

Modification and Manipulation of Layered Materials Using Scanned Probe Microscopies

Charles M. Lieber

**Department of Chemistry and Division of Applied Sciences
Harvard University, Cambridge, Massachusetts 02138**

ABSTRACT

Scanned probe microscopes, including the scanning tunneling microscope and the atomic force microscope (AFM), are promising techniques for manipulating matter on the atomic to nanometer length scales. Herein, recent work from the author's laboratory that has utilized the AFM as a technique to affect the direct modification and manipulation of layered materials on the nanometer scale is reviewed. The AFM has been used to machine linear and more complex patterns in thin layers of MoO_3 grown on the surface of MoS_2 . The pattern lines have been formed with less than 10 nm resolution using conventional Si_3N_4 tips. These structures can also be inspected without perturbation by imaging the surface with a small applied load. Nanometer scale MoO_3 structural objects, which were defined by AFM nanomachining, have also been manipulated over distances of several hundred nanometers using the AFM tip. The immediate and future applications of these results are discussed.

1. INTRODUCTION AND BACKGROUND

The controlled assembly of matter into structures on the atomic to nanometer scales is an important objective of researchers in the field of nanotechnology.^{1,2} Underlying the successful achievement of this goal is the need to develop methods that can be used to modify and manipulate matter reproducibly on nanometer and shorter length scales. The scanned probe microscopies, including scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are general techniques that have shown considerable promise for manipulating materials on the nanometer scale. Utilization of STM and AFM thus represents an attractive approach for assembling matter into nanometer scale structures.

To date, a number of interesting examples of STM- and AFM-based manipulation have been reported. On the atomic scale STM has been used to remove single atoms and clusters of atoms from the surfaces of several distinct materials,³⁻⁶ to deposit and position atoms on surfaces^{3,4} and to create an atomic switch.⁷ On the nanometer scale STM has also been used to create structures by field-assisted diffusion,^{7,8} to develop organic resists,^{9,10} to expose passivated semiconductor surfaces,¹¹ and to deposit material from the probe tip.^{12,13} STM has also been used to dissociate a single molecule on the surface of silicon.¹⁴ The AFM has also been used with success to manipulate matter on the nanometer length scales. For example, several groups have used AFM to modify organic layers and transition metal dichalcogenide surfaces on a ≥ 50 nm scale.¹⁵⁻¹⁸ More recently we have shown that AFM can be used to machine features in thin oxide layers with 5-10 nm resolution, and that distinct structural objects with nanometer dimensions can be manipulated on the surface.^{19,20} These examples of materials modification and manipulation using STM and AFM serve to illustrate some of the unique capabilities of probe microscopies for nanotechnology. Several of these areas are discussed in greater depth in other chapters within this volume. Herein, we review the recent efforts in our research program that focus on the modification and manipulation of layered materials using AFM.

To date, our research program has focused on the modification and manipulation of layered materials, including transition metal dichalcogenide (MX_2) solids and aniso-tropic thin films grown on these solids.^{16,17,19,20} A schematic view of these systems are illustrated in Fig. 1.

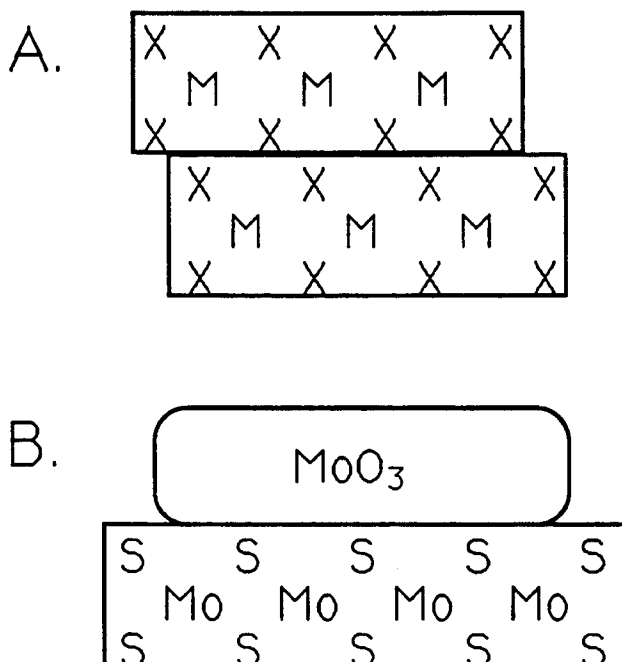


Figure 1. (A) Schematic side-view of a transition metal dichalcogenide (MX_2) material. (B) Illustration of a specific MX_2 material (MoS_2) with an oxide (MoO_3) film grown on the surface.

The MX_2 materials have a number of features that make them attractive for controlled studies of atomic to nanometer scale surface modifications; these features include: (1) single crystals can be cleaved between adjacent X/X sheets to yield atomically flat and ordered chalcogenide surfaces; (2) atomically flat thin films can be grown or deposited onto the surfaces of these materials; and (3) the electronic properties of the solid (surface) can be varied from metallic (e.g., NbSe_2) to semiconducting (e.g., MoS_2) through changes in M and X. On the one hand, the ability to prepare atomically flat surfaces facilitates controlled high-resolution experiments on these solids. The ability to vary the fundamental nature of the surface through the growth of atomically flat thin layers or through changes in M and X also provides a flexible approach to systems with unique electronic and optical properties. Below we review the status of our research program directed towards the modification and manipulation of these interfaces (section 2) and also suggest potentially exciting directions in which these investigations may proceed (section 3).

2. MODIFICATION AND MANIPULATION OF LAYERED MATERIALS

2.1. Nanomachining with the AFM

In force microscopy, a surface is imaged by scanning a surface below a probe that is attached to a cantilever; deflections of the cantilever are related to surface features. The force(s) that cause the cantilever deflections define the mode of imaging. For example, when the tip is in contact with the surface repulsive electrostatic forces usually are the dominant interaction; this contact regime is termed repulsive mode imaging. Alternatively, if the tip is removed from the surface, a van der Waals attractive interaction may be the dominant force between the sample and tip; this case is termed attractive mode imaging. All of our AFM studies reviewed below were carried out in the repulsive mode using a modified commercial instrument.²¹ Si_3N_4 cantilever-tip assemblies were used for both imaging and modification studies. An illustration of the experimental apparatus is shown in Fig. 2.

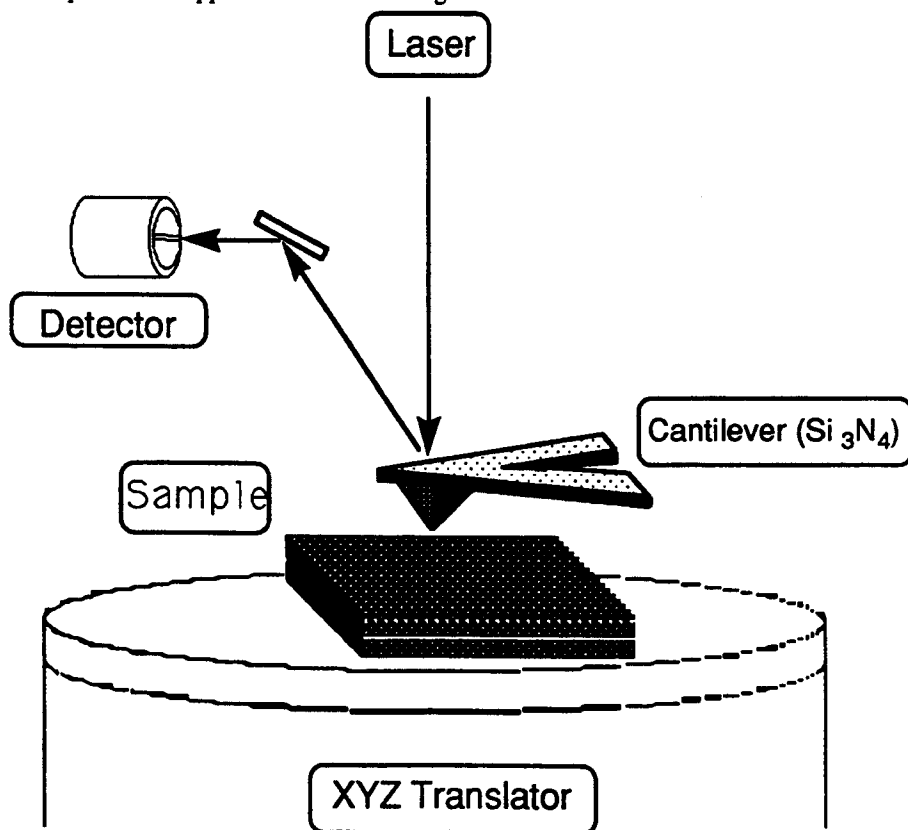


Figure 2. Schematic view of the atomic force microscope.

In general, there are two regimes of repulsive mode imaging: (1) if the forces between the tip and sample are sufficiently small then tip-sample sliding can occur without wear; alternatively, (2) at higher loads tip-sample motion leads to wear. It is this latter regime that we seek to exploit in our studies of layered materials.

Previous AFM studies of MX_2 materials carried out in our laboratory and elsewhere have shown that the tip can be used to modify the surfaces of these materials in air.¹⁶⁻¹⁸ In Fig. 3 we show the effect of continuous scanning of the AFM probe over the surface of NbSe_2 .

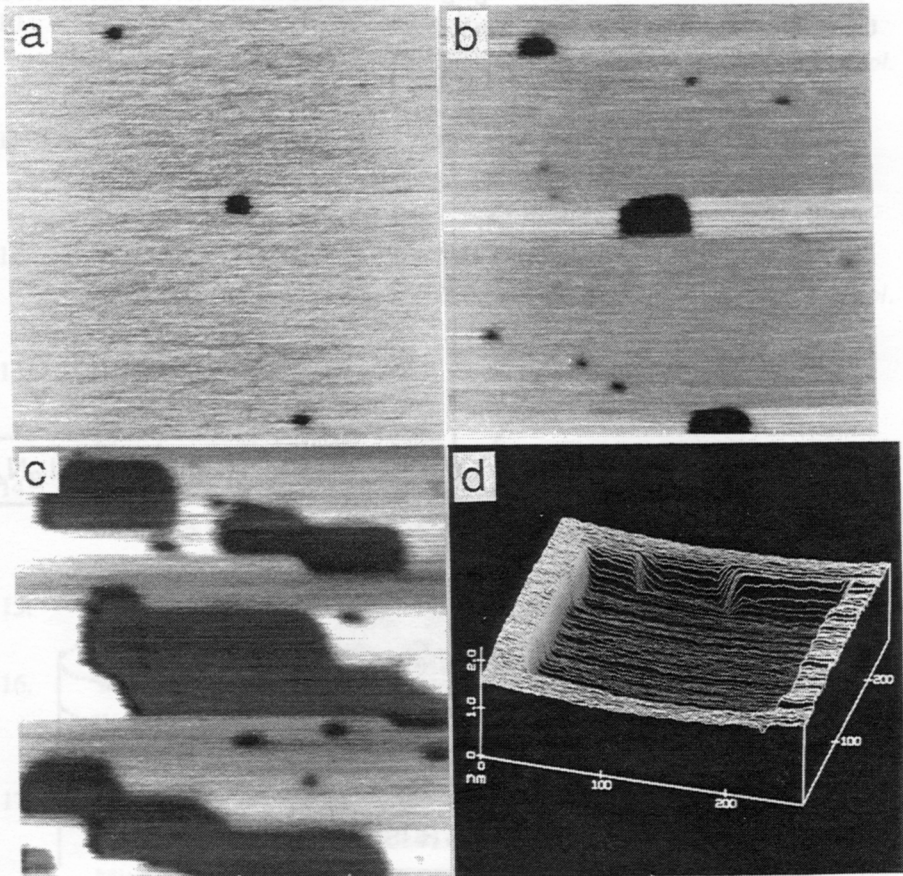


Figure 3. Removal of material from the surface of NbSe_2 while imaging in the repulsive mode with a force of $\approx 10^{-8}$ N. Images a, b, c and d were recorded after ≈ 0 , 490, 1720 and 3350 s of scanning. The top-view images a-c are $200 \times 200 \text{ nm}^2$.

This series of images illustrates that the AFM can be used to pattern a structure in the surface of NbSe₂ (and other MX₂ solids), although the structures have sizes greater than 10 nm. It is also apparent from this series of images that the modification process is not well controlled. That is, scanning in air continuously removes material from the surface regardless of the imaging force, and thus it is not possible to modify and then non-destructively image and probe resulting nanostructures. Similar results have also been observed during AFM imaging of MoS₂ in air (Fig. 4).^{16,20}

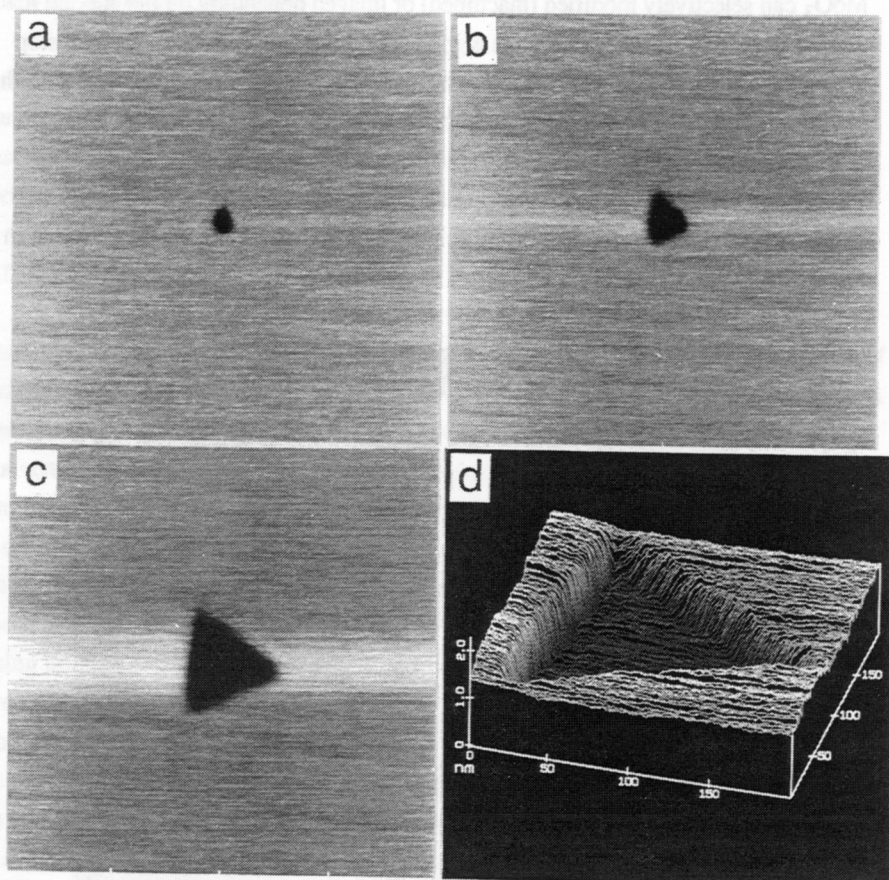


Figure 4. Removal of material from the surface of MoS₂ while imaging in air with a force of $\approx 10^{-8}$ N. Images a, b, c and d were recorded after $\approx 0, 590, 1760$ and 8500 s of scanning. The top-view images a-c are 200×200 nm².

Scanning the MoS₂ surface also results in removal of material from the surface, although on this compound surface modification occurs preferentially along three

crystallographic directions. Hence, we believe that the MX_2 materials themselves are not suitable systems to explore direct AFM-based surface modification. STM can, however, be used to reproducibly modify and probe the surfaces of MX_2 materials in an ultrahigh vacuum environment.⁵

To extend significantly the applicability of AFM to controlled, high-resolution surface modification we have therefore developed a new system that consists of a thin metal oxide film (MoO_3) on the surface of the metal dichalcogenide (MoS_2).^{19,20} This thin film/substrate system has several unique features in comparison to materials studied previously, including: (1) the MoO_3 thin film is rigid and non-deformable; (2) MoO_3 can selectively modified (machined) or imaged depending on the applied load; and (3) the MoS_2 substrate, which is a good solid lubricant, acts as an integral stop layer that automatically sets the depth of features. Important results obtained with this system are described below.

2.2 Nanomachining $\text{MoO}_3/\text{MoS}_2$.

An image of a MoO_3 crystallite grown on the surface of MoS_2 is shown in Fig. 5.

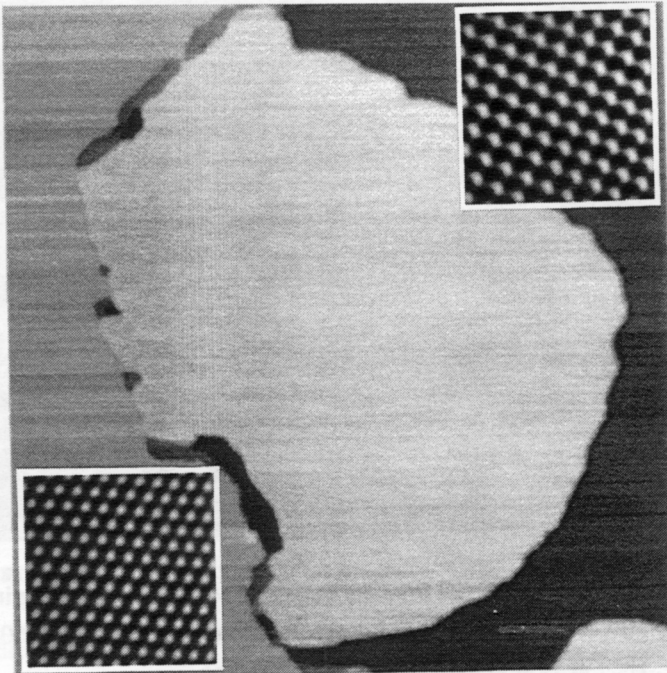


Figure 5. 500 nm x 500 nm AFM image of a 1.5 nm thick MoO_3 crystallite on the surface of MoS_2 . The upper and lower insets show the atomic structure of MoO_3 and MoS_2 , respectively.

The MoO_3 is oriented with the *a-c* axes parallel to the (0001) MoS_2 surface¹⁹ and has a thickness of approximately 1.5 nm (corresponding to one unit all along the *b*-axis). The regions around the edges of this image are MoS_2 . An essential point concerning this thin-oxide layer and MoS_2 substrate is that they are completely stable to repetitive scanning in an inert atmosphere when the imaging force is $\leq 10^{-8}$ N. Hence, it is possible to explore controlled surface modification with this system.

Notably, when the applied load is increased to $> 5 \times 10^{-8}$ N, we have shown that the MoO_3 layer (and only this material) can be machined with nanometer resolution in a controlled manner.^{19,20} A line 150 nm long machined in the MoO_3 crystallite of Fig. 5 is shown in Fig. 6. This line has width of 10 nm at the MoO_3 surface and a width of only 5 nm at the $\text{MoO}_3/\text{MoS}_2$ interface.

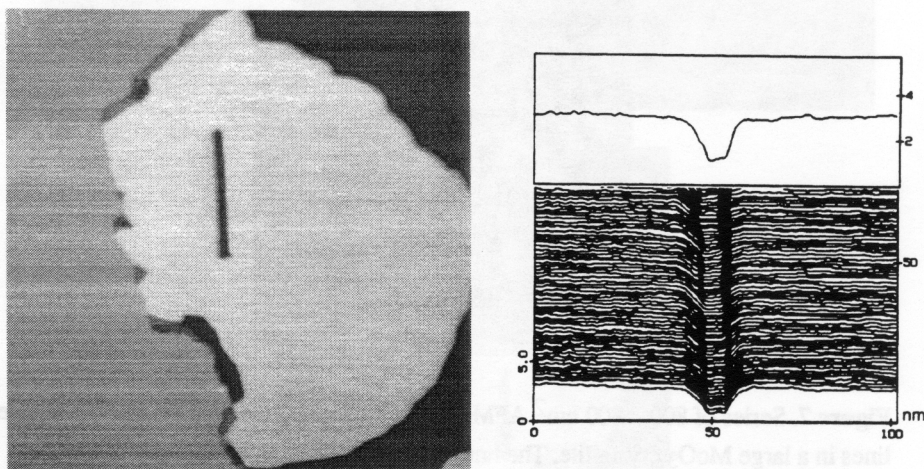


Figure 6 500 nm x 500 nm top-view image illustrating the line machined in the MoO_3 layer using a force of 5×10^{-8} N, and a line-scan view that illustrates the three-dimensional characteristics of this structure.

The line-scan data also show that modification results in a microscopically smooth structure in the MoO_3 . Since the rate at which structures such as this line are formed is proportional to applied load ($> 5 \times 10^{-8}$ N) and scan rate we have termed the modification process, by analogy to macroscopic processes, nanomachining.

To explore the versatility of nanomachining with this system and its potential applications to nanotechnology we have created a number of different structures. For example, we find that a series of high aspect ratio line-structures can be readily created in the MoO_3 layers as shown in Fig. 7.

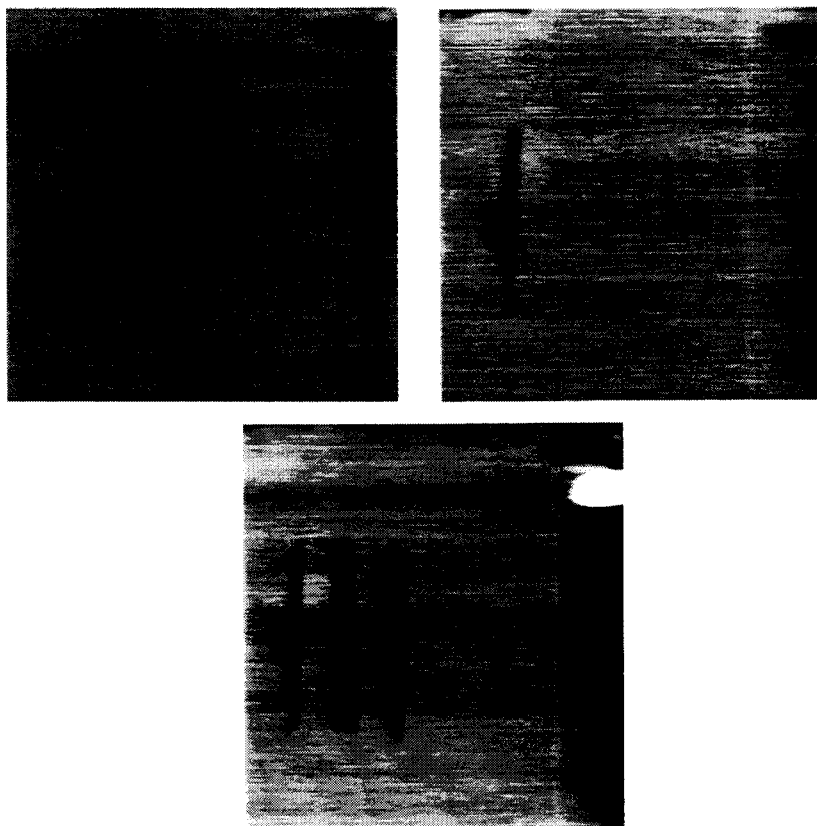


Figure 7. Series of $800 \times 800 \text{ nm}^2$ AFM images illustrating the nanomachining of three lines in a large MoO_3 crystallite. The lines were created using an applied load of $1 \times 10^{-7} \text{ N}$. The images were recorded with a load of 10^{-8} N .

These line structures are 400 nm long, $\approx 20 \text{ nm}$ wide and 30 nm deep. While these features are typical of the linear structures we have created in the MoO_3 layers, we do not believe that they represent the limit of this technology. Recent advances in the fabrication of integrated tip-cantilever assemblies suggest that it may be possible to achieve $< 5 \text{ nm}$ resolution in the future. Notably, the ability to create readily arrays of closely spaced linear structures suggests that these techniques may be useful for producing nanometer resolution gratings.

In addition, it is possible to produce more complex structures in these MoO_3 layers without a loss of resolution. A series of nonparallel lines that were nanomachined to define the initials "H U", which stands for Harvard University, are shown in Fig. 8.

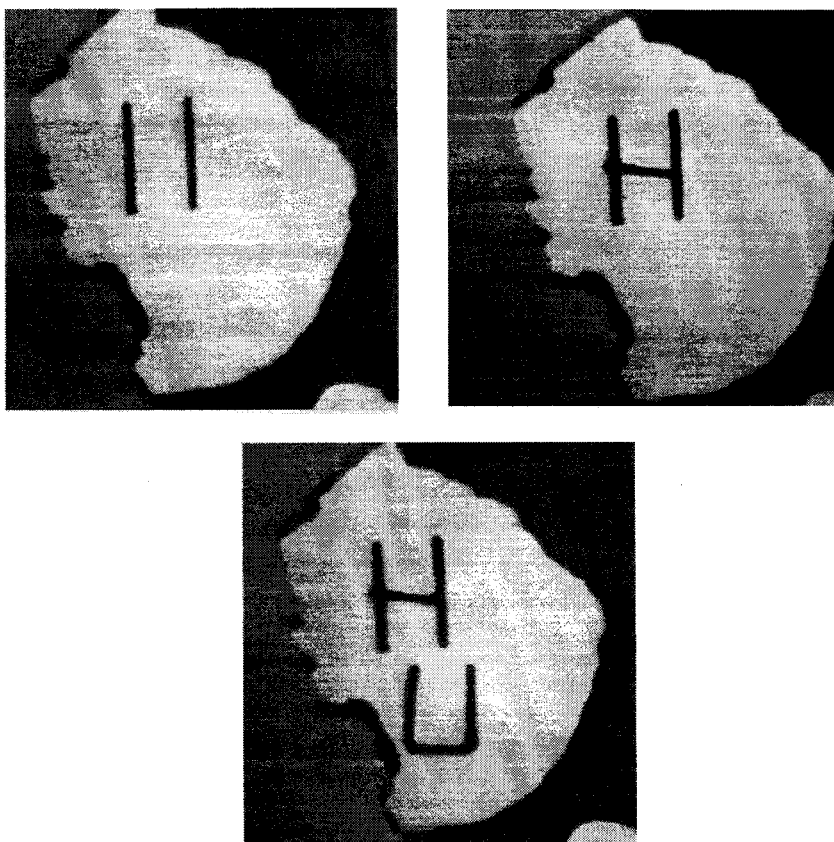


Figure 8. A series of 500 nm x 500 nm AFM images that illustrate nanomachining operations to define the pattern HU.

This sequence of images shows that it is possible to define patterns with intersecting lines, in addition to the parallel features shown in Fig. 7. The resolution (width) of all of these features is approximately 10 nm, although we believe that better resolution will be attainable using higher aspect ratio tips. In the future it may be possible to utilize complex patterning of MoO₃ (or other thin films) to prepare masks for high-resolution X-ray lithography (see below).

2.3 Manipulation of MoO₃ Structures.

We have also shown that it is possible to go beyond the level of nanomachining a series of lines or a complex pattern in the MoO₃ thin layers, and make distinct structures that can be manipulated on the surface.¹⁹ The underlying basis for structure manipulation in the MoO₃/MoS₂ system is that the MoO₃ material is not strongly bound to the MoS₂ substrate. Hence, it is possible to machine a MoO₃ structure, separate this object from the MoS₂ substrate, and then manipulate the structure on the surface. This series of operations is illustrated in Fig. 9.

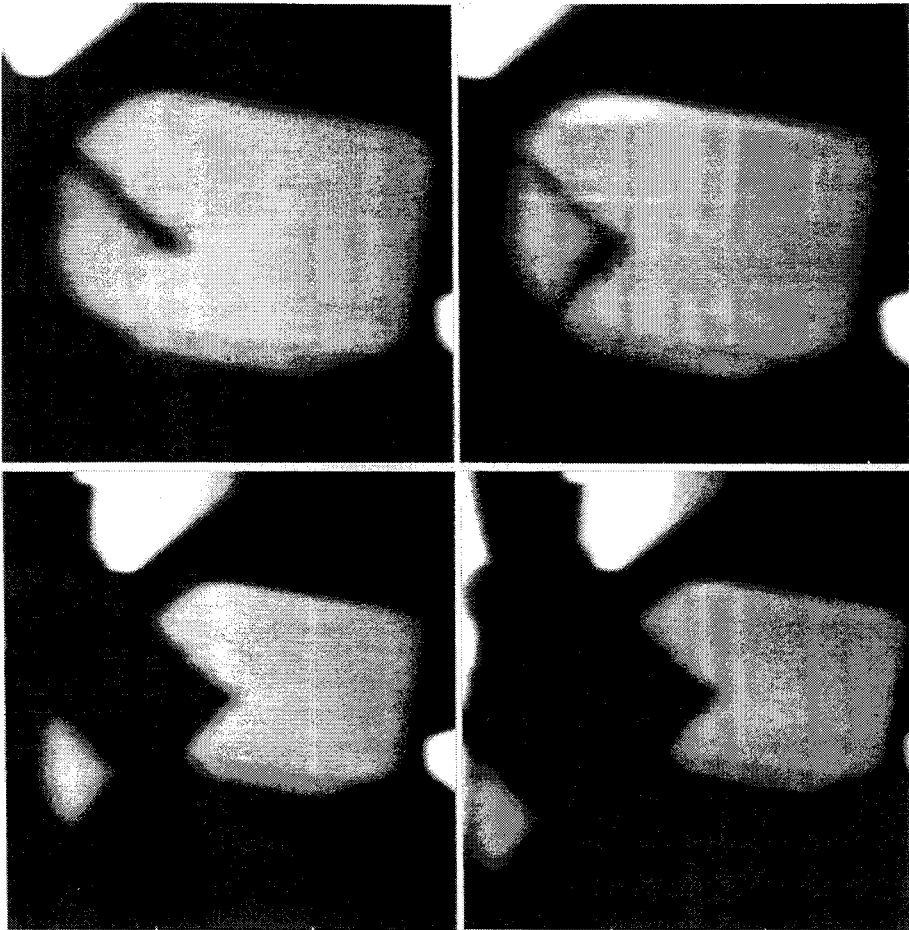


Figure 9. Sequence of AFM images that illustrate (1) the formation of two lines at the edge of a MoO₃ crystallite to define a triangular structure, and (2) the manipulation of the triangular structure across the MoS₂ surface. The triangular MoO₃ object is approximately 60 nm on edge. The two upper images are 450 x 450 nm², and the two lower images are 600 x 600 nm².

An exciting feature illustrated in Fig. 9 is the ability to manipulate nanometer scale objects on surface with the AFM. We have found that it is possible to move small structures across the surface by applying a high load ($\approx 1 \times 10^{-7}$ N) with the tip and then translating the object using the tip. It is also possible to image the manipulated structures without perturbation using a small applied load ($\leq 10^{-8}$ N). Since the electronic and optical properties of MoO_3 can be readily varied by doping we believe that this system and the manipulation techniques described above represent a promising approach for the fabrication of nanostructures with novel properties.

3. FUTURE DIRECTIONS

It is also interesting to consider potential applications of this work to nanotechnology and future directions in which this research may evolve. Below we discuss areas in which we believe these studies could have an immediate impact, as well as longer range and more speculative ideas.

3.1. Direct Applications of $\text{MoO}_3/\text{MoS}_2$ to Nanotechnology.

We believe that the ability to pattern the MoO_3 thin layers with < 10 nm resolution could have an immediate impact in several areas, including the fabrication of nanometer scale diffraction gratings, and X-ray lithography masks. To date, the longest line structures that we have fabricated are 400 nm. Practical gratings and masks for conventional technologies will, however, require longer features. We believe that 100 μm long high-resolution patterns can be obtained through several straight-forward modifications of our procedures. First, larger area MoO_3 layers will have to be grown on the MoS_2 substrates. At the present time the MoO_3 crystallites that we grow by thermal oxidation are usually $< 1 \mu\text{m}$. Large area MoO_3 layers can, however, be grown using thin film techniques such as pulsed laser ablation. Secondly, larger area scanners are needed for tip control over the 1 nm to 100 μm length scale. Recent advances in both commercial and custom instruments indicate that such scanning requirements will be met in the near future, and thus the scan range should not limit future applications. In addition, it will be important to extend further the complexity of the patterns that we machine with the AFM. For example, it would be interesting and useful to nanomachine structures such as a Fresnel zone-plate lens (Fig. 10).

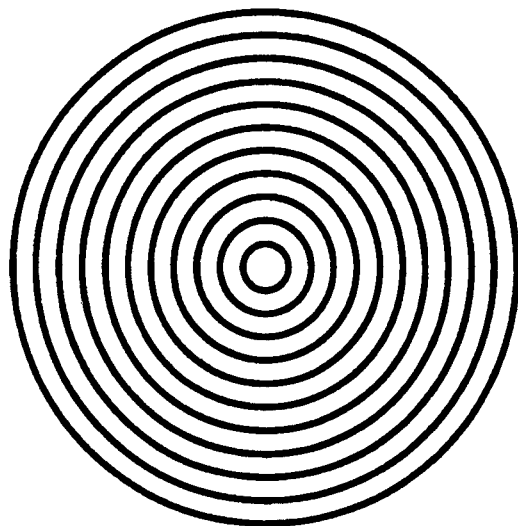


Figure 10. Schematic illustration of a Fresnel zone-plate lens consisting of a pattern of concentric rings.

The zone-plate lens could have interesting application to both X-ray and atom optics. It is unlikely, however, that conventional sample manipulation will lead to successful nanomachining of this complex structure. We believe that an attractive approach will involve using the new sample translation method reported by Mamin and Rugar.²² Application of this method to our system would involve spinning the sample on a precision drive, and then machining the MoO_3 at specified radial distances from the rotation axis.

Other approaches may also enable our system to be used for the fabrication of complex high-resolution masks. A current limitation to the direct application of our techniques to this problem is the need to maintain registry over very large distances (e.g., mm). It may be possible, however, to combine conventional photolithography with AFM to produce unique structures. Conventional photolithography could be used to define the basic mask pattern on the $10\text{ }\mu\text{m}$ to 1 mm scale. AFM could then be used to nanomachine intricate details and interconnects in this pattern, and thereby yield a novel mask structure.

3.2. Other directions.

We believe that it also should be possible to generalize the attractive features of the $\text{MoO}_3/\text{MoS}_2$ system and our nanomachining ideas to other materials. For example, the major requirements to achieve controlled and reproducible nanomachining

are (1) that the thin layer wears more rapidly than the substrate, and (2) that the AFM tip is stable during the machining operation. There are many choices of systems that meet these requirements, although we believe two are particularly interesting. These systems are SiO_x/Si and copper oxide superconductor/ SrTiO_3 . The SiO_x/Si system would be interesting due to the central role these materials play in microelectronics; however, cantilevers with diamond probes may be needed for reliable modification. Preliminary work also indicates that the layered high- T_c copper oxide materials can be machined on the nanometer scale. Hence, it may be possible to make novel junction structures and devices by using AFM to nanomachine these superconductor materials.

In addition, we believe it will be important in the future to exploit our ability to manipulate MoO_3 structures (and perhaps other materials on the nanometer scale). For example, it will be interesting to consider whether it is possible to construct a nanomotor. An armature and gears could be readily machined on the < 100 nm scale and then used to assemble a motor on the surface. A motor on this scale would represent several orders of magnitude size reduction compared to the structures that can be obtained using micromachining techniques.²³ One obstacle that would have to be overcome in fabricating such a device would be the development of methods to "lift" parts, such as the gears, during assembly. We believe that it may be possible to lift small objects with the tip using electrostatic clamping. We must also consider how a nanomotor would be powered and/or observed. Finally, we believe that it will be possible to explore many other types of structures, such as those that exploit quantum confinement and/or the photochromic properties of MoO_3 , as we continue to explore the applications of scanned probe microscopies to nanotechnology.

4. ACKNOWLEDGMENTS

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