Manipulation of Matter at the Atomic and Molecular Levels

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Introduction

The concept of the atom as the fundamental component of matter was first proposed by the Greek philosopher Leucippus and further developed by his student Democritus in the 5th century B.C. The concept of the molecule as a distinct group of atoms is believed to have been introduced by Asklepiades of Prusa at about 100 B.C.[1] With few exceptions, these precocious Greeks and their ideas were largely forgotten, until atomism was revived in the 1600s by Newton, Bernoulli, and others. Later, Dalton (1803) used the atomic theory to construct a conceptual basis for chemistry. By the beginning of the 20th century, the basic constituents of the atom—the electron and the nucleus—were discovered. This was followed by the development of quantum mechanics, so that by 1930 the theoretical description of the behavior of atoms and electrons was essentially complete. Nevertheless, atoms remained beyond the realm of the senses, and the reality of an individual isolated atom or electron was challenged even by pioneers of quantum theory. As recently as 1952, Erwin Schrödinger wrote:[2] "We never experiment with just one electron or atom or molecule. In thought-experiments we sometimes assume that we do; this invariably entails ridiculous consequences", further adding that "we are not experimenting with single particles, any more than we can raise ichthyosauria in the zoo." Others were more optimistic and saw great scientific and technological opportunities if one could experiment with individual atoms and molecules. In 1960, Richard Feynman in a prophetic article on miniaturization wrote:[3] "...I am not afraid to consider the final question as to whether, ultimately—in the great future—we can arrange the atoms the way we want: the very atoms, all the way down!" Feynman asserted that "the principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom" and concluded that "the problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level is ultimately developed."

The "far future" of Feynman began to be realized in the 1980s. Some of the capabilities he dreamed of have been demonstrated, while others are being developed. Although we are still far from having a general and reliable "atomic technology", progress in the last 15 years or so has been tremendous. Here we describe some of these developments, starting with

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the isolation and manipulation of individual atoms. We then concentrate on atomic and molecular manipulation using the powerful scanning proximal probe techniques, such as the scanning tunneling microscope.

Manipulation of Isolated Atoms and Molecules

The first particle to be isolated and manipulated was the electron. In 1976 Dehmelt and his co-workers at the University of Washington succeeded in trapping a single electron[4] and later a positron[5] in a Penning trap (a combination of electric and magnetic fields) and kept them isolated for months. Pauli traps subsequently were used to trap other charged species such as atomic ions. In 1986 Dehmelt and co-workers[6] and Wineland and co-workers[7] trapped single Ba^+ and Hg^+ ions, respectively. Moreover, by pumping the ions to electronically excited states it was possible to photograph them using their own fluorescence!

Neutral atoms and molecules have also been trapped and manipulated in a variety of different trapping devices. All of these traps act by strongly perturbing, via electric and/or magnetic fields, the energy levels of the atoms or molecules in a spatially-dependent manner. Unlike charged species, however, neutral species involve very weak trapping energies. For example, the confining well depth for an atom with a magnetic moment of 1 μ_B and a trap with 2 T field variation corresponds to a temperature of only ~1 K. Similarly, small trapping well depths are generated by laser traps. Thus, trapping and manipulation of neutral atoms requires that the atoms first be cooled to ultralow temperatures in the millikelvin range. These and even lower temperatures have been achieved by laser cooling.[8,9]

There are two types of forces that light can exert on an atom which can be used in cooling and manipulation: a "dipole force" is produced when light with a frequency near an electronic transition is used. The light field polarizes the atom to produce a dipole **p** which interacts with the gradient of the electromagnetic field. The second interaction, the so-called "scattering force", involves incoherent photon absorption and emission processes. When an atom absorbs

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a photon of wavelength λ, and therefore of momentum $p = h/\lambda$, it receives a momentum impulse along the direction of the incident photon. When the excited atom emits a photon, it receives an impulse opposite to the direction of the emitted photon. However, since there is no preferred direction for the emission process, the net average velocity change for the atom per scattered photon, Δv, is opposite the direction of the incident photon with $\Delta v \sim h/\lambda M$, where M is the mass of the atom. The validity of this approach was demonstrated in 1985 by two groups at the National Bureau of Standards Laboratories,[10] which were able to cool an atomic beam of Na initially at ~ 300 K to $50-100$ mK by irradiating it with a laser beam propagating in the opposite direction. Significantly lower temperatures were achieved by Chu and co-workers[11] using two counterpropagating laser beams. Since then, new cooling mechanisms have been demonstrated,[12] and it is now possible to cool atoms to temperatures below 10^{-6} K! Such cold atoms can then easily be trapped and manipulated.

The simplest way to manipulate a precooled neutral atom or molecule involves the dipole force produced by a single focused laser beam tuned to a frequency just below an electronic transition. If $\mathbf{p}$ is the induced dipole, its energy in the laser field E is $W = -\mathbf{p} \cdot \mathbf{E}$. When the dipole is in the same direction as the field, the energy will be minimized by moving the atom into the high-intensity focal spot of the laser beam. When the focal spot is moved, the cooled atom follows it. When, instead of atoms, larger particles ranging from ~ 10 μm to ~ 20 nm are considered, the induced polarization force can be large enough to allow manipulation at room temperature and even in water solution. With this approach, dubbed "optical tweezers", one can manipulate effectively and without damage individual bacteria and objects within a living cell such as organelles or filaments of protoplasm.[13,14] Biomolecules which are too small to be manipulated directly at room temperature have been manipulated by attachment of appropriate polarizable "handles" to them. As an example, DNA was attached to a polarizable polystyrene sphere and also stained with a fluorescent dye. In this way, the DNA molecule could be manipulated by the laser beam and imaged by its own fluorescence.[15]

We also note here that, in addition to the physical manipulation of individual atoms, their excited state dynamics can be modified by their being placed in very small cavities with reflecting walls. These cavities constrain the wavelengths of the photons that can be absorbed or emitted and, thus, the transitions that the atom or molecule can undergo. Using this approach, so-called "cavity quantum electrodynamics", one can slow down spontaneous transitions, halt them, accelerate them, or even reverse them entirely.[16,17]

Atom and Molecule Manipulation in the Condensed Phase

In parallel with the development of techniques for trapping and manipulating individual atoms in isolation, work has proceeded on atomic imaging and manipulation in the condensed phase, primarily at solid surfaces. In the condensed phase, although the atoms are not isolated, one can image the surface of a solid with atomic resolution and individual atoms can be selected and manipulated. Since the manipulated atoms are bonded to some extent to a substrate, the structures formed by manipulation are relatively stable and the ultralow temperatures required for the trapping and manipulation of isolated atoms are not, in general, needed. The relative stability of atomic structures in the condensed phase, compared to the gas phase, has raised prospects for the development of atomic and nanometer technologies, involving, for example, atomic scale electronic devices.

An essential requirement for the successful control of materials on the atomic scale is the ability to observe and manipulate them at the same time. Conventional optical microscopy is certainly not an atomic imaging technique. Recently, however, great improvements in resolution were brought about by the exploitation of near-field optics.[18] In conventional microscopy, interference and diffraction lead to a resolution limit of about $\lambda/2$. If an object smaller than $\lambda/2$ emits light, its details are lost after the light travels a distance of the order of λ. This limit can be bypassed by use of a light source of dimensions smaller than λ and placement of the sample very close (tens of nanometers away) to it, i.e., in the near field. Traveling over such short distances, the light has no opportunity to diffract and take on its asymptotic far-field characteristics.[18] A number of different experimental arrangements are now being utilized to perform near-field optical microscopy, and the results are very encouraging. Betzig and Chichester[19] were the first to image isolated dye molecules with a resolution of 50 nm. Spectra[20,21] of individual molecules and lifetimes[22] have also been obtained. There is every expectation that the resolution of near-field microscopy can be improved significantly and could be used for molecular modification, for example, by performing "near-field photochemistry".

The first true atomic resolution images of solids were produced by Müller using the field ion microscope (FIM)[23] which he invented. A certain type of atomic manipulation, i.e., atom desorption, is in fact possible in the FIM and forms the basis of the atom-probe FIM.[24] However, the limitations on the nature (primarily refractory metals) and shape (sharp tip) of the sample limit the applications of this technique.

Proximal Probe Imaging and Manipulation Techniques

Of all the different approaches to atomic and molecular manipulation, scanning proximal probes offer,

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so far, the simplest and most general approach. One important advantage is that manipulation and atomic resolution imaging can be performed using the same apparatus. Thus, one is able to image the surface of a material, zoom in on a particular feature of interest, induce an atomic scale modification, and then image and study the properties of the new structure.

The first scanning proximal probe technique, the scanning tunneling microscope (STM), was developed by Binnig and Rohrer[25] in 1982, followed soon after by the atomic force microscope (AFM)[26] and a score of other variants.[27] 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 piezo-electric transducers. When the gap between tip and sample is ≤1 nm, the wave functions of the tip and sample overlap and electrons can tunnel through the gap. The application of a voltage bias between tip and sample leads to the flow of a tunneling current. The ability of the STM to image surface topography with atomic resolution is based on the fact that this tunneling current is a very sensitive, exponential function of the tip—sample distance. For typical values of work functions, ~4 eV, the current changes by almost an order of magnitude for a change in tip—sample distance of only 1 Å. 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.

The most common mode of operation of the STM is to obtain constant current images of surfaces. As Tersoff and Hamann showed,[28] such images have, provided certain conditions are fulfilled, a simple physical interpretation: they represent surfaces of constant local density of states, LDOS (r,E). Note that we use density of states to describe the electronic structure because we are dealing with solids which have continuous spectra. The measurement is local in that it refers to a specific location on the surface determined by the position of the tip, r, and also at a specific energy, E, determined by the applied bias. By placement of the tip over a feature of interest and measurement of the current as a function of bias, local electronic spectroscopy can be performed with atomic resolution.[29] As an example of STM imaging we show in Figure 1 images of naphthalene molecules adsorbed at 300 K on a Pt(111) surface along with the shapes of the relevant molecular orbitals and calculated densities of states.[30]

As is true for most other imaging techniques, there are interactions between the sample and the probe (STM tip). These interactions are 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 different physical or chemical interaction mechanisms through which tip and sample interact, select the appropriate interaction, control its magnitude and location, and use it to bring about the
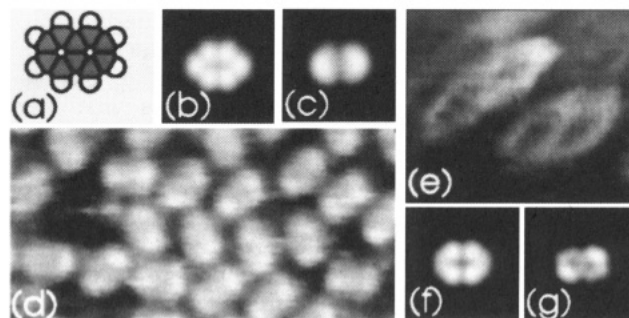

Figure 1. Naphthalene molecules on Pt(111). (a) Schematic of isolated molecule. (b) Lowest unoccupied orbital (LUMO) of the isolated molecule, 2 Å above molecular plane. (c) Logarithm of the unoccupied state density, ϱ_H, at 2 Å. This density was obtained by integrating the calculated unoccupied density of the adsorbate—substrate complex within 1 eV of the Fermi energy, and convoluting with a 1 Å wide Gaussian to simulate the effect of a finite radius tip. (d) Low-resolution STM image; the molecular van der Waals length is 8.1 Å. (e) High-resolution STM image. (f) LUMO for isolated molecule, 0.5 Å above molecular plane. (g) ϱ_H at 0.5 Å above molecular plane. Reprinted with permission from ref 30. Copyright 1993 American Institute of Physics.

desired atomic or molecular modification/manipulation.[31,32] The tip—sample interactions that can be used for this purpose can be grouped in two broad categories: (A) forces that act on the sample because of the proximity of the tip even in the absence of a voltage bias and tunneling current, as in the case of AFM experiments, and (B) effects caused by the electric field generated between tip and sample by the bias voltage, or the current flowing through the gap region. Yet another application of the STM involves the use of one or more of the above types of sample perturbations as a way to control the spatial distribution of thermal surface reactions.

(a) Forces between Tip and Sample and Atomic Manipulation. When the tip is at a typical tunneling position, i.e., ~0.5—1 nm away from the sample, in a vacuum environment, the forces acting on the sample are long-ranged van der Waals forces. Their magnitude at these distances is typically of the order of 10^{-10} N. When the tip approaches closer to the sample, stronger chemical interactions come into play. At even closer distances, strong repulsive forces develop. At contact, the attractive forces balance the repulsive forces, leading to large local stresses which can cause local damage and modification of the material. For example, using the AFM, Hansma and co-workers were able to image and cut DNA molecules.[33] Similarly, Lieber and co-workers[34] used the AFM to cut sections of thin oxide layers.

The forces, even the weak van der Waals force, between tip and sample can be controlled and used to move atoms or molecules laterally on a surface. This process is usually referred to as "atom sliding". The energy barriers to lateral motion depend on the nature of the surface and of the adsorption bond. Metal surfaces are rather smooth, and the adsorption bonds are not very directional. As a result, the diffusional

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barriers are low, typically 5–20% of the energy of the adsorption bond.[35] At semiconductor surfaces, on the other hand, adsorption bonds are strong and directional, so that for semiconductor surfaces with open structures, such as the much studied Si(111)-7×7 surface, the barriers for diffusion are of comparable magnitude to the binding energy. Indeed, early experiments on Si(111)-7×7 showed that the tip can induce the desorption and lateral displacement of adsorbates with comparable probabilities.[36] Metals, however, offer a much better substrate for performing atom sliding. This capability was demonstrated in an elegant experiment by Eigler and Schweizer,[37] who were able to arrange Xe atoms in a variety of patterns on a Ni(110) surface. Xe is weakly adsorbed on Ni-(110), with a binding energy ∼250 meV, while the energy barrier for diffusion along the close-packed direction is only ∼20 meV. So in order to maintain a given arrangement of Xe atoms on the surface, the experiment was performed at 4 K.

The mechanism by which the Xe atoms can be moved is illustrated by the potential energy curves shown in Figure 2.[38] The top panel shows the atomic arrangement for tip and sample used in the calculations. Figure 2B shows the energy as a function of the distance normal to the surface for Xe on Ni(110), at a sequence of tip–sample separations, while Figure 2C shows the potential energy as a function of the lateral displacement of Xe in the absence and presence of the tip. When the tip is far away, the Xe atom experiences a weakly corrugated potential in the close-packed direction. When the tip is lowered (tip–sample distance of 4.3 Å), a deep van der Waals minimum develops which confines the Xe atom to the region under the tip. If the tip is moved parallel to the surface without the tip–sample distance being changed, the Xe atom will follow. When the desired location on the surface is reached, the tip is withdrawn, leaving the Xe atom in that position. We can call this arrangement for atom/molecule sliding a "van der Waals atom trap". The same scheme but with smaller tip–sample distances can be used to move more strongly adsorbed (chemisorbed) species such as metal atoms or molecules on a metal surface. A nice demonstration of this capability by Crommie et al.[39] is given in Figure 3, which shows an arrangement of 48 individual Fe atoms produced by atom-sliding on a Cu(111) surface at 4 K so that they form a circle with a diameter of ∼142 Å. The picture also shows that this circle of Fe atoms encloses circular waves. These are electron standing waves produced when the surface electrons are reflected by the Fe atoms and interfere with themselves. The same phenomena are observed in other confining structures such as narrow terraces and metal islands[40] and provide a striking demonstration of the wave–particle nature of the electron.

Besides the assembly of weakly interacting units, one can imagine using the atom/molecule sliding process to bring together species that would react chemically. A first attempt in this direction involved bringing together a chemisorbed oxygen atom and a CO molecule in the hope of forming a CO_2 molecule.[41]
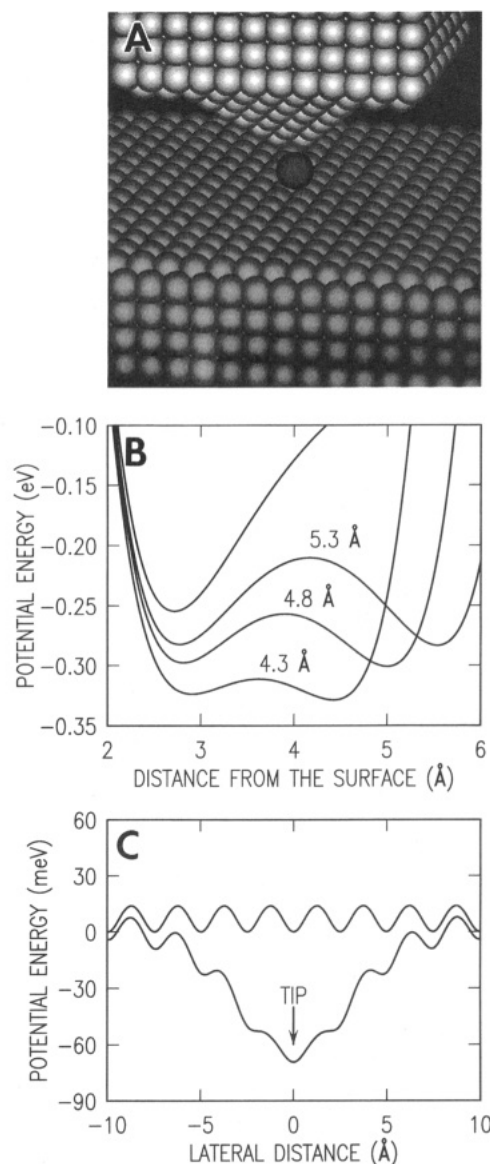

Figure 2. Potential energy curves illustrating the van der Waals interaction between a xenon atom and an STM tip. (A) Atomic arrangement of the tip and sample used in the evaluation of the potential energy curves. (B) The energy as a function of distance normal to the surface for xenon adsorbed on nickel(110), with a sequence of tip–sample separations. (C) The potential energy as a function of lateral displacement. From ref 38.

However, the low temperature (4 K) used to immobilize the adsorbates also prevented the reaction from taking place. It is clear that the sliding process at low temperature must be coupled with a local activation process in studies of chemical reactions. In section c we will discuss possible activation mechanisms.

(b) Electric-Field-Induced Manipulation. The application of a bias voltage between the STM tip and the sample generates an electric field, which can also be used for atomic and molecular manipulation and for inducing novel chemistry. As in the case of isolated atoms, for an electrically neutral adsorbate, the dominant field-dependent forces arise from the polarizability and dipole moment. Thus, the potential energy of an adsorbate with a polarizability α and a dipole moment $\mathbf{p}$ is modified in the presence of a field E by an amount $W_{E(r)} = -\mathbf{p}\cdot\mathbf{E} - (1/2)\alpha E(r)^2$. If, as in the

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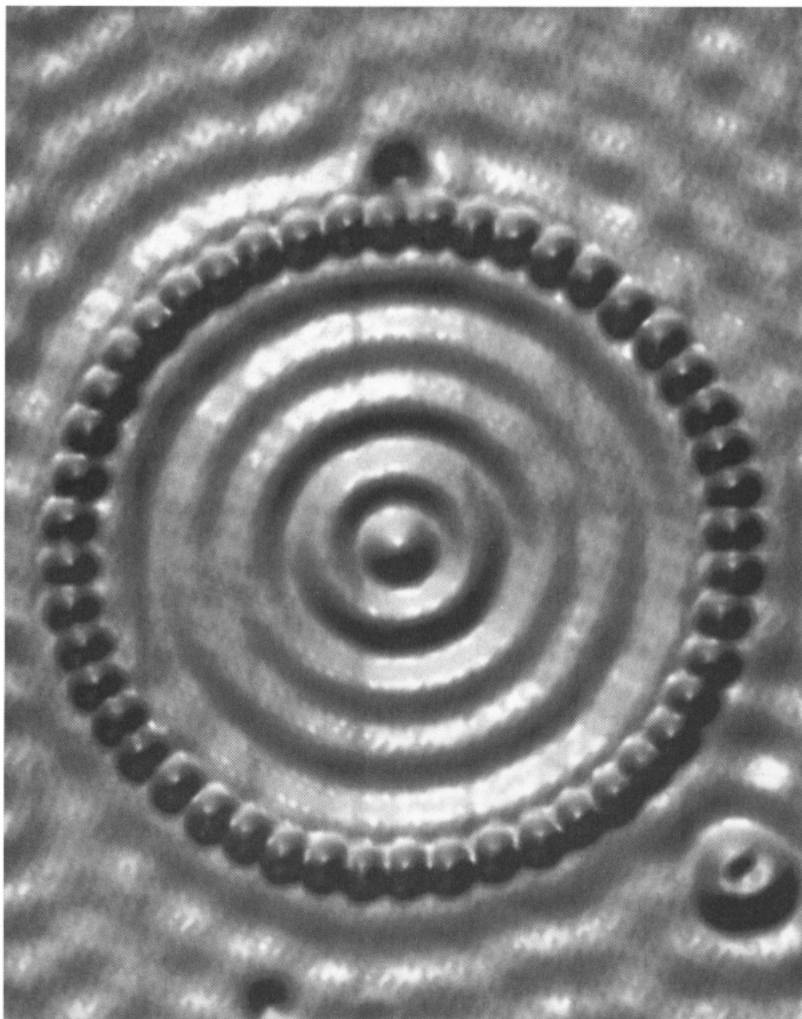(41) Eigler, D. M. Unpublished results.

Figure 3. STM image of the confined electron states of a "quantum corral". The corral was formed by arranging with the STM tip 48 iron atoms to form a ring with an average diameter of 143 Å. The sample temperature was 4 K, the sample bias voltage 0.01 V, and the current 1.0 nA. Reprinted with permission from ref 39. Copyright 1993 American Association for the Advancement of Science.

case of STM, the field is nonuniform, the adsorbate will experience a potential energy gradient, i.e., a force. If the polarizability term dominates, the adsorbate will move toward the region of maximum field strength, i.e., underneath the apex of the tip. When the dipole term dominates, the direction of movement can be controlled by the direction of the E field (polarity of the voltage bias). Thus, an electrostatic adsorbate trap is formed, and the adsorbate can be moved by controlling the tip motion. The electric field present in an STM experiment can be quite high, $\sim 10^7$ V/cm, and this leads to sizable trapping well depths. For example, for a Cs atom on a GaAs sample and a field of 10^7 V/cm, the well depth is ~ 0.1 eV. Whitman et al.[42] have in fact been able to manipulate Cs atoms on GaAs using the electric field of the STM. In comparing the electrostatic STM trap with the van der Waals or chemical traps we note that its resolution is somewhat lower due to the fact that the field strength drops rather slowly with the distance from the apex of the tip.[43]

Even higher fields of the order of 10^8 V/cm can easily be generated in the STM by applying voltage pulses while maintaining the small tip–sample distance.

Such fields are comparable to those experienced by valence electrons in atoms and molecules. In the STM they could lead to a redistribution of electrons among the orbitals of the sample, resulting in changes in bonding and chemistry. Whether bonding is enhanced or diminished depends on whether bonding or antibonding orbitals are mostly affected. For adsorbed species, there may be charge transfer between the adsorbate and the substrate or intra-adsorbate changes. By removing charge from the orbital involved in the chemisorption bond, one can break this bond and induce the desorption of the adsorbate (see below). Conversely, if the field increases the occupation of a bonding orbital, field-enhanced adsorption can take place. Even the most inert of all atoms, He, can be chemisorbed on a metal surface at fields of about 5×10^8/cm.[44] At such fields, excited states of He are populated by electrons from the metal.[44] If the field induces charge transfer to intra-adsorbate antibonding orbitals of an adsorbed molecule, field-induced dissociation may take place. For example, NO adsorbs molecularly on Pt at room temperature, but enhanced charge transfer to the $2\pi^*$ level at a field of about 0.4×10^8/cm is known to lead to dissociation.[45] Dissociation of Sb_4 molecules on Si and manipulation of the

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resulting Sb_2 dimers by a mechanism that apparently involves the electric field of the STM was reported recently.[46]

In the previous section we saw how van der Waals and chemical forces can be used to transport laterally (slide) atoms and molecules on "metal" surfaces. The electric field in the STM allows a different type of transport, vertical transport, in which adsorbed or substrate atoms are removed and transferred to the STM tip. The STM tip, under computer control, can then deliver the transferred atoms to another location and, at least in principle, redeposit them there. The transfer of the atom(s) to the tip involves breaking the bonds to the substrate, a process that requires significant activation. The process by which the transfer can be achieved involves field desorption (for adsorbed species) or field evaporation (for substrate atoms).[24] Field desorption and evaporation have been studied extensively in field-ion microscopy (FIM).[24] They involve biasing the sample in the form of a sharp tip with a very high positive voltage so that fields of the order of several electronvolts/angstrom are generated. The field leads to the depopulation of a low-lying bonding molecular orbital, and the resulting positive ion is accelerated by the electric field and desorbs. In some cases, negative ion desorption can be affected by biasing the sample with a high negative bias. The STM configuration with the sample and tip in close proximity leads to an important modification of the field-desorption/evaporation process. The potential energy diagram for atom transfer now involves two minima, as the atom can be bonded to either the substrate or tip (see also Figure 2). The activation energy involved and, therefore, the critical field for desorption are functions of the tip–sample distance, decreasing sharply as this distance is decreased.[47] While field desorption/evaporation can certainly be accomplished at large tip–sample distances by simply using higher voltage pulses, there are other reasons why one may want to use a short tip–sample distance. As we have already indicated, the electric field strength falls off rather gradually with lateral distance from the apex of the tip. As a result, one may not be able to choose the atom to be removed. Instead, if different kinds of atomic sites exist under the tip, the atom(s) with the lowest desorption energy will be removed preferentially. This was demonstrated in the case of the Si(111)-7×7 surface.[48] A solution to this problem is to combine chemical and electrostatic forces.[49] One brings a sharp STM tip over the atom to be removed and decreases the tip–sample distance so as to induce a chemical interaction (bonding) between the selected atom and the tip. This interaction reduces the activation energy required for desorption of the interacting atom so that when a voltage pulse is applied this atom is selectively removed. This hybrid process has been termed[49] "chemically-assisted field-desorption" and has been analyzed theoretically by Lang[47] and Hirose and Tsukada.[50] In Figure 4 we demonstrate this manipulation scheme by selectively removing strongly-bound Si atoms from the surface of Si(111)-7×7 and

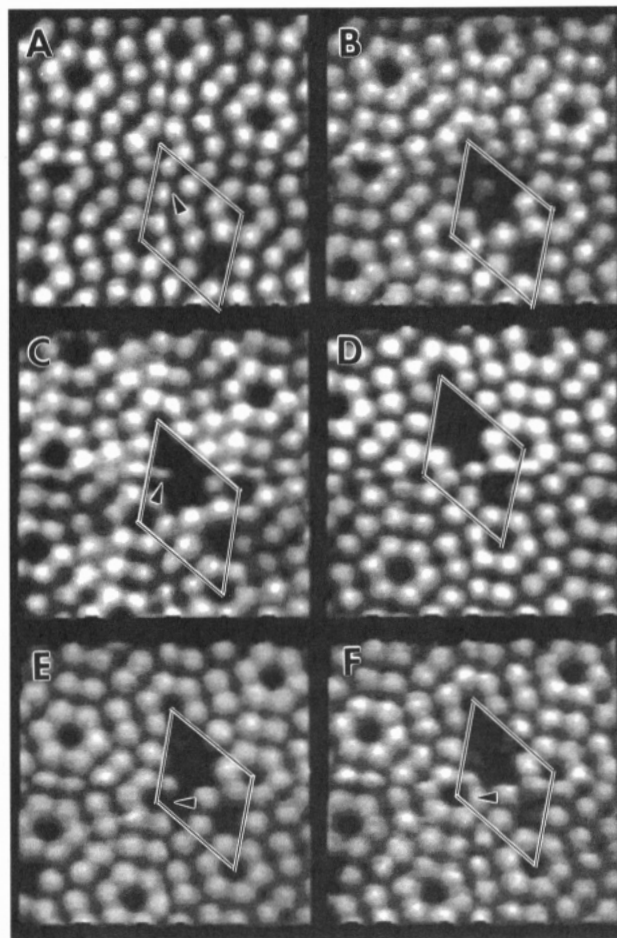**Figure 4.** Selective breaking of covalent chemical bonds: a series of atomic scale manipulations of Si(111)-7×7. (A) The STM tip is placed at ~0.1 nm from electronic contact over the site indicated by the arrow. (B) A 1 V pulse removes three atoms, leaving a fourth under the tip. (C) The first attempt to remove this atom leads to its migrating to the left (see arrow) and bonding as a center Si adatom. (D) A second pulse removes this fourth atom. (E) A new pulse over the adjacent corner Si adatom removes this atom, and then (F) this adatom is placed back in its original position. From ref 51.

redepositing them.[51] Similar approaches have been used to manipulate layered compounds[52] and metal surfaces.[53] This latter work brings attention to the important issue of the stability of atomic structures. The metal surface atoms are elastically coupled to each other, so if, for example, a number of atoms are removed from a particular location, the resulting perturbation is felt by atoms far removed from the original site. In the case of Au(111) it was found[53] that the removal of a few atoms led to large-scale atomic rearrangements and a modification of the reconstruction of the surface.

(c) Effects of the Electric Current. The simplest way in which the electric current flowing through the gap region can affect the sample is by inducing local heating. The maximum temperature rise in the STM due to current flow is given by $\Delta T = IV/4\pi kd$, where I and V are the tunneling current and bias voltage, respectively, k is the thermal conductivity, and d is the mean free path of electrons in the sample. For most crystalline materials, k and d are sufficiently

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large that the temperature rise is negligible ($\ll 1$ K) under ordinary STM imaging conditions. However, one can achieve substantial heating by applying voltage pulses to materials with low thermal conductivity. Such a heating process has been used to crystallize locally amorphous materials and to melt metallic glasses.[54]

A more promising use of the STM current to induce material modification involves the vibrational (or electronic) excitation of the sample by inelastic tunneling. During inelastic tunneling, the tunneling electron loses energy by exciting a vibrational mode of the sample. Two different excitation mechanisms for adsorbates have been discussed in the literature: [55,56] (a) the interaction of the electric field of the moving electron with the transition dipoles of vibrational modes and (b) a resonance scattering mechanism in which an incident electron is captured by an adsorbed species to form a transient negative ion. One can quantify the importance of inelastic tunneling in terms of the inelastic fraction, f, which is equal to the ratio of the inelastic to elastic tunneling conductance. Values of f in the range $10^{-3}-10^{-4}$ are predicted by mechanism (a) for dipole active modes.[38] The contribution of resonance scattering depends on the specific electronic structure of the adsorbate, but it can, in principle, give rise to a significant inelastic tunneling fraction.

Another important factor to consider is the very high current densities that are present in the STM due to the extremely small cross section of the STM beam. Compared with a conventional electron beam with the same current, the current density in the STM can be $10^{11}-10^{12}$ times higher. As a result of the high current densities, not only single vibrational excitation but even multiple vibrational excitation is possible, with the extent of vibrational excitation depending largely on the vibrational lifetime.[38,57] Vibrational heating can have a number of consequences for an adsorbed species; it can lead to desorption, transfer to the tip, enhanced diffusion, dissociation, or the activation of surface reactions. For example, in Figure 2B we saw that as the STM tip approaches an adsorbed Xe atom, a new potential energy well corresponding to bonding to the tip is generated. At a distance of 4.3 Å the barrier separating the two wells is only ~ 15 meV. Eigler et al.[58] found that they can transfer the Xe atom to the STM tip and from the tip back to the sample by applying voltage pulses of opposite polarity. The Xe atom was found to move in the same direction as the tunneling electron flow, and the transfer rate to depend on the tunneling current in an exponential fashion. Walkup et al.[38,57] and Gao et al.[59] interpreted these findings in terms of multiple excitation of the Ni—Xe vibrational mode. The directionality of the transfer process was ascribed to the effect of the electric field present in the gap region acting on the electric moment **p** produced by the adsorption process.[38,57] While in the case of Xe/Ni(110) the vibrational lifetime is short, and as a result the temperature rise is small, significant heating is predicted in

systems with long lifetimes and high vibrational frequencies. Walkup et al.[38] proposed that this would be the case for the Si—H surface species formed by the hydrogenation of silicon. Due to the high frequency of the Si—H stretch, the vibrational lifetime is very long, $\tau \gtrsim 1$ ns.[60] Indeed, recent experiments by Shen et al.[61] show that H desorption from Si(100) can be achieved with electron energies below the onset of electronic transitions and that the desorption probability is an exponential function of the current. The findings could be accounted for by a model involving multiple-vibrational excitation by the STM.[38] Thus, it appears that vibrational heating by inelastic electron tunneling can provide in certain systems a means to activate local chemical reactions.

Dissociation induced by tip-emitted electrons has been extended down to the limit of individual adsorbed molecules. In one example, Dujardin et al.[62] dissociated individual decaborane ($B_{10}H_{10}$) molecules adsorbed on Si(111). Such dissociation processes could be used to deposit dopant atoms such as boron on selected areas of semiconductor surfaces with dimensions as small as ~ 1 nm^2. Electrons from the tip can also desorb atoms or molecules from surfaces via electronic excitation. This has been demonstrated for hydrogen adsorbed on Si(111) by Becker et al.[63] using field-emitted electrons with energy ≥ 6 eV.

(d) STM Tip as a Means of Controlling Thermal Reactions. The STM also can be used to control the spatial distribution of thermal reactions. For example, the tip can be used as a catalyst to enhance locally surface chemical reactions. Such an application was demonstrated recently by McIntyre et al.,[64] who used a Pt—Rh STM tip to dissociate locally H_2 to atomic hydrogen and effect the hydrogenation and removal of carbonaceous deposits on a Pt(111) surface.

In another application, Lyding et al.[65] took advantage of the fact that Si surfaces become unreactive when the Si dangling bonds are saturated by hydrogen to generate a chemically inert Si(100) surface. They then used the STM tip to desorb the hydrogen from selected areas of the surface and thus restore locally the chemical reactivity of the Si atoms. Exposure of such a selectively depassivated surface to various gases led to reaction in only the depassivated areas.[65] This mode of controlling the spatial distribution of surface chemistry appears very promising in terms of technological applications. While desorption at high energies via field-emitted electrons has a resolution of several nanometers, the use of multiple-vibrational excitation for desorption[38] can provide near single-atom manipulation capabilities. An example of a selectively depassivated Si(100)-2×1:H surface is shown in Figure 5. The grid of bright lines involves Si atoms whose dangling bonds have been restored through the STM-induced H-desorption process. For parts of their length, the lines are ≤ 1 nm wide.

As a final example of the use of STM and AFM to influence the spatial distribution of surface processes

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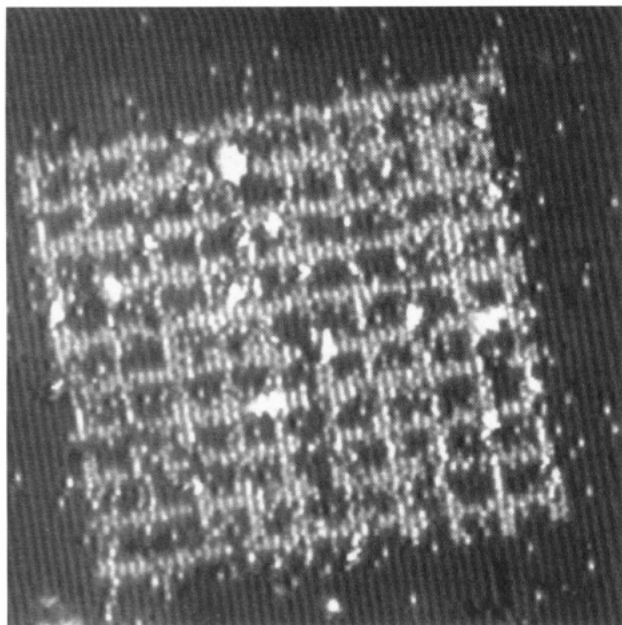
Figure 5. Pattern resulting from selective, STM-induced hydrogen desorption from a Si(100)-2×1:H sample. The lines are about 10 Å wide. The pattern was written with a tip bias of −4.5 V, a current of 2.0 nA, and a line dose of 2 × 10⁻³ C/cm. See ref 61.

we mention the control of electrodeposition. In this case, the STM or AFM tip was used to generate surface defects, which then acted as selective nucleation centers for the electrochemical deposition of metal atoms.[66]

Conclusions and Future Prospects

The isolation and manipulation of individual atoms have important implications in basic science and applications. For example, the long observation times allowed by a trapped electron have made possible extremely accurate measurements of its properties, which in turn have raised questions about the very nature of the electron itself.[67] Ultracold atoms provide the basis for an even more accurate measurement of time than is currently possible, while devices such as atom interferometers probe fundamental questions of quantum mechanics. While, so far, most of the work has been performed on isolated atoms, it is expected that the techniques developed will in the future yield unique information on molecular structure and interactions. For molecules in excited states, control of the vibrational and, in some cases, electron dynamics can be achieved by the use of the coherence properties of the excitation pulse or train of pulses. This is currently a very active research area.[68]

Controlled manipulation of atoms and molecules in condensed phases can lead to many technological applications. Techniques such as STM and AFM are extremely effective as probes and manipulation tools for surface systems. However, such studies need not be limited or relevant only to surface chemistry. A

surface can be chosen to be inert to the molecular systems of interest which are laid on it, as on a chemical bench, for study or to fabricate desired structures. The issue of the mobility of weakly adsorbed molecules can be circumvented by cooling to low temperatures. Moreover, proximal probes can be used in a variety of environments: from UHV to high-pressure cells to aqueous solutions.

Currently, the biggest limitation in atomic and molecular manipulation is the fact that the structure and composition of the tip used is not, in general, known or reproducible. Techniques such as FIM can be used to characterize the tip beforehand, but during its use a number of forces act to change its structure. Surface tension, thermally-activated atom diffusion, stress induced by the applied bias, and heating via the so-called Nottingham effect all contribute to its instability. There is a great need for tips with a well-characterized and stable apex structure. In some cases this can be achieved by functionalizing the tip with stable molecular groups.[69]

Another limitation is the slowness of the atomic manipulation process. This is partially because manipulation is performed in a serial manner. Nevertheless, "writing" speeds of several micrometers/second have been achieved recently in nanometer scale patterning.[70] A different approach to this problem would be to utilize not an individual tip but an array of tips moving in unison. Thus, to write a line, each individual tip will only have to move a small fraction of the length of the line. Microfabrication of such tip arrays is currently being pursued.[71]

To a great extent, the present progress in atomic and nanometer scale modification and manipulation of materials was brought about by advances in microfabrication. Microfabrication itself was developed as a result of the continuous drive for miniaturization of electronics, the technological legacy of the 20th century. What would the corresponding role of a future nanotechnology be? It is clear that the drive for miniaturization will continue. At some point, however, the physics underlying the operation of currently used devices will no longer function; new device concepts will be needed. One promising candidate for the electronics of the 21st century is "single electronics", circuits in which single electrons are manipulated.[72] The basis of "single electronics" is the phenomenon of "Coulomb blockade", which involves the finite charging energy of a very small conductor. Already the feasibility of several devices has been demonstrated.[72] The goal is to be able to produce and manipulate nanostructures with capacitances of the order of ~10⁻¹⁸ F. Logic circuits based on such structures will have switching times of the order of 10⁻¹³ s and involve minimal power dissipation. It is clear that the development of "single electronics" or, for that matter, any other type of nanoelectronics would hinge on the development of reliable nanofabrication techniques.

The applications of atomic manipulation and nanomanipulation are certainly not limited to electronics; chemistry and biology are expected to be major beneficiaries of the new technology. Analytical techniques based on sensors with single-molecule sensitivity, DNA sequencing, and manipulation ("molecular surgery") are among the areas currently being investigated.

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