Nanostructuring on WSe$_2$ with the atomic force microscope by a potential controlled electrochemical reaction

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We present a method for the controlled fabrication of stable nanostructures under ambient conditions. The surfaces under consideration, WSe$_2$, are imaged by an atomic force microscope. By applying a voltage between the tip and the sample, we can control an etching process at the surface: different voltage thresholds for the creation and the growth of structures of one monolayer (Se–W–Se) depth are observed. Our measurements on p-doped WSe$_2$ strongly support an electrochemical corrosion reaction in a physisorbed water film. This method allows the *in situ* preparation and characterization of individual nanometer-sized structures on WSe$_2$ and other metal dichalcogenides. © *1996 American Institute of Physics.* [S0003-6951(96)00539-6]

During the past few years scanning probe techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been reported as useful tools to modify surfaces on a nanometer or even atomic scale.[1] In particular, it has been demonstrated that metal dichalcogenide surfaces are suitable for the fabrication of regularly shaped depressions, when being manipulated by a STM or AFM tip.[2-5] The depth of these depressions equals one single molecular layer; their lateral extensions are on a nanometer scale. On the layered semiconductor WSe$_2$, for example, triangular holes can be induced with their shape representing the triangular symmetry of a single molecular layer.[2] The manipulation of the surface has been achieved either directly by the tunneling voltage or an additional voltage pulse applied to the probing tip (in case of the STM)[2,3] or by varying the mechanical load of the AFM tip.[4,5] Although these manipulations have been shown to work successfully for several metal dichalcogenides, the origin and the details of the subsequent development of the induced structures are controversial. The mechanisms suggested are attributed either to the electric field, the electric current, or the direct mechanical tip–sample contact.[3,4]

Recently the influence of the electric field between a probing STM tip and the surface on the growth of induced triangular depressions on WSe$_2$ has been observed by Boneberg *et al.*[6] It has also been demonstrated that these structures could be generated successfully in ambient conditions but not, for example, in high vacuum conditions or in an atmosphere of dry oxygen. Therefore, the authors suggested an etching process, involving physisorbed water, induced by charge carriers, particularly holes (h^+), for the origin of these growing triangles:

$$WSe_2 + 9H_2O + 14h^+ \rightarrow WO_3 + 2SeO_3^{2-} + 18H^+. \qquad (1)$$
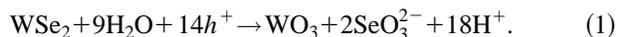
This reaction can be regarded as a two-stage process: First, water is oxidized toward free oxygen, which then reacts with WSe$_2$ toward soluble tungsten trioxide and selenite ions. Taking both reactions together WSe$_2$ is oxidized in the presence of a physisorbed water film. The presence of holes is provided by tip induced band bending.

In order to confirm this model, a detailed study of the voltage dependence of this process would be necessary. Unfortunately, STM-experiments are restricted in varying the electric field between tip and sample to those values that are appropriate for operating the STM. As a consequence, in the experiments mentioned above, the individual structures grew laterally during their observation. However, by using an AFM with a conducting cantilever, an electric field can be applied independently from the imaging process in contrast to the application of a STM. In the present study, we exploit this possibility in a first step to study the etching mechanism in detail and then to use this knowledge for creating individual nanostructures with preserved crystalline order.

The investigations were performed on p-type WSe$_2$ single crystals ($p = 10^{16}$ cm^{-3}), which have been grown using the vapor phase transport method.[7] The samples were mounted with conductive silver paste onto the sample holder and connected to a dc supply. All experiments were performed in air at room temperature using a home-built AFM setup[8] with highly doped Si cantilevers (spring constant $k = 0.07$ N/m). Working in the contact mode, the applied forces have been typically in the order of 1 nN. After cleaving the sample with an adhesive tape, the tip of our AFM was positioned on an atomically flat area of the surface.

Mechanical force induced etching phenomena on some metal dichalcogenides with the AFM had been reported by Parkinson and co-workers.[4] While etching had been observed on, e.g., TaS$_2$ and SnS$_2$, no etching occurred on WSe$_2$. Our experiments with applied forces up to 200 nN confirmed the results of Parkinson on WSe$_2$: we did not succeed in generating any structures mechanically.

In order to examine the influence of an electric field, we applied a bias voltage between the sample and the AFM tip during the scanning process (the cantilever was kept on ground potential). No changes of the surface topography could be observed up to a threshold voltage U_1 of (1.2 ±0.05) V. At this bias voltage, triangular structures started to grow at several sites on the surface (Fig. 1). Upon changing the bias below or above the threshold, the growth could be stopped or continued. Triangles that were not scanned with voltages above threshold could be observed for several months without changing their shape or size. At negative bias the surface structure remained undisturbed up to −7 V.
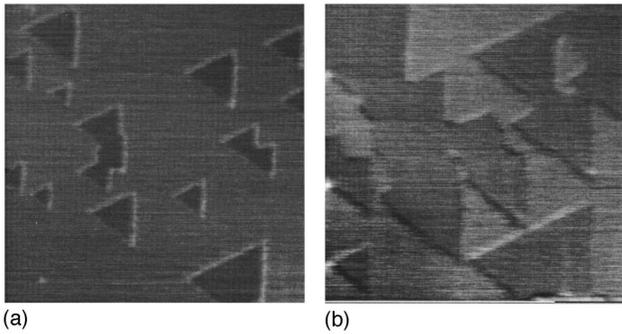
FIG. 1. Evolution of triangles of approximately 6.5 Å depth, corresponding to a single (Se–W–Se) layer, on a previously atomically flat area of WSe$_2$ induced by scanning with applied bias voltage. Image sizes: 500×500 nm^2.

FIG. 3. AFM image of a nanostructure on WSe$_2$ created by choosing the appropriate scan area and bias voltage. The line indicates the cross section. Image size: 400×400 nm^2.

Beyond this voltage the previously atomically flat surface was severely damaged.

In a first interpretation we supposed that this growth process starts at surface defects (e.g., missing atoms or dopant sites). Since we wanted to create structures deliberately at any site on the surface, we started the next experiments at areas where no growth had been observed even at voltages slightly above U_1 (implying that these areas were free of surface defects). This time the tip was positioned in the center of the scanning area and was not scanned during the application of the bias voltage. After applying the bias for several seconds (2 V for the example shown here) an image of the surface was taken. In contrast to the results of similar STM experiments, where a triangular *depression* evolved, and in contrast to the experiments above, an *elevated* triangular structure could be observed in the center of the picture [Fig. 2(a)]. The height of this triangle was about 21 Å. In opposition to the depressed triangles created in the experiments described before, this structure was found to be sensitive to mechanical abrasion. That means, by scanning the surface without any external bias, the material of the elevated triangle was ''wiped'' off the actual scan area. Using this technique the elevated structure could be completely removed, and at its former position a depressed triangle with the same lateral extension as the elevated one appeared. Its depth of 6.5 Å corresponds to one single molecular layer [Fig. 2(b)]. Once more we studied the voltage dependence of such a nucleation process and determined a nucleation
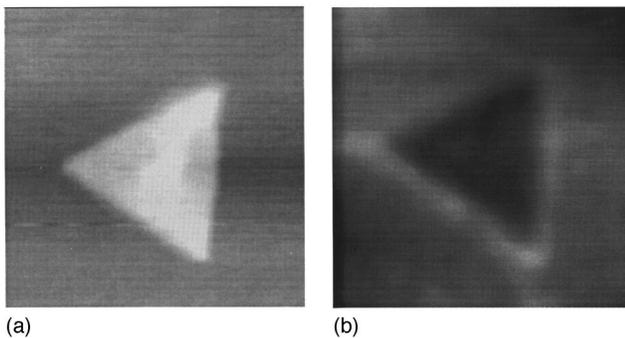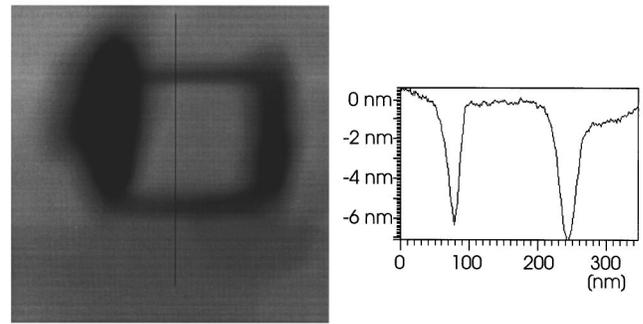

FIG. 2. Triangular structure on WSe$_2$ induced and imaged by an AFM: (a) directly after nucleation by applying a bias voltage of 2 V, and (b) after mechanical removal of the elevated structure by the AFM tip. Image sizes: 500×500 nm^2.

threshold U_2 of (1.5±0.1) V. The knowledge of this nucleation threshold enables one to nucleate triangular structures at any site of the surface.

In order to create individual nanostructures of not necessarily triangular but arbitrary shape, we used the result of previous STM measurements, which had shown that the growth is restricted to a certain area below the tip.[6] An example of a nanostructure created by choosing the appropriate scan area and bias voltage is shown in Fig. 3. This structure does not represent the crystal symmetry any longer, but we observed that its stability was comparable to that of the triangular ones.

Two mechanisms have been favored so far in the literature to explain the observed etching phenomena on metal dichalcogenides: (1) mechanical abrasion via direct sample–tip contact,[4] and (2) an electric field induced corrosion reaction.[6]

On one hand, our experimental results on the van-der-Waals surface of WSe$_2$ have clearly shown that in the force regime used here (1–200 nN) mechanical contact between tip and sample is not sufficient for creating any structures. As already mentioned above this behavior agrees with the measurements of Parkinson and Delawski.[4] Furthermore, we do not observe any mechanical abrasion even at steps.

On the other hand, the model that suggests a field induced electrochemical reaction at the WSe$_2$ surface is in agreement with our observations: etching occurs only at positive bias, where holes are accumulated at the surface region below the tip. In a next step, we want to show that the observed threshold voltages are determined by the energetic position of the band edges at the surface.

At first we are considering the nucleation of triangles with a bias voltage applied at a fixed tip–sample contact. The corrosion reaction (1) described above will start if (a) holes (h^+) are accumulated at the surface according to a suitable band bending, and if (b) their energy is equal to or higher than the redox potential of the reaction $H_2O + 2h^+ \Leftrightarrow O + 2H^+$, (−5.7 eV with respect to the vacuum level). However, without an external bias the position of the valence band edge is at about −5.4 eV (Ref. 9) and, therefore, the latter condition is not fulfilled.

Upon contact between tip and sample the work function at the samples' surface is altered as the contact potential induces additional band bending and/or changes in electron

affinity (neglecting effects such as Fermi level pinning). From our measurements of the contact potentials between several tip and sample combinations, we deduce the Fermi level of the tip to (-4.4 ± 0.2) eV with respect to the vacuum level.[10] Thus, the minimum bias voltage for starting the electrochemical reaction has to be in a first approximation the difference between the Fermi level of the tip and the redox potential of the water reaction, that is (1.3 ± 0.2) V. This value agrees well with the measured threshold bias for nucleation U_2 of (1.5 ± 0.1) V. As this value is directly determined by the Fermi level of the tip, any change of it should lead to a different threshold bias in a predictable manner. In recent experiments we used Pt/Ir coated tips with a Fermi level of (-5.0 ± 0.1) eV (Ref. 10) to study the nucleation of these triangles. In this case, we determined the threshold bias for nucleation U_2 to (0.9 ± 0.1) V, which suits very well to the predicted value of (0.7 ± 0.1) V.

Of course, this consideration on the band scheme is simplified, because it does not take into account the influence of Fermi level pinning, electric current, reaction products or Helmholtz double layer on the band structure, and the position of band edges. Nevertheless, it is a first approximation that principally allows an understanding of the experimental findings.

For defects and steps existing on the surface of a layered semiconductor as WSe$_2$ it is generally assumed that the electron affinity is altered and/or additional band bending is induced, leading to an accumulation of holes at the disturbed surface.[11] Therefore, the threshold bias for the growth U_1 of existing triangular depressions should be lower than for their nucleation, as measured.

We have shown so far that the proposed model of an electrochemical etching process satisfies the experimentally observed threshold voltages for structuring the surface. The nature of the elevated triangles formed during the nucleation process is not completely clear so far. From macroscopic corrosion experiments performed in electrochemical cells, it is well known that the reaction products are tungsten oxides of different stoichiometry.[12] Therefore, we suppose that these elevated triangles are formed by low conductive tungsten oxides. This assumption is supported by the fact that elevated structures have never been observed in STM measurements.

To summarize, we have demonstrated a method for creating nanostructures with the AFM on WSe$_2$. The advantages of these nanostructures are their stability even during observation and the possibility of fabricating artificial nanostructures of any shape but with preserved crystalline order just by choosing the appropriate scan area and applied voltage. We believe that the proposed electrochemical corrosion reactions can be utilized to create nanostructures on a wide class of layered metal dichalcogenides because of their similar chemical behavior. Thus, a simple method for the creation of nanostructures in ambient conditions is provided.

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