Field-induced surface modification on the atomic scale by scanning tunneling microscopy

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(Received 13 March 1992; accepted for publication 22 July 1992)

Scanning tunneling microscopy has been used to study the modification of tin diselenide ($SnSe_2$) and molybdenum disulfide (MoS_2) surfaces in ultrahigh vacuum. We have shown that there are positive bias voltage pulse thresholds that must be exceeded to remove material from the surfaces of $SnSe_2$ and MoS_2. The voltage threshold for modification of $SnSe_2$ ($+1.4$ V) is significantly smaller in magnitude than the threshold for modification of MoS_2 ($+3.5$ V). These threshold results and tip-sample distance dependence data suggest that modification occurs by field evaporation. Additionally, near threshold pulses create stable atomic sizes defects that can be erased by high voltage scanning.

Currently, there is an intense effort in the scientific community directed towards the development of scanning tunneling microscopy (STM) as a technique to modify and manipulate matter on the nanometer to atomic scale.[1-6] Promising results obtained to date with STM include: (1) the deposition of gold clusters,[1] (2) the removal and deposition of small silicon clusters,[2] and (3) the manipulation of single xenon atoms.[3] These data demonstrate the potential power of STM for modifying surface structure, however, additional studies are needed to explore new systems and to understand the physics of the modification process in greater detail.

Metal dichalcogenide materials are unique systems to investigate for modification since crystal cleavage reproducibly yields atomically flat and ordered chalcogenide surfaces,[7] and since the metal-chalcogenide bonding can be changed through variations of the metal and chalcogenide. Previous STM studies in air have shown that voltage pulses can be used to create ring-like structures and holes on WSe_2,[8,9] and that repeated scanning can remove material from surface defects.[9,10] While these results are interesting, they have not addressed the mechanism of modification. Herein, we describe new STM lithography studies of two metal dichalcogenide materials, tin diselenide ($SnSe_2$) and molybdenum disulfide (MoS_2), that were carried out in ultrahigh vacuum (UHV). Our data demonstrate for clean surfaces and tips that well-defined bias voltage thresholds must be exceeded to remove material from these surfaces, and that the modification threshold voltage is significantly greater for MoS_2 than $SnSe_2$. These results are consistent with electric field induced surface modification. In addition, near threshold pulses create stable atomic size defects that can be erased by high voltage scanning.

The experiments were carried out using a custom UHV-STM system with a working pressure of $\approx 3\times10^{-10}$ Torr. Crystals of $SnSe_2$ and MoS_2 were obtained from chemical vapor transport growth[7] and from natural sources (MoS_2). *n*-type and *p*-type MoS_2 and *p*-type $SnSe_2$ samples were used in these studies. The crystals were cleaved *in vacuo* prior to the start of an experiment. Images were acquired in the constant current mode using Pt-Ir alloy (80%–20%) tips; similar results were also obtained using clean W tips. Square wave bias-voltage pulses ($\leqslant 1$ ms) were used to modify the surfaces. The pulses were applied after opening the feedback loop and moving the tip ≈ 0.5 nm towards the sample surface.

Images of $SnSe_2$ and MoS_2 surfaces cleaved at $\approx 10^{-10}$ Torr are atomically ordered [Figs. 1(a) and 1(b)]. Both surfaces are also stable during repetitive imaging in UHV, and are thus ideal for modification studies. To this end we have investigated the effects of applying short voltage pulses between the sample and tip. In these experiments the feedback loop was stabilized for tunneling resistance of 10^8 Ω; this sets the relative tip-sample separation. Rectangular pulses 500 μs in duration were then applied after opening the feedback loop and moving the tip ≈ 0.5 nm towards the surface. We find that there are distinct pulse height thresholds to remove material from the surfaces of $SnSe_2$ and MoS_2. The modification threshold using the above pulse sequence is $+1.5\pm0.2$ V for $SnSe_2$ (bias relative to the sample) and $+3.6\pm0.3$ V for MoS_2.[11] Notably, we find that pulses applied close to these modification threshold values can remove single atoms from the surfaces of both materials [Figs. 1(c) and 1(d)]. Typically, holes consisting of 1–4 vacancies are produced on the $SnSe_2$ surfaces, although single atom vacancies can be made on the MoS_2 surfaces. Studies of WSe_2 showed previously that features can be made by bias-pulsing.[8,9] In one study pulsing induced a deformation of the lattice, but did not remove material from the surface.[8] A later study of WSe_2 showed that material could be removed from the surface, however, the features obtained in this work were $\approx 10\times$ larger than produced in the present investigations. Our new studies demonstrate that there is a threshold for producing atomic size holes, and that this threshold depends strongly on the nature of the metal-dichalcogenide material.

The distinct pulse height thresholds to remove material from the surfaces of these materials indicates that an electric field based mechanism is operative. This conclusion is further supported by the fact that similar amplitude pulses

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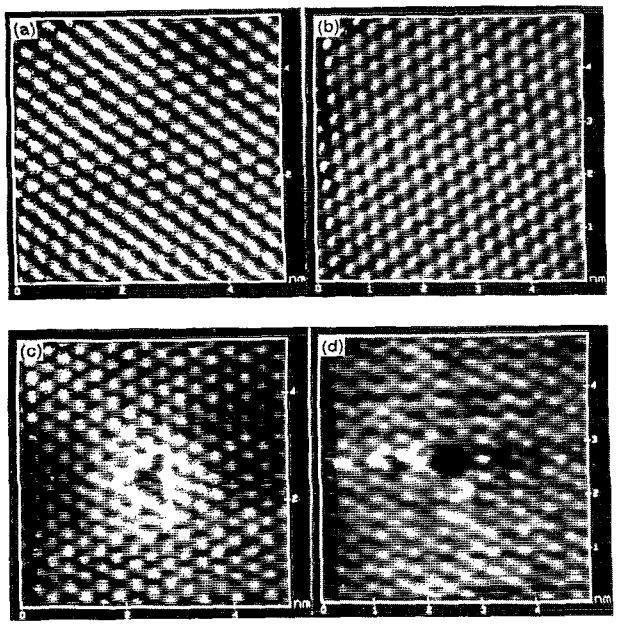

FIG. 1. Atomic resolution STM images of (a) $SnSe_2$ and (b) MoS_2 cleaved surfaces recorded in UHV. Image of the (c) $SnSe_2$ and (d) MoS_2 surfaces following the application of $+1.4$ V and $+3.5$ V pulses, respectively. The $SnSe_2$ images were recorded with a bias voltage of 50 mV and a tunneling current of 1 nA. The MoS_2 images were recorded with a bias of 200 mV and a tunneling current of 1 nA. The axes on these images are marked in nanometers.

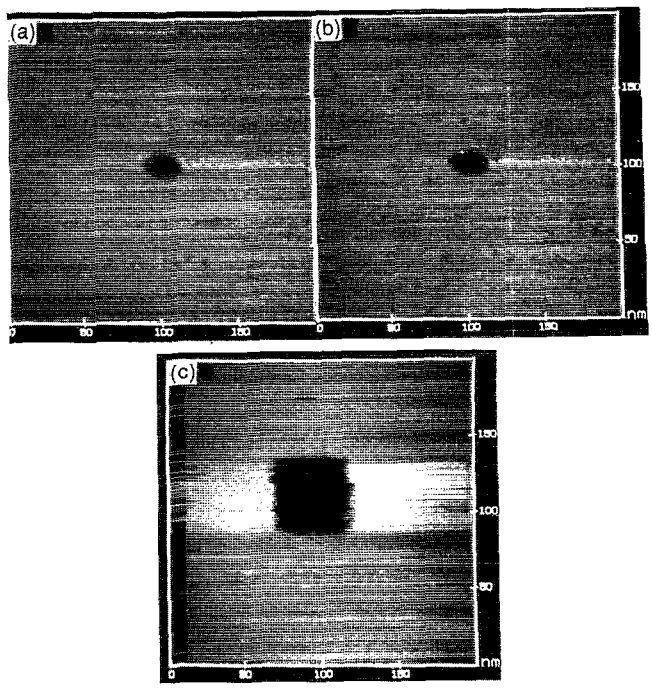

FIG. 2. (a) Image of $SnSe_2$ exhibiting a defect created by bias pulsing. (b) Image of the same surface area recorded after 1 h of scanning at 900 mV; the surface defect is unchanged by this scanning. (c) Image of the same surface region recorded after scanning a 50×50 nm^2 area in the image center with a bias of 1980 mV. This high bias scanning erases the defect by removing a layer of material within this 50×50 nm^2 scan window. Images (a), (b), and (c) are 200 nm$\times$200 nm and the axes are marked in nanometers

applied without moving the tip towards the surface do not modify the surface. Although we have not yet quantitatively mapped out the distance dependence of the threshold voltage, these data do suggest that the magnitude of the electric field is important in the modification process.[12] The most straightforward mechanism involving the electric field would be field evaporation of positive ions or clusters. This mechanism has recently been suggested to explain modification of Si(111) surfaces,[2] and is consistent with the distinct positive bias threshold that we observe. It is also possible that field emission of electrons from the tip and subsequent heating contribute to the modification process; however, it is unlikely that this is the dominant pathway since the threshold for modification of $SnSe_2$ and MoS_2 are so different. Studies designed to probe the possible role of field emission and local heating are currently in progress. These and other experimental and theoretical investigations will be needed to address fully the mechanism and energetics of modification.

It is important to note that the threshold for modification is significantly larger on MoS_2 versus $SnSe_2$. This observation is consistent with the substantially stronger Mo—S versus Sn—Se bonding in these materials, and recent atomic force microscopy (AFM) studies which show that tip-induced wear proceeds more slowly on MoS_2.[13] In addition, high bias voltage scanning (below) provides evidence supporting this conclusion. These results have several important implications. First, they suggest that the bias voltage pulsing technique can be used to assess (at least qualitatively) surface stability and the strength of surface-adsorbate bonds. Additionally, the material dependent modification thresholds indicate that material selective nanolithography will be possible in heterostructures derived from these solids.

Last, we find that these atomic size holes are stable under normal UHV imaging conditions.[14] These features can thus be envisioned as memory bits. This is not only a write-once/read-many-times type of memory since it also possible to erase the features by scanning at high bias voltages. Imaging $SnSe_2$ and MoS_2 at bias voltages >1.7 and >4.5 V, respectively, leads to the removal of MX_2 layers within the scan window in a layer by layer process (Fig. 2). The observation of a threshold for material removal when scanning further supports the intrinsic nature of the voltage pulse threshold discussed above. Because material removal at these high voltages occurs only if a surface feature/defect is present, it is possible to write (by pulsing) stable features that can be read by low bias voltage imaging, and then erase the system under high bias scanning. Since the erasing process ideally corresponds to the removal of a single layer (≈6 Å) a 1-mm-thick film could yields 10^6 cycles.

In conclusion, we have used an UHV STM to study the modification of $SnSe_2$ and MoS_2. We have shown that there are positive bias voltage pulse thresholds that must be exceeded to remove material from these surfaces, and that the threshold for modification of $SnSe_2$ is significantly smaller than MoS_2. Voltage pulses applied near threshold were also shown to create stable single atom defects on

both surfaces. In addition, our results indicate that material selective nanolithography could be carried out on metal dichalcogenide heterostructures and that erasable features can be written on these surfaces. Thus, we believe that the metal dichalcogenides should be considered further for STM-based lithography processes in the future.

We thank T. T. Tsong for communication of results prior to publication. C. M. L. acknowledges support of this work by the David and Lucile Packard Foundation, Air Force Office of Scientific Research, and Camille and Henry Dreyfus Foundation.

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