Reports

Scanning Tunneling Microscopy and Nanolithography on a Conducting Oxide, $Rb_{0.3}MoO_3$

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The scanning tunneling microscope has been used to image and modify the surface of a conducting oxide ($Rb_{0.3}MoO_3$) in ambient atmosphere. Individual octahedral MoO_6 units of the oxide can be imaged, and under certain conditions defects can be created in the surface that are stable in air. The ability to produce nanometer-sized structures on the surface of an oxide is demonstrated and discussed with reference to nanolithographic applications.

The scanning tunneling microscope (STM) is a valuable tool for studying surface topographic and electronic properties (*1*). One proposed application of the STM is to use the atomic scale control of a sharp tip by piezoelectric-based positioning devices to produce pat terns on samples for nanometer-sized device fabrication or data storage. The STM has recently been used to create defects on or in metals (*2–4*) and insulators (*5*). We report results that demonstrate nanolithography and near-atomic scale imaging on single-crystal samples of $Rb_{0.3}MoO_3$, a conducting oxide. Oxides are more stable than most transition metals and semiconductors in air or modest vacuum, hence STM-based nanolithography on oxides may be more practical than on other materials in technical applications.

All of the STM experiments were performed in air with a tube-type scanner (*6*). The single-crystal $Rb_{0.3}MoO_3$ sample was prepared by the gradient flux technique (*7*) and then cleaved in air just prior to imaging. A schematic of the crystal structure of $Rb_{0.3}MoO_3$ is presented in Fig. 1. This oxide has unit cell dimensions of **a** = 18.6354(3) Å, **b** = 7.555(1) Å, and **c** = 10.094(2) Å (number in parentheses is the error expressed as the variation in the last digit), space group *C2/m*, and contains 20 MoO_6 octahedra per unit cell (*7*). Similar to other compounds in this class of so-called blue bronzes, $Rb_{0.3}MoO_3$ is a metallic conductor at room temperature, and it undergoes a one-dimensional charge density wave (CDW)–driven distortion at 180 K (the CDW is not relevant to this study).

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We present STM images taken with near-atomic resolution over a 7.4 nm by 7.4 nm and a 4.2 nm by 4.2 nm area (Fig. 2). Good images were observed for 50- to 500-mV bias and 100- to 300-pA tunneling current. The features in Fig. 2 can be associated with MoO_6 units but not with individual atoms. Repeat distances determined from the images or their Fourier transform agree with the known crystallographic distances along the **b** and [102] axes. The primary features running across the surface correspond to the **b** axis (see Fig. 2A). The distortions of the octahedral units evident in the STM image are a confirmation of the results obtained by single-crystal x-ray diffraction analysis (*7*).

In Fig. 3A we show an example of steps on the surface over a 100 nm by 100 nm area. Single- and double-height steps were observed, and their heights agree with known interplanar spacings. The flatness of the terraces varied considerably between samples. Some regions of the surface were quite rough and displayed irreproducible behavior typical of surfaces that have patches of conductive and insulating areas.

While experimenting with different bias voltages, we observed that indentations could be produced on the surface. Some of the features we engineered are displayed in Fig. 3, B through D. In Fig. 3B, a hole 15 nm to 20 nm across and ~2 nm deep is shown. This feature was created by scanning a 10 nm by 10 nm area of the surface at 10 mV and 0.25 nA for 10 min. Its deviation from a square shape was possibly caused by thermal, piezo, or electronic drift and fluctuations. Features as small as 0.3 nm deep and 6 nm across could be etched in the surface, although we note that the shape of the observed features represents a convolution of tip and surface morphology. We found that the best way to produce these kinds of features was to lower the bias voltage to ~10 mV and then to scan across the surface in a predetermined pattern. We believe that under these low bias conditions, the tip was forced to penetrate the first layer to maintain

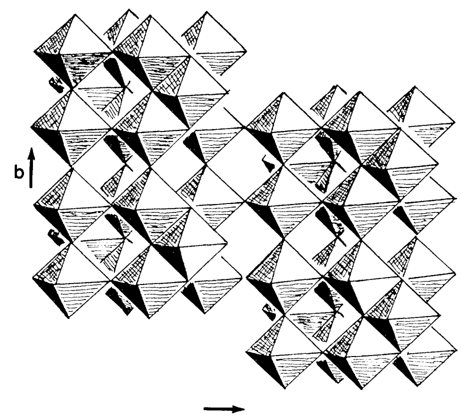

Fig. 1. Schematic diagram of the structure of $Rb_{0.3}MoO_3$. The octahedra represent MoO_6 units; infinite layers of MoO_6 octahedra are made up of corner- and edge-sharing octahedra along the **b** ([010]) and [102] directions.

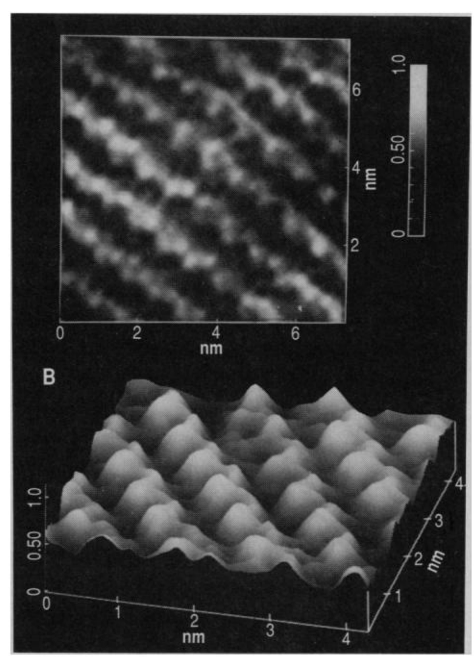

Fig. 2. (**A**) Near-atomic scale STM image of $Rb_{0.3}MoO_3$, 7.4 nm by 7.4 nm. Bright spots correspond to MoO_6 octahedra. The long chains are along the **b** axis. Current image; bias +240 mV, current set point 0.3 nA. (**B**) As in (A), but 4.2 nm by 4.2 nm topographic image at +100 mV, current set point 0.3 nA.

the required tunneling current. By moving the tip parallel to the surface, features could then be written in the surface. A much larger square feature was produced in the surface (Fig. 3C) with dimensions ~100 nm by 100 nm across and 10 nm deep, again created by lowering the bias voltage and scanning a predetermined shape. In addition to square features, lines (Fig. 3D) and other shapes were produced on the oxide surface. The lines in Fig. 3D were ~150 nm long, ~8 nm wide, and <1 nm deep. These lines demonstrate the potential applicability of the technique for nanolithography.

A second way we explored writing on surfaces was to move the tip to a predetermined position, lower the voltage from 200 mV to 10 mV for a short time, and then raise it again. By moving the tip to a series of locations we could pattern a group of holes on the surface. The features produced by both approaches were quite stable and did not degrade within the time frame of the experiment (up to 4 hours). In previous work on metals, surface features changed within minutes or hours, and in fact led to studies of dynamics of surface migration (*3*).

Several questions arise concerning the mechanism of writing. Although they are not mutally exclusive, we have considered four mechanisms: (i) local heating, (ii) processes induced by a single "hot" electron, (iii) electrochemical reactions, and (iv) abrasion (*5*). During fabrication of these features (that is, on switching from the topography to writing modes), the current was often held constant, and the voltage was decreased. This procedure implies that the local classical Joule heating (current times voltage) should actually decrease while writing, although this effect might be compensated by tunneling into a smaller area. (The concept of a local temperature, however, is questionable, as the electrons tunneling into a few atoms are not in thermal equilibrium with phonons between the same few atoms.) Most hot electron or electrochemical-induced processes would require electrons of sufficient energy to break bonds (>1eV); thus these two mechanisms are also unlikely. We favor atomic scale abrasion as the probable cause of etching. The metallic bonding within the tip (W or Pt-Ir) is much stronger than that in the $Rb_{0.3}MoO_3$ (as estimated from heats of sublimation); thus the surface should be etched without significantly damaging the tip if the tip penetrates or is dragged along the surface.

Another important consideration is the fate of the excess molybdenum, oxygen, and rubidium atoms formed when creating the depression in the surface. Under certain conditions, we observed mounds (deposits) on the sides of the features we created on the surface. Although these features clearly represent some of the material that was displaced, the composition and stoichiometry of the mounds could not be determined. Often no deposits were observed in the vicinity of the holes, and atomic scale images such as in Fig. 2 could be observed at the bottom of an etched area. In these instances, some of the etched material might have been deposited on the tip. If it deposited as the original oxide, this would be unstable toward further abrasive etching. If, however, the molybdenum oxide was reduced when transferred to the tip, it would be more stable than $Rb_{0.3}MoO_3$ and would permit continued abrasive etching.

The ability to engineer nanometer-sized objects on a surface has potential for important applications, primarily in the creation of electronic devices in which the size of the conducting, semiconducting, or insulating elements are in the range where quantum transport and confinement effects can be observed, controlled, and exploited (*8*). Two critical problems must be solved before most applications can be realized. First, the positioners must be able to rapidly move the tip or surface over a wide range of distances and to return to within 1 nm of the same position (on a typical surface this would require control of lateral distances over seven orders of magnitude). Second, one must be capable of reproducibly making strong sharp tips of a small (and preferably known) shape.

The STM can be used to image a conducting oxide with near atomic resolution and also to create stable nanometer-scale indentations on the surface.

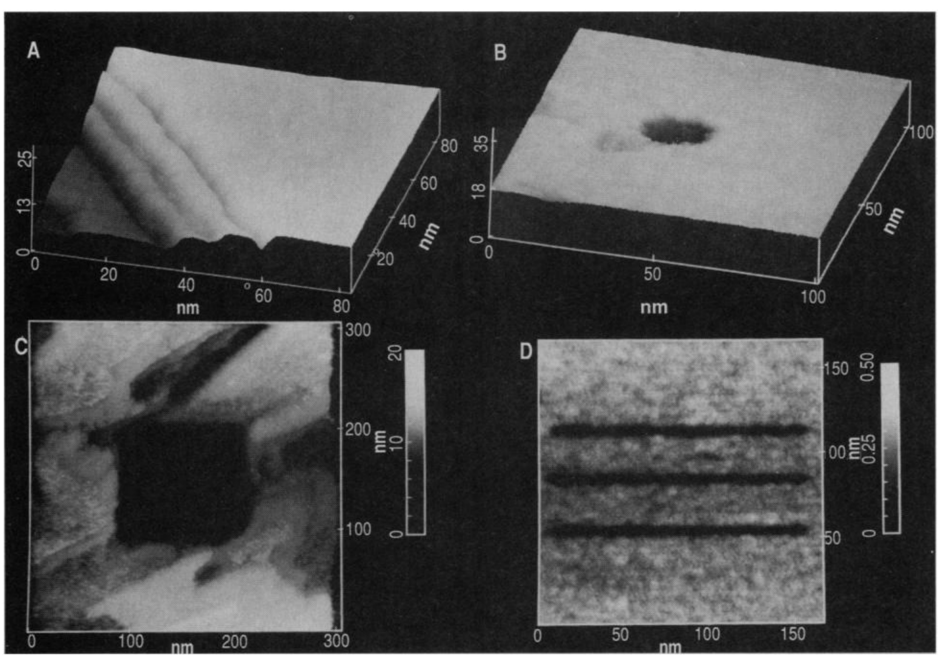

Fig. 3. (**A**) STM Image of single- and double-height steps on $Rb_{0.3}MoO_3$. Topographic image at −250 mV, 0.05 nA. In (B) through (D), the indentations were produced at 10-mV bias and 0.5-nA tunneling current conditions. (**B**) Hole abrasively etched in $Rb_{0.3}MoO_3$ sample by scanning a 10 nm by 10 nm area for 10 min. Topographic image obtained at +100 mV, 0.12 nA. (**C**) Square (100 nm by 100 nm) etched in $Rb_{0.3}MoO_3$ sample. Although the surface was rough prior to etching, the bottom of the square was quite flat. Topographic image at +275 mV, 0.12 nA. (**D**) Three lines etched by scanning across the surface in a single direction.

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