

## Research News

# Nanomachining and Manipulation with the Atomic Force Microscope

By Charles M. Lieber\* and Yun Kim

### 1. Introduction

The field of nanotechnology is emerging as an exciting area of fundamental and applied research.<sup>[1-3]</sup> Central to efforts in this field is the development of approaches to manipulate matter on the nanometer scale. The scanned probe microscopies, such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), are general techniques that show considerable promise for this purpose.<sup>[4-14]</sup> For example, STM has been used to remove single atoms and clusters of atoms,<sup>[9, 10]</sup> to deposit and position single atoms<sup>[11]</sup> and to create an atomic switch.<sup>[12]</sup> Such atomic-scale manipulations may in the future lead to a new generation of devices. The STM has also been used as a collimated source of electrons to develop resist layers on the nanometer scale<sup>[13, 14]</sup> analogously to electron beam lithography. More recently, we have shown that AFM can be used to machine complex features in thin oxide layers with nanometer resolution and, furthermore, that AFM can be used to manipulate distinct nanometer scale structures on a surface.<sup>[4]</sup> Nanometer scale manipulations can bridge the gap between molecular scale structures and those produced by conventional lithography and thus could have immediate application to conventional technologies as well as long-term utility to emerging nanotechnologies. Below we review the underlying basis, scope and applications of nanomachining.

### 2. Surface Modification by AFM

In AFM, a tip attached to a cantilever is brought into contact with a sample surface, and the sample is rastered beneath the tip while detecting displacements of the cantilever.<sup>[15]</sup> The force on the sample surface is readily estimated using Hooke's law,  $F = -kz$ , where  $k$  and  $z$  are the spring constant and displacement, respectively.

There are several possible consequences of tip-surface contact while scanning. First, for small forces (typically  $10^{-8}$ – $10^{-9}$  N) the sample can be scanned beneath the tip/cantilever without damaging the surface. In essence, the

imaging force is less than the force associated with chemical bonds in the material. For larger forces it is possible to inelastically deform soft materials (e.g., polymers<sup>[7, 8]</sup>) or more generally to affect material wear.<sup>[4-6]</sup> In a rigid solid, the resolution of features made by the removal of material through a wear process will be limited by the size of the tip (5–10 nm) and depth of the feature. Hence, nanometer-scale structures should be readily achieved in thin solid layers by controlling the force of the tip on the surface; this process can be termed nanomachining.

### 3. The MoO<sub>3</sub>/MoS<sub>2</sub> System

The choice of substrate material is critical to controlled high-resolution nanomachining with AFM. We have found that a novel material system that exhibits properties ideal for high-resolution nanomachining consists of thin ( $\leq 5$  nm) MoO<sub>3</sub> films grown on a MoS<sub>2</sub> substrate. Key features of this material system are as follows: the thin MoO<sub>3</sub> layer is rigid and non-deformable; MoO<sub>3</sub> can be selectively imaged or machined, depending on the force; and the MoS<sub>2</sub> substrate serves as an integral depth stop since it does not wear under the conditions used to machine MoO<sub>3</sub>.

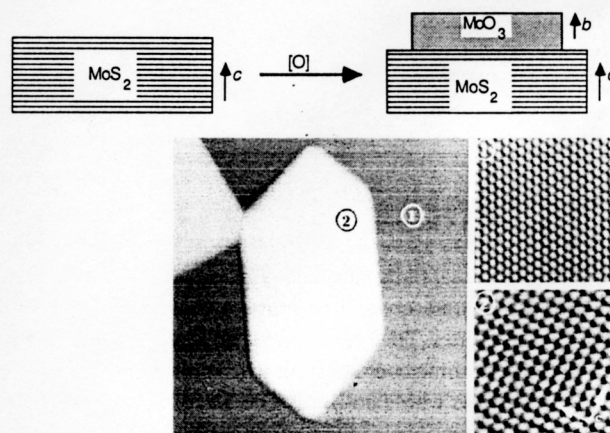


Fig. 1. (Top) Schematic view of the MoS<sub>2</sub> substrate before and after oxidation. The MoO<sub>3</sub> crystallite grows with its  $b$  axis perpendicular to the MoS<sub>2</sub> surface. (Bottom, left)  $450 \times 230$  nm<sup>2</sup> AFM image of a MoO<sub>3</sub> crystallite (2) on the MoS<sub>2</sub> surface (1). The atomic resolution images (bottom, right) readily identify the MoS<sub>2</sub> (1) and MoO<sub>3</sub> (2) materials.

[\*] Prof. C. M. Lieber, Dr. Y. Kim  
Department of Chemistry and Division of Applied Sciences  
Harvard University  
Cambridge, MA 02138 (USA)

Thin crystallites of  $\text{MoO}_3$  can be readily grown on the surface of single-crystalline  $\text{MoS}_2$  by thermal oxidation.<sup>[16]</sup> Reaction of  $\text{MoS}_2$  with oxygen at 480 °C for 5–10 min typically produces  $\text{MoO}_3$  crystallites of 300–500 nm edge length and 1.5–4.5 nm thickness. These structural features can be readily determined from AFM images acquired with a small imaging force ( $\leq 10^{-8}$  N) and are illustrated in Figure 1. Interestingly, the high resolution imaging capabilities of AFM enable the rapid identification of crystallographic orientations of the  $\text{MoO}_3$  films relative to the substrate; the  $\text{MoO}_3$  grows exclusively with the [010] direction parallel to [001] of  $\text{MoS}_2$ .

#### 4. Pattern Formation on the Nanometer Scale

When the imaging force is increased to  $\geq 5 \times 10^{-8}$  N, the  $\text{MoO}_3$  surface (but not  $\text{MoS}_2$ ) can be machined in a controlled manner with high resolution.<sup>[4, 16]</sup> A line 150 nm long is shown in Figure 2. Investigations of the rates of nanomachining as a function of the force on the surface and scan rate confirm that structures are created by tip-induced wear of the  $\text{MoO}_3$  film.

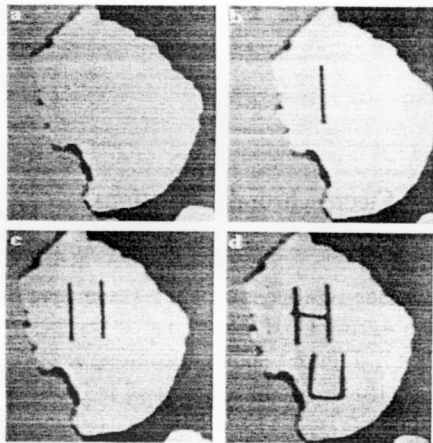


Fig. 2. Series of  $500 \times 500 \text{ nm}^2$  AFM images showing the machining of the pattern "HU" in a  $\text{MoO}_3$  crystallite. The images were recorded non-destructively using an applied load of  $1 \times 10^{-8}$  N; nanomachining was carried out using forces  $\geq 5 \times 10^{-8}$  N.

The width of the line in Figure 2b is 10 nm at the  $\text{MoO}_3$  surface and only 5 nm at the  $\text{MoO}_3/\text{MoS}_2$  interface. The average aspect ratios of this structure is thus on the order of 20:1; in fact, linear features with aspect ratios in excess of 40:1 have been created. It is also clear from the examination of three-dimensional views of these trenches that they are microscopically smooth. An immediate application that one can envision for high-resolution linear structures would be diffraction gratings.

In addition to simple linear features it is possible to use the nanomachining process to create significantly more complex

structures. We illustrate this point with the pattern HU, which stands for Harvard University, that was created by machining a series of lines in a  $\text{MoO}_3$  crystallite (Fig. 2). It is important to note that the nanomachining resolution does not degrade during the sequence of operations and that the resulting structure is stable during repetitive imaging for forces  $\leq 10^{-8}$  N. Hence, it is possible to create reasonably complex and durable structures in  $\text{MoO}_3$  films with a resolution which exceeds that attainable by conventional lithography. The ability to machine complex nanometer patterns in  $\text{MoO}_3$  could lead to a new method for constructing high-resolution masks for X-ray lithography.

#### 5. Manipulation of Nanostructures

With the  $\text{MoO}_3/\text{MoS}_2$  system we have shown that it is also possible to extend the application of AFM from nanomachining and patterning to the controlled manipulation of nanostructures. The underlying basis for structure manipulation in the  $\text{MoO}_3/\text{MoS}_2$  system is that the  $\text{MoO}_3$  material is not strongly bound to the  $\text{MoS}_2$  substrate. It is thus possible to pattern a  $\text{MoO}_3$  structure, separate this structure from the  $\text{MoS}_2$  substrate, and then manipulate the object on the  $\text{MoS}_2$  surface. This process is illustrated in Figure 3 for a triangular object of approximately 80 nm edge length. As

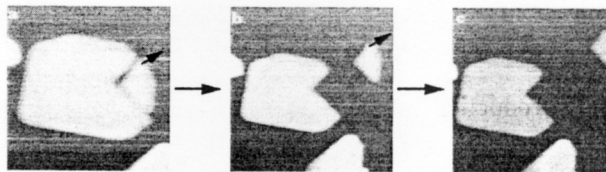


Fig. 3. A series of AFM images exhibiting the manipulation of a triangular  $\text{MoO}_3$  object on the  $\text{MoS}_2$  surface. The two translations each correspond to a distance of ca. 100 nm.

with the nanomachining process, it is possible to move the triangular structure using a relatively large force ( $\sim 10^{-7}$  N) and image the resulting translation without further perturbation using a small force. Hence, it is possible to monitor the manipulation process in situ; this enables exquisite control and precise positioning during the manipulation process. In terms of future applications, it is notable that the objects we can create and manipulate are several orders of magnitude smaller than those currently produced by micro-machining.<sup>[17]</sup>

#### 6. Future Directions and Applications

We have shown that it is possible, using AFM and a novel material system, to pattern complex structures and to machine and manipulate free objects all with nanometer resolu-