *Highlights in Condensed Matter Physics and Future Prospects*; Esaki, L., Ed.; Plenum Press: New York, 1991. Avouris, Ph. *J. Phys. Chem.* **1990**, *94*, 2247.

(6) Avouris, Ph., Ed. *Atomic and Nanometer Scale Modification of Materials: Fundamentals and Applications*; Kluwer Academic Publishers: Dordrecht, 1993.

(7) Quate, C. A. In *Highlights in Condensed Matter Physics and Future Prospects*; Esaki, L., Ed.; Plenum Press: New York, 1991.

Phaedon Avouris received a B.S. degree in chemistry from the Aristotelian University in Greece and a Ph.D. degree in physical chemistry from Michigan State University. After postdoctoral work at UCLA and AT&T Bell Laboratories, he joined IBM Research as a research staff member in 1978 and in 1984 became manager of the Chemical Physics of Surfaces group. His current research interests include studies of the electronic structure and chemistry of surfaces, surface dynamics, atomic manipulation, and nanoelectronics. Dr. Avouris is a Fellow of the American Physical Society.

bias. M_{ST} is the tunneling matrix element. Bardeen⁸ has derived an expression for M_{ST} involving the individual wave functions of the tip and sample. For the purposes of this discussion, however, it is sufficient to consider an approximate result (WKB approximation) for the transmission coefficient (T) of electrons of energy E through the energy barrier formed by the work functions of the tip (ϕ_T) and sample (ϕ_S):

$$T(E, V) = \exp\left[-\frac{2s(2m)^{1/2}}{\hbar}\left(\frac{\phi_S + \phi_T}{2} + \frac{eV}{2} - E\right)^{1/2}\right] \quad (2)$$

From eqs 1 and 2 we see that the tunneling current depends on the tip-sample distance s , the bias voltage, and the details of the electronic structure (LDOS) of both sample and tip. Thus, an STM image represents a convolution of geometric and electronic structure. To separate these two contributions one may use the spectroscopic version of the STM: scanning tunneling spectroscopy (STS).⁴ To measure the local electronic structure at a particular site during a topographic scan, the tip is poised over the site of interest, the tunneling distance is fixed, and the feedback loop, which is used to maintain a constant current during topographic imaging, is disconnected. The bias voltage is then ramped, and the tunneling current is measured as a function of the applied bias. The I vs V data are used to obtain the derivative dI/dV ; the ST spectra are plots of dI/dV vs V . However, as can be seen from eq 1, this procedure does not really yield the LDOS of the sample, but rather a convolution of the LDOS of sample and tip and the barrier transmission factor T . It is usually assumed that the tip of LDOS is structureless in the range E_F to $E_F - eV$ so that the observed peaks are due to the structure of the sample LDOS. This, however, need not be true in general, and deviations leading to interesting electrical phenomena have been reported.^{9,10} The transmission coefficient T is also V -dependent. Stroscio et al.¹¹ have shown, however, that by using the quantity $(dI/dV)/(I/V)$ instead of dI/dV , a large part of the transmission coefficient factor is divided out.

A fundamental principle of modern physics is that a moving particle is associated with a wave (de Broglie wave) which has a wavelength λ given by $\lambda = h/p$, where p is the particle's momentum.¹² The momentum p can be written in terms of the wavenumber k as $p = \hbar k$. The tunneling phenomenon on which the STM itself is based is one of the manifestations of the wave nature of the electron. The barrier area corresponds to a region of imaginary index of refraction. In optics, such a situation is encountered in the process of total internal reflection of light, where, as in electron tunneling, an exponential penetration of the light wave from the more dense into the less dense medium is observed.¹² Here we use another characteristic of the wave nature of the electron, the ability to interfere with itself. We will show that it is possible to image with the STM the standing wave patterns that are produced by electron interference effects.^{13,14}

(8) Bardeen, J. *Phys. Rev. Lett.* **1961**, *6*, 57.

(9) Bedrossian, P.; Chen, D. M.; Mortensen, K.; Golovchenko, J. A. *Nature* **1989**, *342*, 258.

(10) Lyo, I.-W.; Avouris, Ph. *Science* **1989**, *245*, 1369.

(11) Stroscio, J. A.; Feenstra, R. M.; Fein, A. P. *Phys. Rev. Lett.* **1986**, *57*, 2579.

(12) See, for example: Bohm, D. *Quantum Theory*; Dover Publications: New York, 1989.

At certain faces of metal crystals, the surface electrons are confined to the surface region by the vacuum barrier (work function) on one side and by a band gap in the bulk states on the other side. The electrons in these so-called surface states are, however, delocalized in the surface plane, behaving very much like a two-dimensional (2D) free electron gas.¹⁵ This is, for example, the case for the (111) faces of the noble metals (Cu, Ag, Au).¹⁶ The energy of these surface electrons is given by

$$E = E_0 + \frac{\hbar^2 k_{\parallel}^2}{2m^*} \quad k_{\parallel} = (k_x^2 + k_y^2)^{1/2} \quad (3)$$

where k_{\parallel} is the wavenumber in the surface plane, k_x and k_y are its components, and E_0 is the onset of the surface-state band. The fact that the electrons are not truly free is accounted for through the use of an effective mass, m^* , which is different from the free electron mass.¹⁵ The electron waves can be scattered by features such as surface steps, other defects, and adsorbed atoms and molecules. Representing these obstacles as potential energy barriers, one would expect from elementary quantum mechanics that, depending on its energy and the characteristics of the barrier, an electron wave would be partially transmitted and partially reflected.¹² The reflected electron wave can interfere with the incident wave leading to oscillations in the LDOS of the surface. This is easy to show by further simplifying the problem to only one dimension, x . A plane wave, e^{ikx} , incident from the left on a barrier will be reflected with a reflection coefficient R , so that the wave function Ψ at the left side of the barrier becomes $\Psi = e^{ikx} + Re^{-ikx}$. Then $|\Psi|^2$ will be given by

$$|\Psi|^2 = 1 + |R|^2 + 2|R| \cos(2kx - \eta) \quad (4)$$

where η stands for the phase shift of the wave. Since $|\Psi|^2$ is related to the LDOS of the surface state band, we deduce from eq 4 that an oscillatory density of states will develop, which if sufficiently strong (i.e., if R is high) could be detected by STS or even directly in STM topographs. The LDOS oscillations predicted by the above one-dimensional model do not decay. However, for a given quantum state in two dimensions, k_x is not well defined (see eq 3); only the sum $k_x^2 + k_y^2$ is fixed. As a result, the LDOS oscillations should decay (at 0 K) away from the barrier as $1/(x)^{1/2}$.^{13,14}

Interaction of Surface Electrons with Steps. As an example of such an electron scattering process, we consider the interaction of surface electrons with a surface step. Steps are always present at surfaces and are usually active sites for atomic and molecular adsorption and chemistry.¹⁷ Specifically, we consider a Au(111) surface which has a well-studied surface state¹⁶ with an onset at ~ 0.4 eV below E_F . In Figure 1 (top) we show an STM image of this surface (sample bias -1 V). The image shows two terraces separated by a monoatomic step. No particular structure is observed

(13) Hasegawa, Y.; Avouris, Ph. *Phys. Rev. Lett.* **1993**, *71*, 1071. Avouris, Ph.; Lyo, I.-W.; Walkup, R. E.; Hasegawa, Y. *J. Vac. Sci. Technol.*, *B*, in press.

(14) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Nature* **1993**, *363*, 524.

(15) See, for example: Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Saunders: Philadelphia, 1976.

(16) Kevan, S. D.; Gaylord, R. H. *Phys. Rev. B* **1987**, *36*, 5809.

(17) Somorjai, G. *Chemistry in Two Dimensions*; Cornell University Press: Ithaca, 1981.

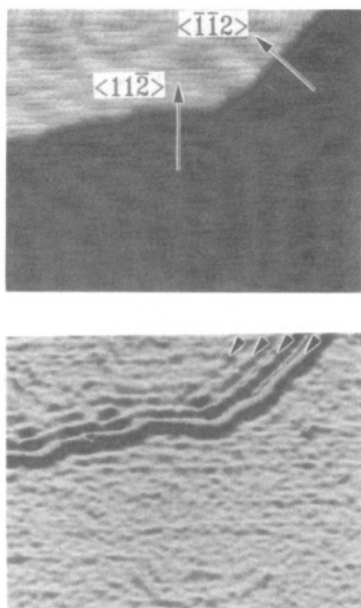


Figure 1. Top: STM topograph of a Au(111) surface showing two terraces (sample bias voltage = -1 V). Bottom: Spectroscopic image ($(dI/dV)/(I/V)$) at $V = 0.15$ V calculated from I - V curves obtained over the same area shown in the STM topograph.

on the terraces except for a weak corrugation (lines normal to the step) due to the intrinsic structure of the Au(111) surface.¹⁸ In addition to the topographic image, we have obtained I - V curves at 2-Å intervals over the same area and used them to generate spatial maps of the quantity $(dI/dV)/(I/V)$ at a given voltage V . Such a map for $V = 0.15$ V is shown in Figure 1 (bottom). In this picture, bright contrast indicates a large value of $(dI/dV)/(I/V)$. As we have pointed out earlier, the value of $(dI/dV)/(I/V)$ provides a rough measure of LDOS. Thus, the image of Figure 1 (bottom) corresponds to a map of the surface LDOS at an energy of ~ 0.15 eV above E_F . This image shows a high LDOS right at the step, which may be an indication of the presence of a localized step state. Most importantly, near the step on the upper terrace side, several bright lines running parallel to the step can now be seen; the LDOS oscillates near the step with a period of about 1.6 nm. These are the standing waves we predicted that will be generated due to the interference between the incident and reflected electron waves by the step.

Another way of displaying the data, which is more amenable to theoretical analysis, is to show the variation of the LDOS along a line normal to the step. This mode is usually referred to as an STM line scan. Line scans can be laterally averaged to further improve the signal-to-noise ratio. Figure 2 shows a set of line scans along a particular crystallographic direction ($\langle 11\bar{2} \rangle$ direction) of the Au(111) surface for a range of energies from 0.27 eV below E_F (bottom curve) to 0.42 eV above E_F (top). We see that the period of the waves becomes shorter with increasing energy (voltage). This is exactly the behavior expected from eq 3. The perturbation that the step exerts on the electronic structure of the surface is seen to extend more than 5 nm from the step. Moreover, as can be seen from Figure 1 (bottom), steps along different crystallographic directions lead to different oscillation amplitudes. Steps made of facets with high atomic density appear to reflect the electron

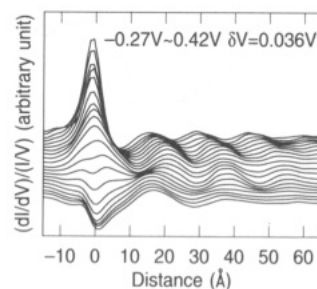


Figure 2. Laterally-averaged $(dI/dV)/(I/V)$ line scans normal to a step of the Au(111) surface for sample biases in the range -0.27 V (bottom curve) to 0.42 V (top curve).

waves more strongly than steps with more open structures. The oscillations are also much stronger on the upper terrace side of the steps (see Figure 1, bottom), indicating that the reflection coefficient depends on the direction of incidence on the step. This behavior is particularly interesting and can be explained in terms of mixing of the otherwise orthogonal bulk and surface states by the perturbation induced by the step. More quantitative information about the interactions involved can be obtained by fitting the data on the oscillations to the appropriate scattering models as discussed elsewhere.^{13,14}

Another important point involves the decay of the oscillations, which is faster than the $x^{-1/2}$ decay predicted for a 2D system at zero temperature (see above). This observation could, in principle, indicate the presence of additional scattering mechanism(s) which damp the oscillations produced by the interference process. Under the conditions of the experiments, however, the observed decay reflects the fact that the STM does not probe a single energy level, but instead it probes a set of states with an energy spread ΔE . This energy spread is determined by the bias conditions and the temperature. The width is largest for large negative sample bias where occupied states are probed, whereas the thermal width of dI/dV is about $3.5k_B T$.¹³ Corresponding to this ΔE spread is a wavenumber spread Δk_{\parallel} determined by the dispersion (E vs k_{\parallel} relation) of the surface state. The Δk_{\parallel} spread is responsible for the observed decay of the oscillations. From the uncertainty principle, the decay length is $l_c \sim 1/\Delta k_{\parallel}$. Thus, we conclude that the actual extent of the perturbation of the surface-state levels by the step is, in fact, longer-ranged than that given by an STS measurement (Figure 2). These long-range oscillations provide a mechanism for the long-range interaction between steps or between adsorbates and steps.

Observation of "Particle in a Box" States. In discussing the oscillations produced by scattering at steps, we have considered terraces with dimensions much larger than the coherence length of the electron waves. As the size of a terrace is decreased down to a few coherence lengths, one has to consider reflections from all boundaries. A more appropriate description of the surface electrons is that of particles confined in a box. Such confinement is encountered, for example, in the case of clusters of metal atoms, small metallic islands formed during metal-on-metal epitaxy,¹³ narrow terraces of stepped surfaces,¹⁹ or artificially made

(18) Hasegawa, Y.; Avouris, Ph. *Science* 1992, 253, 1763.

(19) Avouris, Ph.; Lyo, I.-W. *Science*, in press.

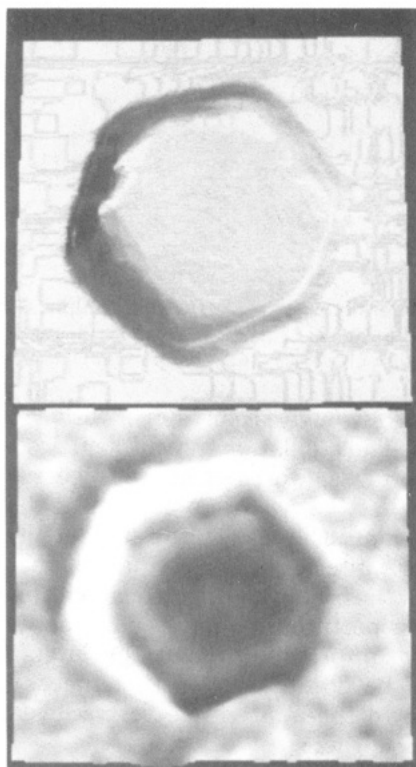


Figure 3. Top: STM topograph of a silver island ("radius" = 4.5 nm). Bottom: Spectroscopic (dI/dV) image of the same island at a sample bias of -0.01 V.

structures,²⁰ and it can lead to discrete atomic-like states. An example of a hexagonal ("radius" ≈ 4.5 nm) silver island grown on silver is shown in Figure 3.¹³ The top panel gives the topographic image, while the bottom shows the dI/dV image at -10 mV. The topographic image does not reveal any structure on the surface of the island, but the spectroscopic image shows clearly a wave structure that is encompassing the entire island. For simplicity, we can approximate the states of the surface electrons of the hexagonal island by the states of electrons in a circular box. The energies and wave functions of the box states are given by²¹

$$E_{n,l} = E_0 + \frac{\hbar^2 u_{n,l}^2}{2m^* a^2} \Psi_{n,l} \propto J_n\left(u_{n,l} \frac{r}{a}\right) \begin{Bmatrix} \cos \theta \\ \sin \theta \end{Bmatrix} \quad (5)$$

where J_n is the n th order Bessel function, $u_{n,l}$ is the l th root of this function, and a is the radius of the box. It is interesting to note the analogy of this problem to that of a vibrating circular membrane.²² The spatial distribution of the state density is analogous to the amplitude distribution of the "normal modes" of the membrane, and the island can be viewed as a nanometer-sized drum!

The spectral image of the island shown in Figure 3 (bottom) corresponds to an energy of about 110 meV above the bottom of the box, i.e., the onset of the surface state (E_0). It shows a nodal pattern characteristic of the $n = 0, l = 2$ box state. The central peak, however, is much weaker than it should be, indicating the presence of another state. Using eq 5 with values of E_0 and m^* from the literature,¹⁶ we find that there are two

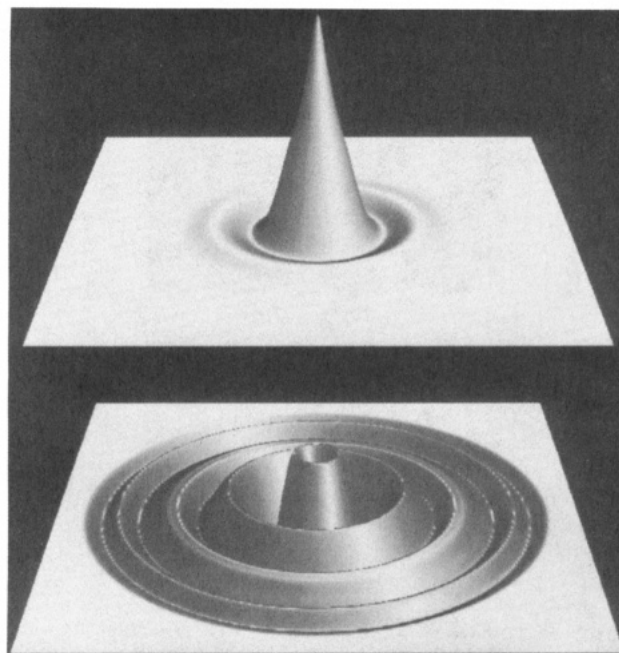


Figure 4. Rotationally-averaged spectroscopic images ($(dI/dV)/(I/V)$) of an adsorbed atom on Ag(111). Top: Occupied states (sample bias = -0.11 V). Bottom: Unoccupied states (sample bias = 0.38 V). The area shown is 18 nm \times 18 nm.

states with an energy of ~ 100 meV: the $n = 0, l = 2$ state (108 meV) and a doubly degenerate $n = 2, l = 1$ state (93 meV). These two states cannot be resolved at room temperature by STS. What we observe is a superposition of both state densities. A good fit is found for a mixture of about 80% of the (2,1) state and 20% of the (0,2) state.

Scattering by Individual Adsorbates. Let us now consider how the 2D electron gas interacts with adsorbed atoms. The "size" of an adsorbed atom is small compared to the wavelength of the surface-state electrons. For example, the wavelengths for Ag and Au surface electrons at their corresponding Fermi levels are 4.9 and 3.6 nm, respectively.¹⁶ Thus the atom cannot probe the detailed structure of the wave and so it scatters it isotropically. The scattered wave has the form of concentric rings, similar to those produced when a pebble is thrown into a pond. The scattering is weak, but the signal-to-noise ratio can be enhanced by performing rotational averaging and using the resulting line scans to regenerate the STS images. Figure 4 provides an example of this type of scattering.¹³ It shows the circular electron waves generated by an impurity (most likely a sulfur atom) on Ag(111). The top panel is a $(dI/dV)/(I/V)$ map of the occupied states ($V_s = -0.11$ V), whereas the bottom panel shows the unoccupied states ($V_s = 0.38$ V).

When a foreign atom is adsorbed on a metal, there is, in general, a transfer of electrons and the atom acquires a net charge. Friedel²³ has shown that the scattering of the metallic electrons by the atom can be considered as the screening process of this charge. The screening picture is very useful because it allows us to determine the charge state of the adsorbed atom. While, in general, it is not easy to discriminate between the intraadsorbate electronic distribution and the induced changes in the substrate LDOS, one may consider the region at the very center of the rings as representative of the adsorbate electronic structure.

(20) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *363*, 524.

(21) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448.

(22) Kauzmann, W. *Quantum Chemistry*; Academic Press: New York, 1957.

We see that there is a peak in the occupied states LDOS centered at the position of the atom (top panel), while there is a hole in the unoccupied states LDOS at the same position (bottom panel). The hole (minimum) in the unoccupied states is surrounded by a cone of increased density of unoccupied substrate levels, and as predicted,²³ further oscillations are seen as the distance increases. The above images appear compatible with an adsorbate that has a net negative charge. A negative species (note peak in occupied states of Figure 4) may not have any low-energy states left unoccupied (note hole in the adsorbate unoccupied states image) and will repel the substrate electrons leading to an increased density (note cone) of substrate unoccupied states surrounding the hole.

Atomic-Scale Manipulation of Surfaces

Tip-Sample Interactions. The interactions between the STM tip and the sample that are useful for surface modification can be grouped into two broad categories: (1) forces that act on the sample because of the close proximity of the tip, even in the absence of a tunneling current, and (2) effects caused by the electric field, the voltage difference, or the current flowing in the region of the tunnel junction. Examples from the first category include the formation of indentations, and uses of the tip to drag or push atoms or molecules along the sample surface. Within the second category are applications in which the STM tip is used to generate localized electric fields and thus induce a variety of processes, or as a localized electron beam for electronic excitation or heating.

Let us first consider the forces acting between tip and sample in the absence of an applied bias. When the STM tip is brought close enough to the sample for electron tunneling to occur (≤ 1 nm) forces develop that act on the tip-sample system. At relatively large distances, $d \gtrsim 0.5$ nm, and in a vacuum environment, these forces are dominated by attractive van der Waals interactions. In spite of their small magnitude, van der Waals forces can play an important role in materials manipulation. For example, van der Waals attraction may be sufficient to allow an atom or molecule that is weakly bound to the sample to slide along the surface and stay directly under the STM tip. This "sliding" mechanism has been demonstrated by arranging Xe atoms to form a variety of structures on metal surfaces at low temperature.²⁴ As the distance between the tip and sample is decreased, much stronger forces develop between them. These forces involve chemical interactions between the tip atoms and the sample atoms that they contact. If the sample and tip atoms have a strong cohesive interaction, then new bonds will be formed when the tip is brought close to the surface.

The STM is also capable of generating electric fields on the order of ~ 10 V/nm usually by applying voltage pulses while keeping the tip-sample distance fixed. Such fields are comparable to the fields inside atoms and molecules; thus they can be used to induce chemical modifications of surfaces. In such strong electric fields, field desorption or field evaporation of atomic and molecular ions can occur. These processes result in

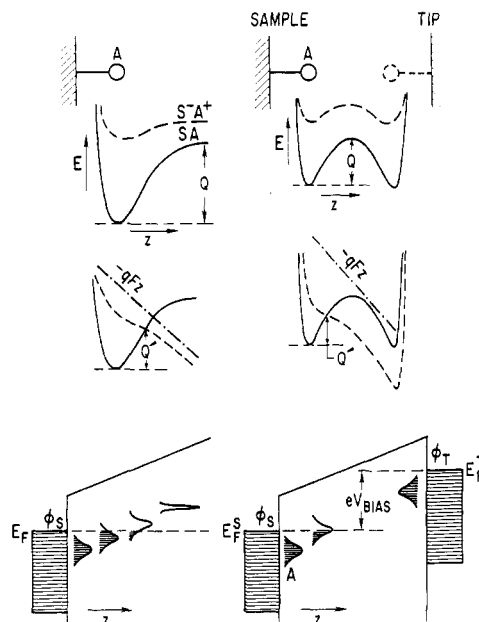


Figure 5. Schematic diagram illustrating the mechanism and energetics of the field evaporation/desorption process in the field-ion microscope (left column) and of the chemically-assisted field evaporation/desorption process in the STM (right column).

the transfer of atoms from the sample to the tip, or in the reverse direction. Similar processes have been extensively studied with the field ion microscope (FIM).²⁵

Chemically-Assisted Field Evaporation/Desorption. A particularly valuable process for the modification of materials and the fabrication of nanostructures involves the ability to zoom in on a particular location on the surface, break strong chemical bonds, transfer one atom or a cluster of atoms to the STM tip, and then perhaps redeposit the atom(s) at another location. A general scheme involving a combination of chemical and electric field effects has been proposed to accomplish this task.²⁶ Mechanistically, the process involved can be described as a chemically-assisted field evaporation process (CAFE).²⁶ The basic principles of this process can be explained by reference to the diagram shown in Figure 5. The left column of the diagram illustrates the field desorption of an adsorbate A from a substrate S, under conditions pertaining to the FIM, while the right column illustrates the transfer of A from sample to tip in an STM experiment. In the FIM, the energy required to desorb a neutral A atom is Q . Above the neutral ground state are ionic states, such as the $S-A^+$ state which upon application of an electric field F is lowered in energy by qFz (q is the charge of the desorbing atom) and crosses the neutral curve so that the barrier for field desorption of A^+ is now only Q' (see middle left panel). In terms of the electronic structure of the system (see bottom panel), a molecular orbital involved in the adsorbate-substrate bonding lying originally below E_F is gradually emptied as atom A moves in the field and acquires a positive charge (bottom left panel).

Let us now consider the STM case (right column of Figure 5). The main difference between field evapora-

(23) Friedel, J. *Phil. Mag. Suppl.* 1954, 3, 446; *Nuovo Cimento, Suppl.* 1958, 7, 287.

(24) Eigler, D. M.; Schweizer, E. K. *Nature* 1990, 344, 524.

(25) Tsong, T. T. *Atom-Probe Field Ion Microscopy*; Cambridge University Press: Cambridge, 1990.

(26) Lyo, I.-W.; Avouris, Ph. *Science* 1991, 253, 173. Avouris, Ph.; Lyo, I.-W. *Appl. Surf. Sci.* 1992, 60/61, 426. Avouris, Ph.; et al. *J. Vac. Sci. Technol., A* 1993, 11, 1725.

tion/desorption in the STM compared to that in FIM is the introduction of a second potential energy well due to the presence of the STM tip.^{27,28} The energy barrier Q for transfer of A from sample to tip is a function of the sample–tip distance. As this distance decreases, the barrier decreases drastically.²⁹ The application of an electric field F further reduces the barrier and can introduce directionality in the atom-transfer process.^{26,29,30} It is important to note that the electric field produced by the application of a voltage bias varies rather slowly over many atomic sites of the sample. Thus, if one wants to induce the transfer of a specific atom, a chemical tip–sample interaction is essential to selectively weaken the bonding to the substrate of the chosen atom or atoms, which are then transferred to the tip by the action of the electric field. Finally, as is illustrated in the bottom right panel, unlike in the FIM, the charge state of the transferred species A changes in a nonmonotonic manner because in the vicinity of the tip the emptying orbital begins to be filled again.

We first consider surface modification on the nanometer spatial scale. Figure 6 shows an example of the modification of the Si(111) surface. Panel A shows the modification generated when a tungsten tip is brought to 0.3 nm from the surface and a 3-V pulse is applied to the sample. This process leads to a surface modification with a characteristic morphology composed of a central hillock surrounded by a depression. In a second step, the cluster of atoms forming the hillock is transferred to the tip by placing the tip over the hillock and applying a second 3-V pulse. The cluster is then redeposited to the left of the hole by applying a -3 -V voltage pulse. The characteristic morphology of the modified surface (i.e., the hillock surrounded by a depression) is primarily due to the fact that the voltage pulse generates a field gradient.³¹ Si atoms move towards the apex of the tip, thus bridging the tunnel gap and connecting the tip to the sample. When the tip is retracted after the voltage pulse, this bridge breaks, leaving behind a central hill.

Let us now consider manipulation on the atomic scale. As we discussed above, in order to remove a particular surface atom, its bonding to the substrate is preferentially weakened by interaction with the tip, and its transfer completed by the application of a voltage pulse. In Figure 7 we show a series of atomic-scale modifications of the Si(111)- 7×7 surface. The tip–sample distance during manipulation is only about 0.1 nm from electronic contact,²⁶ and the voltage pulse is 1 V. Panel A shows a section of the Si surface. This top layer is usually called the Si adatom layer, and the adatoms are separated in two groups. Adatoms situated next to the corner vacancies (see dark sites) are referred to as corner adatoms, while the rest are called center adatoms. The unit cell outlined contains a defect in the lower right which is used as a marker. In panel B a voltage pulse was applied while the tip was centered over the site indicated by the arrow and has led to the

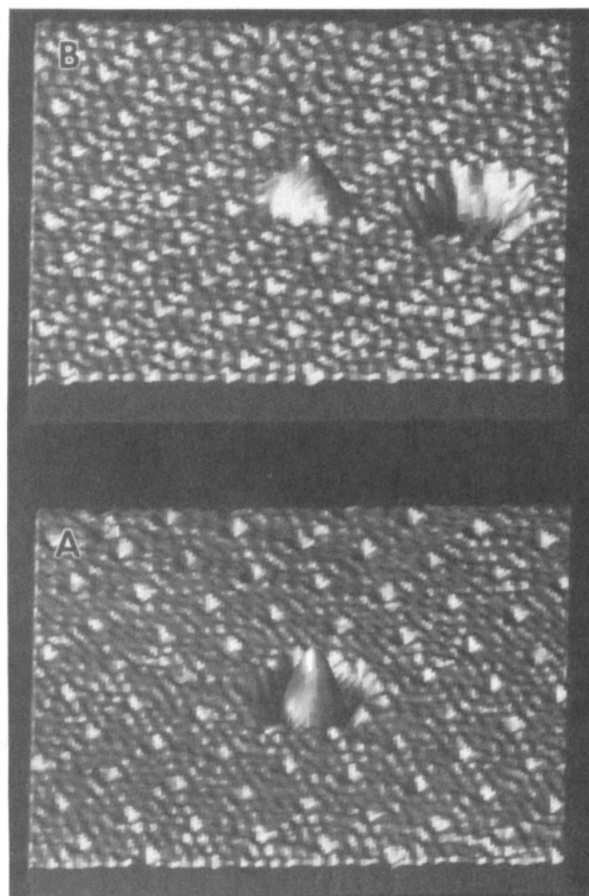


Figure 6. Nanoscale modification of Si(111). (A) A 3-V pulse applied to the sample, at a sample–tip distance of ~ 0.3 nm from electronic contact, leads to the formation of a structure involving a hillock surrounded by a depression. (B) A second 3-V pulse applied with the tip centered over the hillock leads to its transfer to the tip. The tip is then moved to the left of the hole and the cluster is redeposited by applying a -3 -V pulse.

removal of three Si atoms, leaving a fourth under the apex of the tip. This fourth atom is the atomic-scale analogue of the hillock left behind in Figure 6A. This Si atom was in an unstable configuration, and under the influence of the tip it migrated to the left to occupy a center-adatom site of the 7×7 lattice (panel C). This atom was then removed by centering the tip over it and applying a second pulse (panel D). Finally, a neighboring corner adatom was removed (panel E). One question that arises is, Can the STM undo a modification, e.g., can it put back a removed atom or cluster of atoms and re-form the original structure? We find that, for Si in general and especially for larger clusters at room temperature, it is not feasible to do so. The redeposited atoms must overcome an activation barrier to occupy their original sites. However, as panel F shows, in the case of single atom removal, incorporation occasionally can be achieved by bringing the tip over the vacancy site and applying a negative pulse. If, instead of using the CAFE approach as in the above example, one were to apply a large voltage pulse at the normal tip–sample distance used in imaging, then the selectivity of the atom-extraction process would be lost. Under these conditions, other considerations, such as the strength of the bonds holding the atom on the surface, determine which atom will be extracted. In the case of the Si(111)- 7×7 surface, the probability of

(27) Mamin, H. J.; Guether, P. H.; Rugar, D. *Phys. Rev. Lett.* **1990**, *65*, 2418.

(28) Lyo, I.-W.; Avouris, Ph. *J. Chem. Phys.* **1990**, *93*, 4479.

(29) Lang, N. D. *Phys. Rev. B* **1992**, *45*, 13599.

(30) Walkup, R. E.; Newns, D. M.; Avouris, Ph. *Phys. Rev. B* **1993**, *48*, 1858.

(31) Whitman, L. J.; Stroscio, J. A.; Dragoset, R. A.; Celotta, R. J. *Science* **1991**, *251*, 1206.

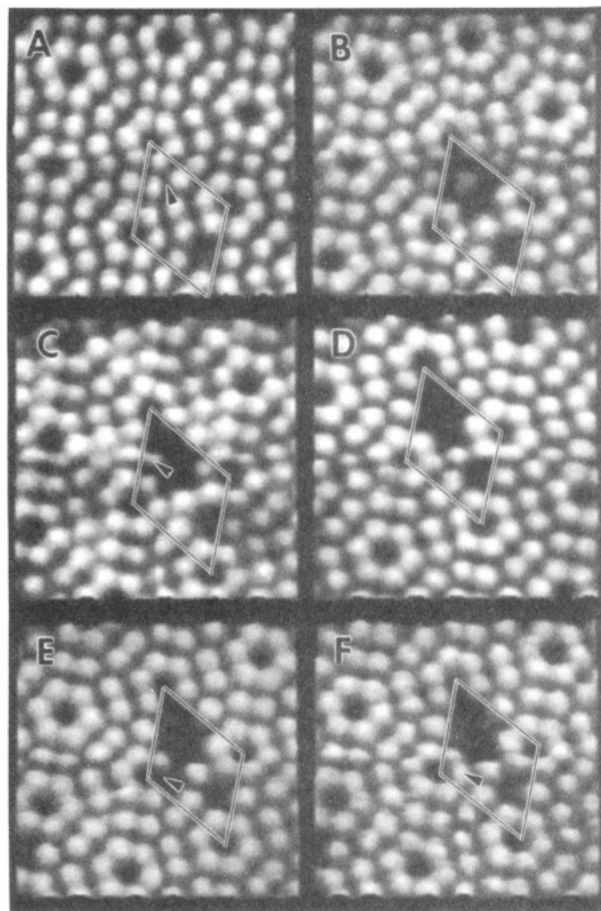


Figure 7. A series of atomic-scale manipulations. (A) The tip is placed at ~ 0.1 nm from electronic contact over the site indicated by the arrow. (B) A 1-V pulse removes three atoms, leaving the fourth under the tip. (C) The first attempt to remove this atom leads to its migrating to the left (see arrow) and bonding as a center adatom. (D) A second pulse removes this fourth atom. (E) A new pulse over the adjacent corner adatom removes this atom, and then (F) this adatom is placed back in its original position.

extracting a center adatom is 1.5 times higher than that of extracting a corner adatom.³²

From the above examples, it is clear that even strongly-bonded materials such as Si can be manipulated on the atomic scale using the CAFE approach. It must be pointed out, however, that currently these manipulations cannot be performed routinely. The main limitation is the structure of the tip, which is largely unknown and difficult to reproduce. There are presently several research efforts in tip "engineering" and functionalization, and hopefully, this problem will soon be overcome. Finally, we should note that while the above results indicate that the area of the surface affected is determined by the area of direct interaction with the tip and the high electric field, this may not be generally true. The Si(111)- 7×7 surface has a very open

(32) Kobayashi, A.; Grey, F.; Uchida, H.; Huang, D.-H.; Aono, M. In ref 6.

structure with little direct interaction between the top layer atoms. In general, however, surface atoms are elastically coupled to each other so that a perturbation at a certain location on the surface is felt by atoms away from that point and could lead to large-scale atomic rearrangements. This behavior has been observed in the manipulation of the Au(111) surface.¹⁸

Conclusions and Prospects

In this Account we discussed two new applications of STM. First we demonstrated that STM/STS can image the standing waves formed by the scattering of surface electrons by steps and adsorbed atoms. The STS images of the standing waves generated provide a striking real-space view of the wave properties of electrons in solids. The electron oscillations are found to extend up to ~ 10 nm from the scattering center. These long-range density oscillations can provide a mechanism for adsorbate-adsorbate and adsorbate-step interactions over large distances.³³ Such interactions may influence the spatial distribution of adsorbates on surfaces and crystal growth processes. The detailed structure (phase shifts) and energy dependence of the oscillations generated by an adsorbed atom is determined by the net charge on the atom.²³ Determination of this charge provides valuable information on the nature of the chemisorption bond. The interference oscillations can possibly be used to distinguish between adsorbed species, currently a major limitation of the STM. The 2D electron gas can also be used to probe the energy states of the adsorbate. These states ("resonances") can be revealed in plots of the phase shifts of the circular waves as a function of energy. The probability distributions of the confined ("particle in a box") electron states of small metal particles and narrow terraces can also be imaged with the help of spectroscopic maps. Such studies can, for example, provide information on the role of the shape and size of the particle and of adsorbates on its surface charge distribution and reactivity.

We have also discussed an approach involving a chemically-assisted field evaporation/desorption process for the atomic-scale modification and manipulation of materials. We have shown that strong covalent bonds can be broken at preselected sites of a surface and individual atoms or clusters of atoms manipulated. This is a unique capability that will undoubtedly have important chemical applications. Atomic manipulation allows the generation of artificial, atomic-scale structures with unique chemical and physical properties. Furthermore, the study of such specially designed structures can provide new insights into interatomic interactions.

I am greatly indebted to my co-workers Yukio Hasegawa, In-Whan Lyo, and Robert E. Walkup for their contributions.

(33) Lau, K. H.; Kohn, W. *Surf. Sci.* 1978, 75, 69.