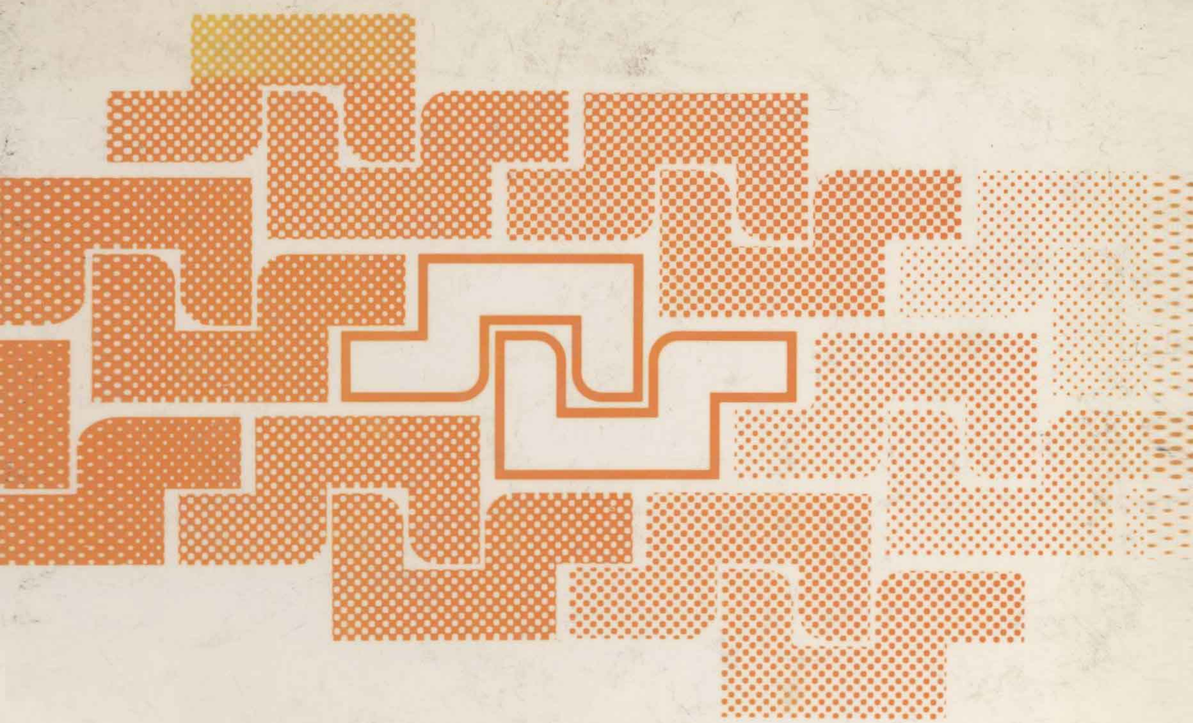

Atomic and Nanometer-Scale Modification of Materials: Fundamentals and Applications

Edited by

Phaedon Avouris

NATO ASI Series

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PREFACE

This volume contains the proceedings of the conference on "Atomic and Nanometer Scale Modification of Materials: Fundamentals and Applications" which was co-sponsored by NATO and the Engineering Foundation, and took place in Ventura, California in August 1992. The goal of the organizers was to bring together and facilitate the exchange of information and ideas between researchers involved in the development of techniques for nanometer-scale modification and manipulation, theorists investigating the fundamental mechanisms of the processes involved in modification, and scientists studying the properties and applications of nanostructures. About seventy scientists from all over the world participated in the conference.

It has been more than 30 years since Richard Feynman wrote his prophetic article: "There is Plenty of Room at the Bottom" (Science and Engineering, **23**, 22, 1960). In it he predicted that some day we should be able to store bits of information in structures composed of only 100 atoms or so, and thus be able to write all the information accumulated in all the books in the world in a cube of material one two-hundredths of an inch high. He went on to say, "the principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom." Since that time there has been significant progress towards the realization of Feynman's dreams. Among the key advances was the development of the scanning tunneling microscope (STM), the atomic force microscope (AFM) and the rest of the scanned proximal-probe microscopes, and the realization that these probes can be used not only for the atomic and nanometer-scale imaging of surfaces, but as tools for the modification and manipulation of materials on the same scale. To affect these modifications one can utilize a variety of tip-sample interactions, including attractive and repulsive forces, electric-fields, and the effect of the electron current. As the papers in these proceedings show, the feasibility of a number of modifications involving small numbers of atoms or even single atoms or molecules has been demonstrated. These manipulations include: sliding and positioning of atoms or molecules on a surface, transferring atoms from a sample to the tip and redepositing them at another location on the sample, dissociating individual molecules, desorbing atoms, and inducing local heating and phase transitions. Moreover, tip-induced modifications can be performed under a wide range of conditions, i.e. in air, in ultra-high vacuum, at a solid-liquid interface, and even at a solid-solid interface (using the ballistic electron emission microscope, BEEM). At the same time our knowledge of the microscopic interaction mechanisms between tip and sample has improved significantly.

While the feasibility of atomic and molecular-scale modification has been proven, it may be some time before the required control and speed with which such manipulations are performed is achieved and a genuine atomic-scale technology is developed. However, atomic manipulation can and is currently being used as a powerful experimental tool for basic science to, for example, isolate or arrange atoms and molecules in precise configurations, probe their electronic structure and interactions with scanning tunneling microscopy (STS), subject them to intense electric-fields or high current densities and thus obtain novel information on inter-atomic and inter-molecular interactions, field-effects on chemistry, etc. Analytical applications, in which the structure of features in STM images is elucidated by taking these structures apart in a step-wise manner and imaging the resulting products, are already appearing. A particularly powerful combination involves low temperatures and atomic manipulation. At very low temperatures, the mobility of adsorbates is eliminated and thus inert substrates can be used as work benches on which, for example, molecular systems can be deposited and operated on with the tip or the tunneling electrons.

In the nanometer (tens of nanometers) regime, the technological implications are likely to be more immediate. Already the STM is used to provide proximity-focused electron beams for lithography. Unlike conventional high-energy electron lithography, the low-energy STM beam reduces the problems associated with electron backscattering and the generation of secondary electrons. A resolution of ~10nm, and exposure rates comparable to those of conventional electron lithography have been achieved. Significant progress has been made in the fabrication of nanometer-scale tip-arrays. The use of such arrays will undoubtedly enhance the lithographic exposure rates and will, in general, facilitate the integration of proximal-probe tools in nanotechnology. The STM electron beam is also being used to locally deposite ultra-small features, such as thin metal lines or nanometer-scale magnets, through the electron-induced decomposition of the appropriate organometallic precursors.

Conventional lithography has been advancing, too. Optical lithography, the workhorse of the field, has greatly benefited from the introduction of new, very high contrast photoresists, phase-shifting masks and other optical technologies. It is, however, unlikely that features below ~100nm can be produced. High energy electron lithography using inorganic resists can lead to a resolution as high as 2nm! However, its throughput, as in the case of the STM, is very low. Currently, the best approach that optimizes resolution and throughput appears to be X-ray proximity printing capable of a 50nm resolution at a 1cm^2/s throughput. In addition to these technologies, a number of new ideas have been introduced and are currently being explored. One such idea involves a "natural nanolithography" in which very fine (nm) spheres (polymers, globular proteins) are rafted together in a Langmuir-Blodgett trough or through self-assembly to form in situ a periodic resist pattern. This pattern is then transferred by implanting or alloying through the interstices.

New ideas have also been introduced and significant advances have taken place in the technology for the growth of low-dimensional structures such as quantum wires (1D) and dots (OD). As 2D heterostructures are easily formed by molecular beam epitaxy (MBE) and chemical vapor deposition (CVD), an obvious way to obtain 1D and OD structures has been through patterning of the 2D structures. However, the etching processes used in the pattern transfer introduce damage that adversely affects the electrical properties. As a result, a number of "softer" fabrication approaches has been introduced. Of particular interest are techniques which utilize MBE and CVD deposition on vicinal (i.e. slightly misoriented) surfaces that form quantum wire structures (tilted and serpentine superlattices) through nucleation at well-organized steps. A very different approach utilizes light-pressure forces to manipulate the density profile of an atomic beam as it impinges onto a substrate. For example, if a 1D standing-wave is generated parallel to the substrate and perpendicular to an atomic beam, the light can, under the appropriate conditions, cause the atoms to become localized in a series of parallel stripes which would then lead to the growth of a series of lines on the substrate. This technique is very new and its potential remains to be evaluated.

Concurrent with the advances in fabrication, there have been advances in the understanding of the basic physics of nanostructures: in particular, of resonant tunneling phenomena and Coulomb blockade. The utilization of these phenomena has made it possible to manipulate single electrons and to build devices such as single-electron turnstiles, pumps and the single-electron transistor. So far, operation is limited to temperatures below 1K; however, with further reductions in dimensions and capacitances, operation at higher temperatures, even room temperature, may be possible. The ability of the STM to probe local electrical properties by establishing point-contacts with the tip has been utilized to study the behavior of conventional electronic devices such as the Schottky-diode at an extreme level of miniaturization. Atomic manipulation at low temperatures with the STM has proven the feasibility of switches involving atomic rather than electronic motion.

A very different approach to nano-fabrication that was discussed in the conference attempts to imitate nature and relies on self-assembly of molecules into supramolecular structures. There are several important advantages in this approach. One is its simplicity and speed, since once the appropriate molecules have been synthesized, self-assembly is spontaneous and does not require the intervention of the technologist. Another important characteristic of self-assembled structures is their extremely low defect density. This is due to the fact that the generated structures are at equilibrium and are thus inherently self-repairing. Finally, when organic molecules are used, the existing extensive knowledge on chemical synthesis can be used to modify and functionalize them, and customize their properties. So far, a number of uses of self-assembled layers including passivation layers, dielectric barriers, and chemical etch resists, have appeared. An exciting new application of self-assembly involves biologically-active proteins (enzymes) on electrode surfaces, where the enzymatic activity is controlled by the electrode potential. These developments raise hopes for the prospect of bio-electronic devices.

As structures and devices decrease in size, the need to precisely control their properties and composition becomes more and more demanding. Specific probes are required and several new proximal probes were discussed. Notable examples include the magnetic-STM which uses ferromagnetic tips and can provide magnetic contrast images with atomic resolution, and the photon-STM, which, by detecting light emission induced by the tunneling electrons, provides valuable insight into the chemical composition of nanometer-scale surface structures.

It appears that Feynman's speculations in the late '50's are rapidly becoming a reality. It is likely that in the next 10 years we will see further dramatic advances that will provide us with a precise control of matter on the atomic and nanometer scales. Nano-devices and nanotechnologies, some imitating natural systems, some based on totally new concepts, could then be realized which would profoundly affect our lives.

The meeting on Atomic and Nanometer Scale Modification of Materials was made possible through the effort of many individuals. Among them, I want to acknowledge and thank James Murday, who co-chaired the Conference, and Calvin Quate, Heinrich Rohrer and Gordon Fisher for their valuable advise and support. I also want to thank the Scientific Affairs Committee of NATO and the Engineering Foundation for their generous financial and administrative support. Additional support was provided by the National Research Foundation, the Office of Naval Research, the Army Research Office and the IBM Corporation. Finally, I would like to take the opportunity to express my gratitude to all participants for contributing to the success of the Conference.

Phaedon Avouris
Yorktown Heights, Sept. 1st, 1992.

CONTENTS

ATOM MANIPULATION WITH THE SCANNING TUNNELING MICROSCOPE

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ABSTRACT. Two processes for manipulating atoms and molecules with the scanning tunneling microscope are discussed along with their underlying physical mechanisms. It is shown how the reversible transfer of an atom between the tip and surface can be used to create a bistable switch. Several applications of atomic manipulation as a laboratory tool are presented.

Introduction

In an article titled *There's Plenty of Room at the Bottom*, Richard Feynman considered the prospect of being able to manipulate matter on the atomic scale.[1] Advances in scanning tunneling microscopy have made this prospect a reality; in certain circumstances we can use the scanning tunneling microscope (STM) to place single atoms at selected positions and build structures of our own design... *atom-by-atom*. In a sense we have learned to use the STM as both our eyes and hands in the world of atoms on surfaces. Here we review the processes that we have developed for manipulating atoms and molecules with the STM and describe how we are using this new capability as a laboratory tool.

Discussion

Our everyday experience leads us to tacitly assume that the process of imaging an object does not perturb the object (quantum mechanics teaches otherwise, and for Schrödinger's cat this is a matter of grave consequence). Similarly, the STM is conventionally thought of as a non-perturbative probe; that is, the act of imaging does not significantly perturb the imaged surface. While this is a reasonable approximation for most circumstances, there exists a regime where this approximation breaks down, namely, when the forces between the STM tip and an adsorbate are comparable in magnitude to the forces between the adsorbate and the surface.

The tip of an STM always exerts a force on the atoms of a surface. At large tip-surface separation this force comes from the Van der Waals interaction between the outermost tip atoms and the atoms of the surface. At closer distance the forces associated with chemical bonding become dominant. The application of a voltage between the tip and the surface will also result in electrostatic contributions to the force between the tip and surface. These forces are usually negligible because the tip is maintained at large enough separation from the surface, the voltages applied are

P. Avouris (ed.), Atomic and Nanometer-Scale Modification of Materials: Fundamentals and Applications, 1–10.

low enough, and the atoms on the surface are bound strong enough. What happens when the force between the tip and the surface is no longer negligible?

We came to be confronted with just this problem while studying the adsorption of xenon on a platinum surface. As a rule of thumb, the energy barrier to diffusion of an atom across a surface will scale in proportion to the adsorption energy. Similarly, the minimum force necessary to move an atom across a surface will scale with the minimum force necessary to pull an atom away from a surface. The bond between the xenon atom and the underlying platinum surface is comparatively weak, just 300 mV (7 KCal), and as a consequence it takes relatively little force to move a xenon atom laterally across a surface. In the process of studying the nucleation and growth of islands of xenon atoms on the platinum surface we were compelled to evaluate whether the presence of the tip was causing the islands to distort and thus invalidate our observations. To answer this question we had to consider the nature of the forces between the tip and the adsorbed xenon. In doing so, it became apparent that we could tune both the magnitude and the direction of the Van der Waals force on the adsorbed xenon due to the tip by controlling the location of the tip. If this force could be made attractive enough then it would be possible to overcome the lateral forces between the surface and the xenon, resulting in the ability to drag a xenon atom over the surface from one location to another without actually lifting the atom off the surface.

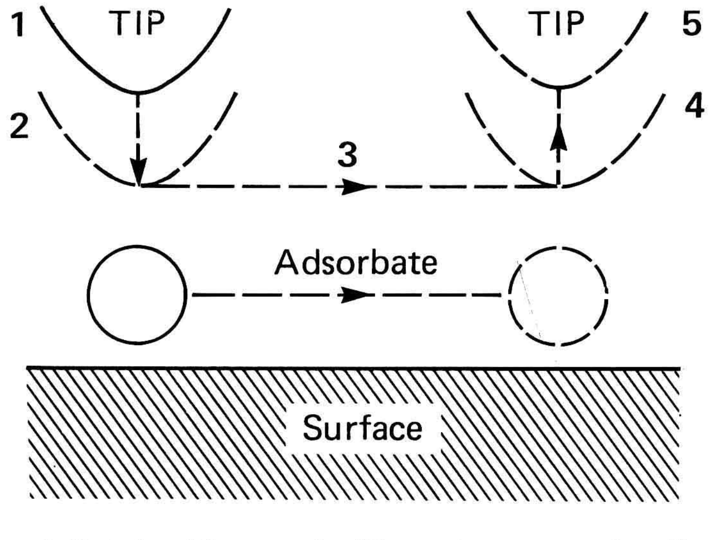

FIG. 1. A schematic illustration of the process for sliding an atom across a surface. The atom is located and the tip is placed directly over it (1). The tip is lowered to position (2), where the atom-tip attractive force is sufficient to keep the atom located beneath the tip when the tip is subsequently moved across the surface (3) to the desired destination (4). Finally, the tip is withdrawn to a position (5) where the atom-tip interaction is negligible, leaving the atom bound to the surface at a new location.

The process for sliding an atom across the surface is shown in figure 1.[2] Here we point out that the essence of this process is to be able to switch between imaging and manipulation modes simply by adjusting the height of the tip above an atom adsorbed on the surface. This process has also been successfully applied to manipulating platinum adatoms on a platinum surface and carbon monoxide molecules on a platinum surface. The sliding process allows atomic-scale precision in so far as we may choose which of any possible stable binding positions we want to place the atom in, and then do so. There are two reasons for this. First, we can control the position of the tip to well within a 1/100th of an atomic diameter. Next, consider that the tip must ultimately exert a force on the atom which overcomes the forces between the atom and the underlying surface. In order to do so the tip must be in near-atomic proximity to the atom. The force between the tip and the atom will thus vary strongly on the length scale of an atom. It is the atomic-scale range of this force that allows us to position atoms with atomic-scale precision.

As mentioned, the force that the tip exerts on an adsorbed atom can have contributions from the Van der Waals interaction, from chemical bonding due to overlap of the electron density of the atom with that of the tip, electrostatic contributions which will depend upon the magnitude of the electric field between the tip and the surface, and possibly from a direct interaction with the electrical current that flows through the atom. We find that the ability to slide a xenon atom over a nickel surface is independent of both the sign and the magnitude of the electric field, the voltage and the current. It does however critically depend upon the separation between the tip and the atom. From this we deduce that it is the Van der Waals interaction, perhaps augmented by chemical binding, that is the dominant interaction between the tip and the xenon atom.

One of the goals of atomic manipulation is to build structures. A limitation of the sliding process is that, so far, all of our attempts to slide an atom over a mono-atomic step on the surface of a sample or to build a three dimensional structure have failed. In order to build three dimensional structures it is desirous to be able to transfer an atom from the surface to the tip of the STM, carry it to a desired location, and then transfer the atom back to the surface, (by now the reader should be discerning a certain correlation between our efforts at atomic manipulation and those of a very young child confronted for the first time with a set of toy building blocks).

Becker, Golovchenko and Swartzentruber[3] found that by applying a voltage pulse between the STM tip and a germanium surface that they could leave behind on the surface an atomic scale perturbation which they suggested might be an atom which transferred from the tip to the surface during the pulse.[4] Following on the ideas of Becker *et al*, we found that by applying voltage pulses we could reliably pick up xenon atoms from a surface, carry them to a new location, and redeposit them on the surface.[5]

To pick up a xenon atom from the surface we first place the tip of the STM directly above the atom. We find that if the tip is held close enough to the xenon atom, then when we apply a +1 V voltage pulse to the tip we cause the xenon atom to jump from the surface to the tip. We may then use the tip to carry the xenon atom to any desired location. If we then reverse the sign of the voltage pulse we can cause the xenon atom to jump back to the surface at any location we choose.

We have studied the delay between the onset of the voltage pulse and the change in junction conductance due the motion of a xenon atom from a bare nickel (110) terrace to a particular STM tip. For a fixed tip height and pulse voltage, the distribution of delays is a decaying exponential, which indicates a fixed probability of transferring per unit time, i.e. there is a characteristic transfer rate. Figure 2 shows that the transfer rate for this particular 906 KΩ junction has a power law dependence on the pulse voltage, and consequently on the tunnel current, according to $I^{4.9 \pm 0.2}$. We were unable to measure the dependence of the transfer rate on the tip-sample separation because at smaller separations (with a junction resistance $R < 700$ KΩ) the xenon atom moved spontaneously to the tip without having to apply a positive voltage pulse. At larger separations ($R > 1.5$ MΩ) the xenon atom tended to hop among several nearby sites on the nickel surface before transferring to the tip, and sometimes escaped from the junction region entirely.

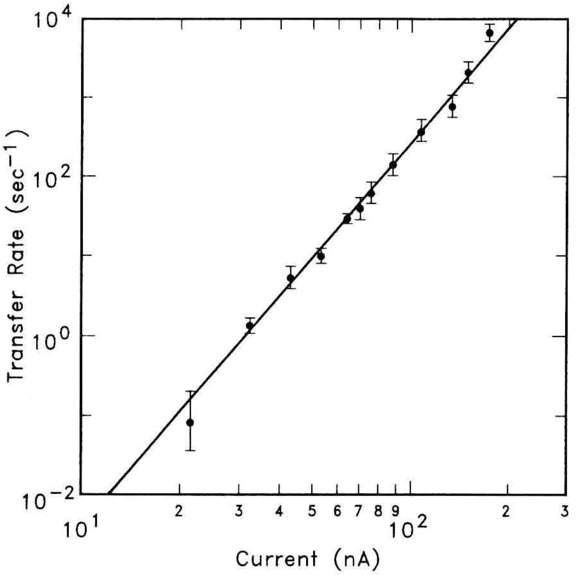

Fig. 2. The measured transfer rate of a xenon atom from the nickel (110) surface to the STM tip as a function of the current during the applied voltage pulse. The transfer rate varies as $I^{4.9 \pm 0.2}$ for this tunnel junction. (For this junction V/I = 906 KΩ plus or minus 2% while the xenon atom is on the surface for the full range of voltages employed.) A heating-assisted electromigration model is consistent with this behavior.

We now turn to the question of what physical mechanism causes the motion of the atom. Any candidate mechanism must be odd in the applied voltage, have the correct sign, and be consistent with the observed transfer delay statistics.

Lyo and Avouris[6] have suggested that ionization followed by field evaporation is the mechanism responsible for the reversible transfer of Si atoms between the tip and Si surface of an STM. This mechanism does not explain the xenon transfer since we find that the motion of the xenon atom is always towards the positively biased electrode.

Mamin *et al*[9] have argued that negative ion formation and subsequent field evaporation can explain the transfer of gold atoms from a negatively-biased gold tip to a substrate. Haberland et. al.[12] have recently presented evidence for the existence of a negative xenon ion with a lifetime greater than 1×10^{-4} seconds. Negative ion formation is unlikely to be the mechanism, however, because we do not observe the