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Nanorobotic Assembly of Two-Dimensional Structures

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Abstract

Precise control of the structure of matter at the nanometer scale will have revolutionary implications for science and technology. Nanoelectromechanical systems (NEMS) will be extremely small and fast, and have applications that range from cell repair to ultrastrong materials. This paper describes the first steps towards the construction of NEMS by assembling nanometer-scale objects using a Scanning Probe Microscope as a robot. Our research takes an interdisciplinary approach that combines knowledge of macrorobotics and computer science with the chemistry and physics of phenomena at the nanoscale. We present experimental results that show how to construct arbitrary patterns of gold nanoparticles on a mica or silicon substrate, and describe the underlying technology. We also discuss the next steps in our research, which are aimed at producing connected structures in the plane, and eventually three-dimensional nanostructures.

Introduction

Microelectromechanical systems (MEMS) have reached the marketplace, with annual sales of several million pressure sensors and accelerometers, primarily to the automotive industries. Research and development in MEMS is under way at many institutions. It is now time to begin studying nanoelectromechanical systems (NEMS), which are the new frontier in miniaturization. Nanometer-scale devices have dimensions comparable to the atoms and molecules that make up all matter, living or inanimate. Control over the structure of matter at the atomic or molecular scale will undoubtedly trigger a major revolution in man-made artifacts.

NEMS will decrease systems' space and energy requirements and increase speed of operation simply because they are smaller than any other electromechanical systems previously built. But these are not their most important characteristics. More interestingly, they open two new areas of potential applications that cannot be tackled with current technology. First, they can be used in applications that require very small sizes. For example, typical cells in living organisms have dimensions on the order of a few micrometers. To penetrate into a damaged cell and repair it requires devices with dimensions on the nanometer scale. Second, macroscopic materials and devices that are molecularly perfect can be built by assembling successively larger components, beginning with nanometer-scale primitives constructed through precise control at the molecular level. These materials and devices would be orders of magnitude stronger than those produced in today's technology, which have minute imperfections that cause them to fail under stress.

Research in nanoelectronics is taking place at many laboratories worldwide, but little attention is being paid to nanoelectromechanical devices and systems. A few researchers are designing NEMS through molecular simulation techniques. However, none have been built, and fabrication processes for them are unavailable. There is a major need to produce physical prototypes for NEMS to validate simulations and, more importantly, to couple design to manufacture, and to guide design efforts so as to ensure manufacturability.

MEMS are built today through extensions of semiconductor fabrication technology, which is well established but has known size limitations. New techniques are needed to reach characteristic lengths of a few nanometers. Several laboratories are exploring self-assembly approaches, which use chemical processes to build nanostructures. Self-assembly is a promising technique to build highly-repetitive or symmetrical structures, but is unlikely to produce, by itself, the asymmetric structures needed in nanomachinery. It also is ill-suited for rapid prototyping, because device modifications in an iterative design cycle may have major manufacturing-process implications. Our research focuses on a different, and much less studied, approach that seeks to construct NEMS by precisely positioning and assembling molecular-sized components. This approach blends knowledge from macrorobotic manipulation and assembly with the physics and chemistry of nanoscale phenomena.

We are developing techniques for constructing NEMS by manipulating nanosized structures with a Scanning Probe Microscope (SPM). Nanoassembly operations by using an SPM as a robot seem ideally suited for NEMS prototyping, and for fabrication of one-

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of-a-kind devices or small batches. The high-level systems we are developing for programming nanoassembly operations will permit rapid exploration of alternative designs. Mass production of validated prototypes might be accomplished either by using arrays of SPM tips working in parallel, by self-assembly, or by a combination of self-assembly and manipulation techniques.

The remainder of this paper is organized as follows. First we discuss the principles of operation of the Atomic Force Microscope (AFM), which is the specific type of SPM we primarily use in our research. Next, we briefly survey prior work on nanomanipulation with SPMs. Then we present our approach to nanomanipulation and the experimental results obtained thus far. A final section summarizes the results and some of the research directions we are pursuing.

The AFM as a Nanomanipulator

The Atomic Force Microscope (AFM) was invented in the mid 1980s, and has had a major impact on science and technology. The principles of operation of the AFM are shown in Figure 1.

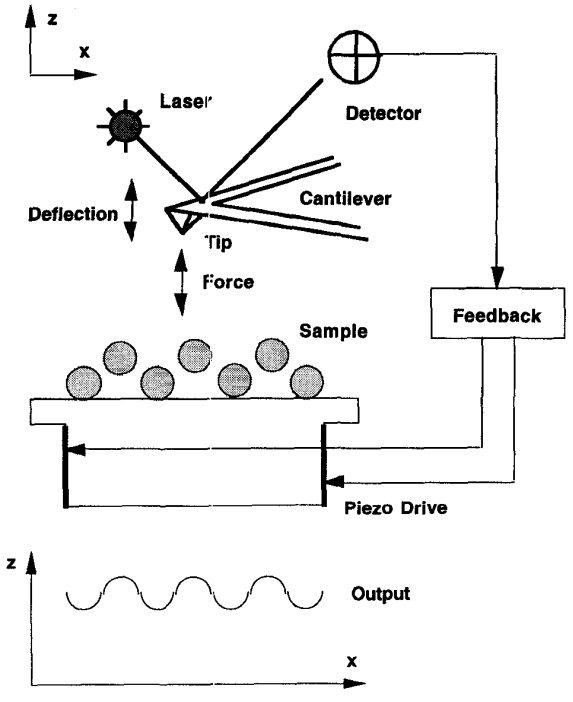


Figure 1 – Principles of operation of the AFM (not to scale).

The forces between atoms in the tip and sample cause a deflection of the cantilever that carries the tip. The amount of deflection is measured by means of a laser beam bouncing off the top of the cantilever. (There are other schemes for measuring deflection.) The tip can be moved vertically with respect to the sample, in the $-z$ or $+z$ directions in the figure, by means of piezoelectric actuators. If the tip of the AFM is brought very close to the sample, at distances of a few Å (1 Å = 0.1 nm = 10^{-10} m), the tip/sample forces are repulsive, and oppose sample penetration by the tip. This mode of operation is called *contact* mode. The force depends on the tip/sample gap—a typical force/separation curve is shown in Figure 2. The force is kept constant by a feedback circuit that controls the piezoelectric actuators. Because of the force/distance relationship, the distance is also constant. Additional piezo motors drive the tip (or, equivalently, the sample) in a xy scanning motion. Since the tip/sample gap is constant, the scanning tip traverses a surface parallel to the sample surface. The result of a scan is a $z(x,y)$ terrain map that follows closely the topography of the sample, as indicated diagrammatically in the figure. (This discussion is an oversimplification; it assumes that the force/ separation curve is constant over the sample, neglects tip-shape effects, and so on.)

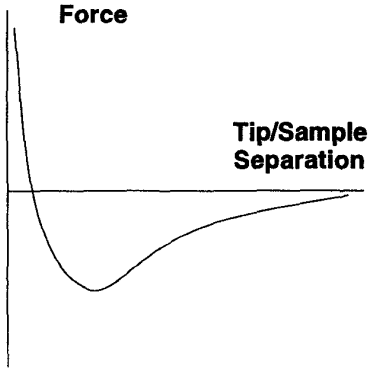


Figure 2 – Typical force between tip and sample as a function of their distance.

Alternatively, the AFM tip can be placed at distances on the order of several nm or tens of nm above the surface, where the interatomic forces between tip and sample are attractive. The cantilever is vibrated at a frequency near its resonance frequency, in the hundreds of kHz range. To a first approximation, the tip/sample force is equivalent to a change in the spring constant of the cantilever, and causes a change in its resonance frequency. In turn, the frequency shift in the resonance curve causes a change in the amplitude of the tip's vibration. This amplitude change can be used as the error signal in the feedback circuit that controls the tip. (There are alternative detection schemes.) This mode of operation is

called *non-contact* mode. A third mode of operation, called *intermitent contact* (or *tapping*) mode, lies betweeen the other two. In this mode the cantilever vibration is such that the tip touches the sample briefly in each cycle. The transition between non-contact and intermitent-contact operation is subtle, and in practice it is often difficult to distinguish between these two modes. Which of the three modes of AFM operation to choose for an imaging task depends on the specific sample and environment. Typically, non-contact or intermitent contact are used for delicate samples, which cannot withstand the higher forces associated with contact mode.

Other scanning microscopes have been developed. The best known is the Scanning Tunelling Microscope (STM), which exploits the quantum-mechanical tunneling effect between conducting tips and samples. For more information on SPM technology see [Chen 1993, Sarid 1994, Wiesendanger 1994].

SPMs are normally used as sensing devices. However, from a robotic perspective, an SPM is a gripper-less robot, operating under force control in z and positional control in x, y. Typically, x, y motions over small regions are done open loop, because of the difficulties (i) in sensing lateral motion with sub-nanometer accuracy and (ii) in reducing the noise in feedback circuits to acceptable levels. This causes complicated calibration problems because the piezo motors' behavior exhibits nonlinearities, creep and hysteresis. In addition, operation is affected by thermal drift due to material inhomogeneities. This drift at room temperature is typically on the order of several atomic diameters per second. Nanomanipulation with an SPM is not unlike macromanipulation on a conveyor belt!

The force/distance curve shown in Figure 2 is highly non-linear, and the behavior of the SPM is difficult to analyze, especially in non-contact or intermitent-contact mode with relatively large amplitudes of cantilever oscillation. We are studying these problems through numerical simulations, and will report our initial results in the near future. Commercial SPM controllers typically are designed through traditional linear-systems methods, but more sophisticated schemes should provide better performance.

It is extremely difficult to sense at the nanoscale. In essence, the only sensor available to us is the SPM itself, which thus functions both as a sensor and manipulator. This raises delicate problems, because we have no access to "ground truth" information for navigating the tip amidst the sample's topography. The time needed for an imaging scan (similar to those shown in Figures 3 and 4) is typically on the order of several minutes, and corresponds to a large amount of drift. In addition, sensing with the SPM involves a filtering process, in which the shape of the tip gets convolved with the shapes of the sample's features. In contact mode, as the tip moves maintaining contact with a feature, it traces a curve that is the Minkowski sum of its own shape with that of the feature. In other words, the *measured* feature is actually the *configuration space obstacle* [Latombe 1991] that corresponds to the actual feature and to a robot that is the SPM tip. This causes significant broadening of sensed objects' shapes, and increases the spatial uncertainty of the situation. To make matters worse, the shape of the tip may change as the SPM moves, especially if there are substantial forces between tip and sample, which often occur in manipulation operations.

The SPM tip is not equipped with a gripper. It may be possible to attach to the tip suitable molecules that will function as grippers and will be able to transport other molecules. This has not yet been demonstrated experimentally, to the best of our knowledge. A major difficulty is that a molecular gripper must be commandable, so as to open and close when needed. In addition, grippers should be non-specific, i.e., capable of interacting with a variety of objects, whereas molecular interactions tend to be rather specific. On the other hand, at the nanoscale one is not limited to mechanical interactions. Thus, for example, electrostatic forces between tips and samples may be exploited to pick up and deposit objects.

In short, an SPM may be viewed as a robot, but it surely is not your garden variety of robot!

Prior Work

Only a handful of labs are pursuing nanomanipulation research. The following works are representative of the state of the art. At IBM Almadén, Eigler's group has been able to precisely position xenon atoms on a nickel surface, iron on copper, platinum on platinum, and carbon monoxide molecules on platinum [Stroscio & Eigler 1991]. Eigler also has succeded in transferring xenon atoms to and from an STM tip. All of this work has been done in ultra high vacuum (UHV) at 4 K. Avouris group, at IBM Yorktown, and Aono's group in Japan have transferred silicon atoms between a tip and a surface in UHV at room temperature [Lyo & Avouris 1991] [Uchida *et al.* 1993]. Samuelson's group at the University of Lund succeeded in pushing galium arsenide (GaAs) nanoparticles of sizes in the order of 30 nm on a GaAs substrate at room temperature in air [Junno *et al.* 1995]. Schaefer *et al.* at Purdue University push gold clusters of sizes 10-20 nm with an AFM in a nitrogen environment at room temperature [Schaefer *et al.* 1995]. These two groups use techniques closely related to ours. Smaller objects have been arranged into prescribed patterns at room temperature by Gimzewski's group at IBM's Zürich laboratory. They push molecules

at room temperature in UHV by using an STM. They have succeeded in pushing porphyrin molecules on copper [Jung *et al.* 1996], and more recently they have arranged bucky balls (i.e., C_{60}) in a linear pattern, using an atomic step in the copper substrate as a guide [Cuberes *et al.* 1996]. C_{60} molecules on silicon also have been pushed with an STM in UHV at room temperature by Maruno *et al.* in Japan [Maruno *et al.* 1993], and Beton *et al.* in the U.K. [Beton *et al.* 1995]. In Maruno's approach the STM tip is brought closer to the surface than in normal imaging mode, and then scanned across a rectangular region with the feedback turned off. This causes many probe crashes. In Beton's approach the tip also is brought close to the surface, but the sweep is done with the feedback on and a high value for the tunneling current. Their success rate is on the order of only 1 in 10 trials. Clearly, nanomanipulation is still in its infancy.

Manipulation Techniques and Experimental Results

Software

SPMs are normally used to image samples. Commercially-available instruments usually are controlled by an IBM-compatible PC, and come with Windows-based software for scanning and image processing. This software is insufficient for manipulation operations. Our main instrument is a Park Scientific Instruments (PSI) AutoProbe CP, which operates in air at room temperature. It is controlled by a digital signal processing board within a PC. The user normally interacts with the SPM through a Windows graphic user interface (GUI). This interface is itself implemented mainly through an Application Programming Interface (API). We implemented our manipulation software through this API.

The API has its own queue of *jobs*, which involve such things as writing user-specified values into the registers, reading output values, and so on. A typical API call places a new job in the queue and returns immediately. The scheduler associated with the API starts the job when resources are available. When the job finishes, a job-end message is produced. Messaging is done mostly by using the facilities provided by the Windows operating system. An application program, such as our Probe Control Software (PCS), cannot assume that a job has been done until it detects the appropriate job-end message. There are no guarantees that a job will be executed within any specified time limits. We have not found any significant practical limitations in this architecture. However, we think it wise to use the SPM PC almost exclusively for sensing and manipulation operations, so as to avoid as much as possible competition for CPU and I/O resources.

The workhorse API function used in PCS is *Wave*, which reads user-specified ramps or steps onto registers. For example, applying two ramps with equal slopes to the x and y registers causes the tip to move in a straight line at 45 degrees. Step inputs can be used to change parameter values. *Wave* applies various ramps and steps simultaneously. The API also has functions for reading output signals from several channels simultaneously. A typical PCS internal procedure calls *Wave* with appropriate parameters so that the tip moves in a straight line between two given x, y positions at a specified speed. During the motion the z feedback may be turned on and off at specified points, or the amplitude setpoint for non-contact operation may be changed to and from specified values, and so on.

PCS is implemented in C++ in the Windows environment, and it has its own GUI. Typically, we start the SPM and engage the tip by using PSI's software and GUI, and then switch to our own PCS for manipulation operations. The two programming systems coexist gracefully, since they both run on top of the same API facilities.

We also have built a server that runs on the PC and listens for requests from the net. A client running on another machine can establish communication with the server through sockets, and, essentially, issue API calls. The server routes these to the API running on the PC, and sends the output back to the client. Data is encoded in XDR (External Data Representation), a de-facto standard for interprocess data exchange. We are currently rewriting the PCS GUI as a Java applet, and will soon be able to control nanomanipulation operations remotely, by using a standard web browser.

Workbench and Objects

Nanoassembly with an SPM must be conducted on top of a suitable substrate, which is the nanoscale analog of a workbench. Unfortunately, often there is a strong relationship between substrates and the objects to be manipulated, and general-purpose substrates may well not exist. The substrate/particle forces must be strong enough to avoid particle motion due to thermal agitation and SPM imaging, and yet not so strong that the tip cannot move the particles. We have been working with colloidal gold (Au) nanoparticles with a thin coating of gold chloride. These nanoparticles are spherical, and are commercially available in various sizes. The chloride-coated particles are slightly negatively charged in air or in aqueous solution, and therefore do not attract each other to form clumps. We have found thus far two successful workbenches for Au balls: mica coated with poly-L-lysine, and silicon coated with a silane self-assembled monolayer (SAM). We have been able to manipulate Au particles with diameters between 5 and 30 nm. Sample

preparation is straightforward and can be done reliably—see [Baur *et al.* 1997] for details.

Manipulation Protocols

We have developed two protocols for moving nanoparticles with the AFM. In both cases we begin by approaching the sample and imaging it by using PSI's GUI and software. Once we have decided which particles to move and where to move them, we switch to PCS. Because it takes a few minutes to image a square with dimensions of a couple of micrometers, and we issue commands in robot coordinates, the particles are no longer in their original positions (in robot coordinates) when the commands are issued. This means that we must track the nanoparticles to compensate for drift. Currently we track them manually. We move the tip to the neighborhood of the nanoparticle and then use several short single-line scans to search for the particle. The actual manipulation protocols are as follows.

Feedback-off protocol – We move in a straight line that goes through the center of the particle, turn off the *z*-feedback just before reaching the particle, and turn it back on after the desired position. Our initial experiments (including those reported below) were done blindly, without acquiring any real-time information during the manipulation operation. Nevertheless, we found that the success rate in moving a particle was nearly 100%. We do not observe balls sliding off the tip. Rarely, a particle may stick to the tip and disappear. In principle, a tip may crash when the feedback is off and the substrate is not sufficiently flat, but flatness can be checked during the preliminary imaging operation. Very recently we conducted a set of experiments and simulations, to be reported elsewhere, that show that the tip is in contact with the particles, and these are mechanically pushed during manipulation. We also succeeded in acquiring real-time data during pushing. These data serve to monitor the progress of the operation, and we expect in the future to incorporate them into more sophisticated manipulation protocols.

Setpoint change protocol – Here we keep the feedback on while we move across the particle, but change the vibration amplitude setpoint so as to force the d.c. value of the tip/sample separation to decrease substantially. We have fewer experimental data with this protocol, and have not studied it as thoroughly as the feedback-off protocol. However, we were able to move smaller particles by changing the setpoint than by turning off the feedback.

After pushing a ball we go back to imaging mode, to verify that the action had the desired effect. Occasionally, the motion does not place the particle in the commanded position, and additional pushing is necessary.

Experimental Results

Figure 3 shows a line pattern created by moving 15 nm Au balls on a mica substrate, using the feedback-off protocol.

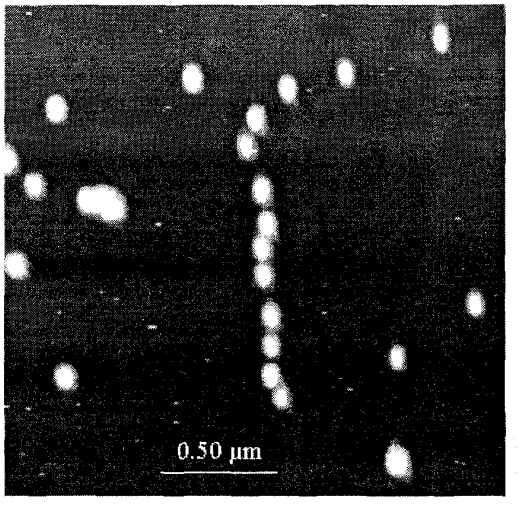
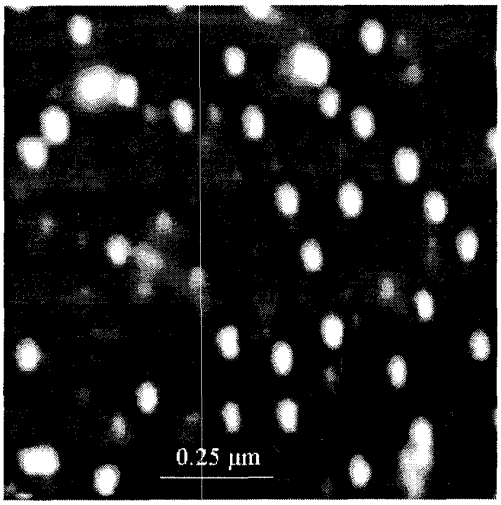


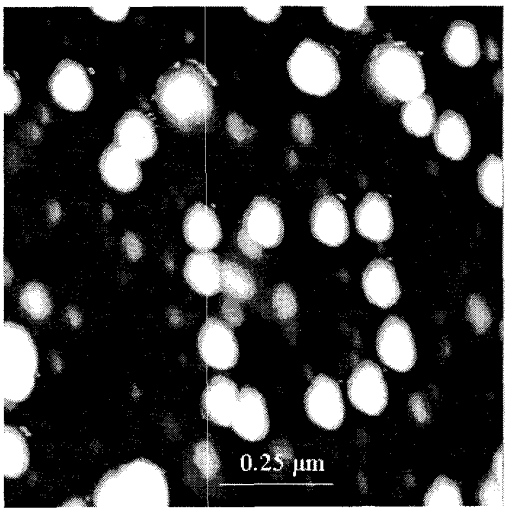
Figure 3 – A line pattern of Au balls on mica.

Figure 4 illustrates the construction of a square pattern with 30 nm balls on a silicon substrate. Figure 4-a is the initial configuration and Figure 4-b is the result of the manipulation. (The small, faded circles are impurities.) This is one of the first patterns we were able to build with a silicon substrate coated with a SAM of an amino-functionalized methoxysilane. Again, the feedback-off protocol was used. We have not yet reached the same experimental proficiency with silicon as with mica.

Experiments with the setpoint change protocol, to be reported elsewhere, are also very encouraging. For example, we were able to construct lines with 5 nm Au balls on mica. Patterns of the complexity shown in the figures typically take several hours to build. Figure 4 also shows the effect of tip shape on imaging. The Au balls look much larger after manipulation because the tip size became larger. The increase in size may be due to material getting adsorbed on the tip, or tip damage during contact.



(a)



(b)

Figure 4 – Construction of a square pattern of Au balls on silicon: random initial configuration (a), and final pattern (b).

Summary and Research Directions

We have shown that the Atomic Force Microscope (AFM) can be used as a manipulator to interact with nanoscale objects. The patterns of gold nanoparticles shown in the figures (and many others obtained in our lab) were generated by manually commanding the AFM through a special-purpose software interface we designed and implemented. Manual operation is tedious and time-consuming. We are now designing automatic tools for manipulation. These require object tracking to compensate for thermal drift, as well as software for correcting non-linearities, creep and other undesirable characteristics of the piezoelectric actuators.

Constructing patterns of gold balls is a fertile testing ground for nanomanipulation. It may also lead to practically useful applications. For example, it has been shown by others [Andres *et al.* 1996, Elghanian *et al.* 1997] that gold balls can be connected by dithiols (which are organic molecules with reactive thiol groups at each end of the chain) or DNA strands. Therefore, we believe that we will be able to construct connected two-dimensional structures with largely arbitrary shapes by first placing gold balls appropriately, and then connecting them. We are ready to begin experimenting with dithiols. These structures may have interesting mechanical and electrical properties. For example, the thiol-connected structures are likely to conduct, and therefore may serve as nanowires of arbitrary geometry. If the structures are sufficiently robust, we may be able to move them and connect them to other sub-assemblies. Patterns of nanoparticles have many other potential applications, which range from high-density digital storage, to single-electron transistors, and as templates for growing nanostructures.

Admittedly, these are small steps towards the production of useful NEMS (nanoelectromechanical systems). However, considering the size of the objects being manipulated, and how reliably we can move them, we find the results very encouraging. NEMS for the masses, as envisioned by Drexler [Drexler 1992] and others, may be still years away, but interesting prototypes may appear in the not-so-distant future in our lab (preferably!) or elsewhere. An important challenge is the assembly of three-dimensional systems. This may require the invention of molecular grippers for picking and placing nanoscale objects. Grippers are high in our research agenda.

Acknowledgements

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