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Real-space imaging of single-layer MoS_2 by scanning tunneling microscopy

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Single layers of MoS_2 have been studied with a scanning tunneling microscope operating in air. The images obtained from films that were prepared by depositing an aqueous suspension of single-layer MoS_2 on a graphite surface show that the unit cell of the single layers corresponds to an approximate $2a_0 \times a_0$ superlattice of the hexagonal $2H$-MoS_2 structure. The unit-cell parameters, in conjunction with previous measurements, imply that the single layers of MoS_2 adopt a distorted octahedral structure. The image of dry restacked MoS_2 transforms back to the hexagonal MoS_2 pattern.

Molybdenum disulfide is a compound semiconductor, consisting of S-Mo-S sandwich layers.[1] In crystalline $2H$-MoS_2, each Mo atom is coordinated by six S atoms in a trigonal prismatic arrangement. The nearest layers are weakly connected with van der Waals bonds so that it is very easy to break these bonds by simply "pulling" off layers to obtain an atomically flat surface, or to intercalate guest atoms between the MoS_2 sandwiches. Recently, it has been shown[2,3] that single molecular layers of MoS_2 can be obtained by exfoliation of lithium-intercalated MoS_2 powder in water. The exfoliated single layers are then "washed" and suspended in water. As an aqueous suspension of single-layer MoS_2 ages, it forms into restacked MoS_2 with two monolayers of water present between parallel but rotationally disordered MoS_2 layers. Such a water bilayer phase may exist for several days at room temperature in air.[3] Detailed studies of the resulting MoS_2 have been performed to examine whether the structure of such alternate forms of MoS_2 are the same as bulk $2H$-MoS_2. Extended x-ray-absorption fine-structure (EXAFS) spectroscopy investigations[3] found two distinct Mo-Mo distances of 2.8 and 3.8 Å for single-layer MoS_2 in suspension, and that the $2H$-MoS_2 lattice constant of 3.16 Å reappeared in the water bilayer MoS_2. The same experiments found that the Mo-S distance in both single-layer aqueous suspensions and water bilayer form is essentially unchanged from that of $2H$-MoS_2. Since EXAFS basically reveals local structural information around individual atoms, the overall structure of the material could not be inferred from the results. X-ray diffraction and Raman-scattering results[4] show that both single-layer MoS_2 in suspension and water bilayer MoS_2 have a structure in which the Mo atoms are octahedrally coordinated in contrast to the trigonal prismatic coordination that pertains in $2H$-MoS_2. In addition, evidence was obtained[4] for the existence of a $2a_0$ superlattice. The question of whether it is 2×2 or 2×1 superlattice is still left uncertain, because both structures would yield a similar x-ray-diffraction pattern and Raman spectra. In dry restacked MoS_2, the structure transforms back to the trigonal prismatic coordination of Mo atoms with the bulk $2H$-MoS_2 lattice constant, and the layers can exhibit partial rotational disorder.[3,4]

In this work, we present atomic resolution images of restacked MoS_2 surfaces that were obtained with a scanning tunneling microscope[5] (STM) operating in air. The real-space image of a water bilayer MoS_2 surface shows a 2×1 superstructure directly and unambiguously. The image of a dry restacked MoS_2 film shows the same structure as that for crystalline $2H$-MoS_2, in good agreement with other experiments previously reported.[3,4]

The preparation of single-layer MoS_2 in suspension has been described previously.[2] In order to form a thin, flat restacked film suitable for imaging the MoS_2 basal plane, a graphite substrate has been used to provide good electrical contact to the MoS_2 layers. The sample electrode is then placed on the graphite, and a tiny drop of the single-layer MoS_2 suspension is spread out on the freshly cleaved surface of the graphite. After a few minutes the drop has adopted a quasiequilibrium configuration with the MoS_2 layers restacked in the water bilayer phase. The thickness of the film is of the order of 10 monolayers of MoS_2 as estimated from the concentration of the single-layer suspension. The sample was imaged within a few hours after preparation. The reason we have selected graphite as the substrate is because it is very inert and it is easy to obtain large regions that are atomically flat. This results in an almost ideal substrate for operating the STM in air, and for obtaining a rather flat restacked MoS_2 film. Since the sample has a bilayer of water between the MoS_2 layers, an ultrahigh-vacuum environment would not be appropriate for such observations. In order to make dry restacked MoS_2, the drying process is accelerated by heating the sample, including the graphite substrate, at 100 °C in a vacuum of $\sim 10^{-3}$ Torr for 5 h.

The STM head used in our experiments was built by Jericho *et al.* at Dalhousie University.[6] The tip holder is fixed on a rigid tripod configuration and its movements are controlled with three piezoelectric bimorphs. The sensitivities of the x and y bimorphs were calibrated using graphite images and were about 8.8 Å/V and 10.3 Å/V, respectively. The sample is glued onto a thin glass plate to insulate it from the sample holder, and then mounted on the horizontal face of the holder with 5-minute epoxy. The feedback circuit is basically the same as that shown in Ref. 6, and a commercial tip scanning circuit and computer software for data acquisition and presentation were used.[7] The commercial 0.25-mm $Pt_{0.8}Ir_{0.2}$ tips[8] were used either directly or after a mechanical resharpening treatment. Every tip was gently washed with 2-propanal before use.

Before imaging the restacked MoS_2 film, we first op-

erated our STM system on a single crystal of $2H$-MoS_2 which was mined in Norway. Figure 1(a) shows the raw data of a gray scale current image of the $2H$-MoS_2 surface, which is taken in the constant-height mode with a positive tip bias of 302 mV (sample virtually grounded), an average tunneling current of 1.2 nA and a scan rate of 1774 Å/sec. The brightness in the image reflects the variation of the tunneling current. The image consists of an array of bright spots with the expected sixfold symmetry. The measured lattice constant is $a_0 = 3.1 \pm 0.1$ Å, which is in good agreement with the crystallographic value of 3.16 Å.[9] The deviation from the ideal hexagonal pattern that is apparent in the figure results from the different x and y scales of the screen from which the photograph was taken. To obtain the lattice constants given in this paper the patterns were calibrated using graphite images.

There are differing opinions that have been published[10,11] on whether the $2H$-MoS_2 image reflects the surface sulfur layer, or the metal layer underneath. This controversy arises because both the S atoms in the top surface layer and the Mo atoms in the middle of the first sandwich appear in equal numbers, and the atomic structures for both layers have the same symmetry. Consequently, an image of either Mo or S atoms would have the same pattern with the same lattice constant. The structure of water bilayer form of restacked MoS_2, however, as indicated by the results of previous experiments,[3,4] is very different from single-crystal $2H$-MoS_2.

Figure 1(b) is a current image of a water bilayer MoS_2 surface, taken with a positive tip bias of 42 mV, an average tunneling current 2 nA and a scan rate of 1830 Å/sec. The image clearly shows an approximate 2×1 structural pattern with a basal plane unit cell containing two bright spots. Previous studies on this material, including x-ray diffraction and Raman scattering, have indicated that there is a $2a_0$ superstructure, but the exact pattern of the structure could not be obtained by either method. The STM image allows us to see the real-space 2×1 form of the lattice directly and unambiguously. The sample has been scanned in perpendicular directions to ensure that the 2×1 pattern is not due to a tip effect. Also, the structure was found to be independent of tip bias polarities. The sample surface was not parallel to the tip scanning plane as indicated by the decrease in image intensity as one moves to the right in the image.

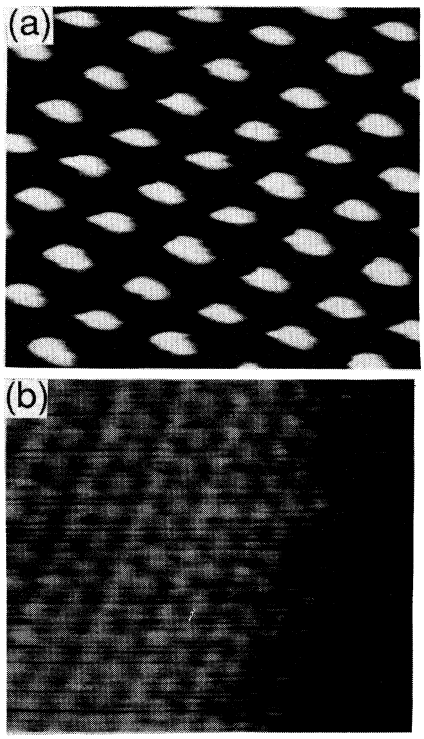

FIG. 1. (a) A constant-height image (~18 Å horizontal by 20 Å vertical) of single-crystal $2H$-MoS_2. (b) A constant-height image (~40×33 Å) of a water bilayer MoS_2 surface. A stripelike 2×1 superlattice structure is apparent.

Figure 2(a) is an image of another sample with the same experimental conditions as for Fig. 1(b). It appears that the surface was not tilted with respect to the tip scanning plane in the central part, but was bent down slightly at both right- and left-hand sides of the image. By superimposing a grid on the image as shown in Fig. 2(b), the 2×1 superlattice is more obvious. The image pattern including the unit cell is presented in Fig. 2(c). After calibrating a number of images obtained from this sample at different surface locations, we measure the lattice parameters as $|\mathbf{a}| = 3.2 \pm 0.1$ Å, $|\mathbf{b}| = 6.1 \pm 0.2$ Å, and $\theta = 53 \pm 1°$. Comparing the lattice constant $a_0 = 3.1 \pm 0.1$ Å obtained from imaging the $2H$-MoS_2 crystal surface as shown in Fig. 1(a), we find that $|\mathbf{a}| \approx a_0$ and $|\mathbf{b}| \approx 2a_0$, hence further confirming the $2a_0 \times a_0$ superlattice structure of the freshly restacked MoS_2 surface. However, notice that the measured θ is about 53°, and thus the $2a_0 \times a_0$ pattern cannot be simply considered as a superlattice of the hexagonal basal plane structure of $2H$-MoS_2 where θ should be 60°.

Figure 2(d) shows a current image of completely dry restacked MoS_2, taken at a positive tip bias of 1 V, an average tunneling current of 2 nA and a scan rate of 3627 Å/sec. The image clearly shows the appearance of the hexagonal structure without any trace of the 2×1 superlattice. The lattice constant is measured to be 3.1 ± 0.1 Å which is in good agreement with the crystallographic value of 3.16 Å, confirming that the trigonal prism layers have been recovered. This result agrees very well with that of previous experiments.[3,4]

We believe that the STM images shown in Fig. 1(b) and Fig. 2(a) reflect the atomic structure of a single layer of MoS_2 at the top surface of the water bilayer phase MoS_2 film. The second MoS_2 layer from the top surface has very little effect on the tunneling image, since there are two monolayers of water between each of the MoS_2 layers which are parallel to each other but rotationally disordered,[3] and our STM observations on different samples and different surface locations of a sample all show the same 2×1 superlattice. Therefore, it is most likely that the structure of the single-layer MoS_2 in suspension has basically the same pattern as that shown in Fig. 1(b) and Fig. 2(a). As Raman-scattering experiments[4] have shown one obtains identical superlattice modes for both single-layer MoS_2 in suspension and a water bilayer MoS_2

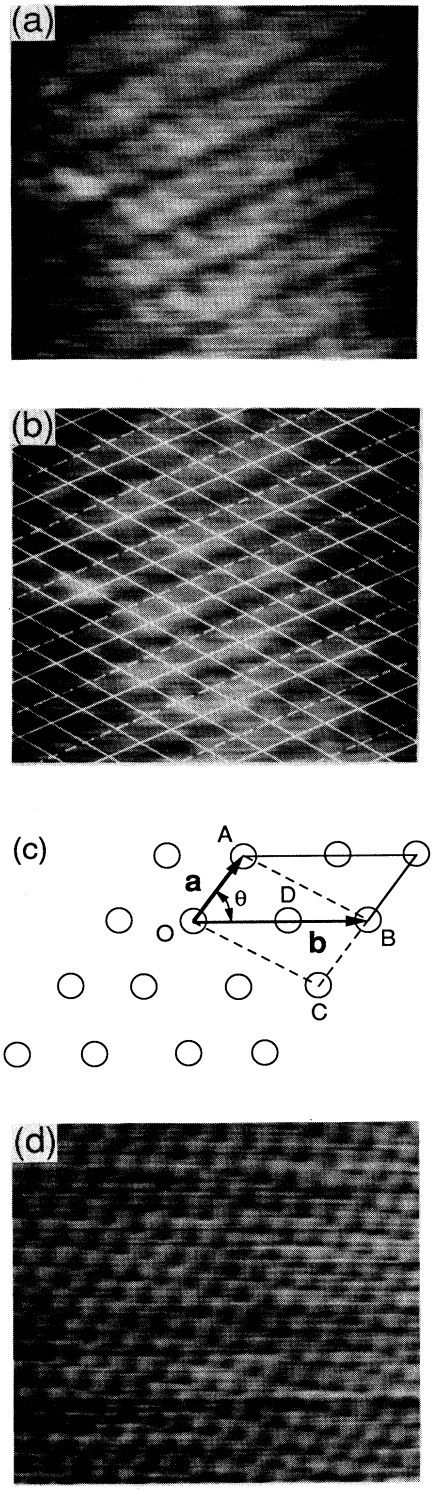

FIG. 2. (a) A constant-height image (~38×30 Å^2) of another water bilayer MoS_2 sample. (b) The same image with a grid superimposed. (c) Schematic representation of the image pattern shown in (a). The open circles represent the bright spots in the current images. The $2a_0 \times a_0$ unit cell is outlined with solid lines. The dashed lines show an alternative definition of a unit cell. (d) A constant-height image (~46×41 Å^2) of a dry restacked MoS_2 surface.

film. EXAFS results for the Mo-Mo distances, 3.8 and 2.8 Å, are also obtained from both forms.[3] However, the structure may not be exactly the same for the two cases due to slightly different water environments. As was shown in the EXAFS experiments, the bulk lattice constant 3.16 Å, which is not observed in the single-layer suspension, reappears in the water bilayer form.[3]

Comparing EXAFS results with our STM measurements for freshly restacked MoS_2, one obvious aspect is that the single-crystal $2H$-MoS_2 lattice constant has been found by both methods. It is more difficult to find a direct correspondence between two nearest Mo-Mo distances 3.8 and 2.8 Å obtained by EXAFS and the lattice constants determined from the STM images. Since the STM probes the local electron density of states around the Fermi level of the surface,[12] the bright spots in the current image do not necessarily correspond to the positions of individual atoms of the surface. On the other hand, the STM image must reflect the projection of the real lattice. As one can tell from Fig. 1(b), the image can be viewed as an array of two rows of spots not quite identical in size and brightness. One possible reason is that the surface is periodically buckled. Combining the $2a_0 \times a_0$ pattern with $\theta = 53°$ measured by STM with the three nearest Mo-Mo distances (3.16, 3.8, and 2.8 Å) given by EXAFS, we can construct a model for the unit cell which is shown in Fig. 3. For $\theta = 53°$, $\overline{OA} = |\mathbf{a}|$, and $\overline{OB} = |\mathbf{b}|$ measured by the STM to be consistent with the Mo-Mo distances measured by EXAFS, one row of Mo atoms has to be displaced vertically by $h = 0.9$ Å. The D' point on the projection plane is then slightly displaced (~0.05 Å) from the $\overline{OB}$ line according to the model. Such a small difference is hard to detect in the STM images shown in Fig. 1(b) and Fig. 2(a). Also, the projected lines $\overline{AD'} = 3.04$ Å and $\overline{D'C} = 2.65$ Å (shown in Fig. 3) calculated with $h = 0.9$ Å are in agreement with the lengths $\overline{AD} = 3.0 \pm 0.1$ Å and $\overline{DC} = 2.6 \pm 0.1$ Å [shown in Fig. 2(c)] measured with the STM.

It is known that WTe_2 possesses a distorted octahedral layer structure,[13,14] whose basal plane projection is similar to the structure shown in Fig. 2(c). In the WTe_2 structure the adjacent rows of W atoms are displaced by 0.21 Å.

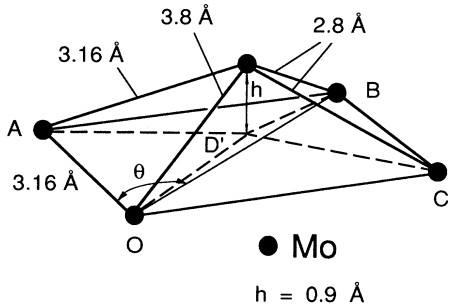

FIG. 3. Schematic 3D model for consistency between results obtained from STM and EXAFS. The solid lines represent the unit cell of Mo atoms based on the bond distances obtained by EXAFS. The dashed lines represent the projections of the corresponding solid lines in the projection plane, where $\theta = 53°$, $\overline{OA} = |\mathbf{a}| = a_0$, and $\overline{OB} = |\mathbf{b}| = 2a_0$, as given by STM.

With the unconstrained single-layer MoS_2 a larger distortion than that found in crystalline WTe_2 is not unreasonable. If it is assumed that the STM images reflect the relative positions of the Mo atoms, an h value of 0.9 Å must be considered to be very large. For example, one might expect a 0.9-Å layer corrugation to result in a current varying by about 1 order of magnitude for a clean tip and surface.[15] However, the possibility of a 0.9-Å corrugation cannot be ruled out. Since we operate the STM in air, contamination on the tip and the sample surface can reduce the effective tunnel barrier height,[15] hence a 0.9-Å corrugation may result in a current variation much less than 1 order of magnitude. Such effects thus make it very difficult to draw any conclusions from the images [Fig. 1(b) and Fig. 2(a)] about the relative heights of adjacent atomic rows and any variation in relative heights that might be suggested by a comparison of different images. On the other hand, it is perhaps possible that the S atom planes are less rippled than the Mo atom planes. The STM images could then be interpreted as support for the view that tunneling is occurring between the tip and the surface sulfur atoms. Additional experimental evidence will be required to resolve this question.

In conclusion, STM observations in air have been carried out on single MoS_2 layers separated by a bilayer of water molecules. The atomic resolution images clearly show an approximate 2×1 superlattice structure for the single layer of MoS_2 at the top of the film surface. One of the basal plane lattice constants is found to have the same value as the bulk $2H$-MoS_2 case, and the other one is about twice that of the bulk value. After drying by heating or aging, the atomic arrangement of restacked MoS_2 layers transforms back to the bulk hexagonal trigonal prism structure.

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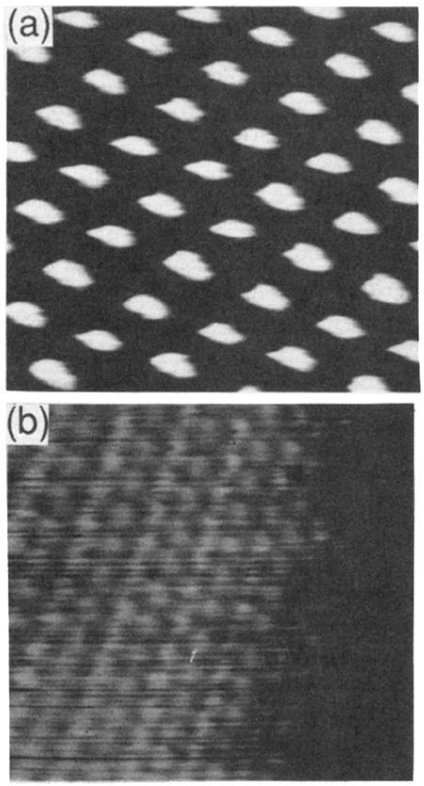

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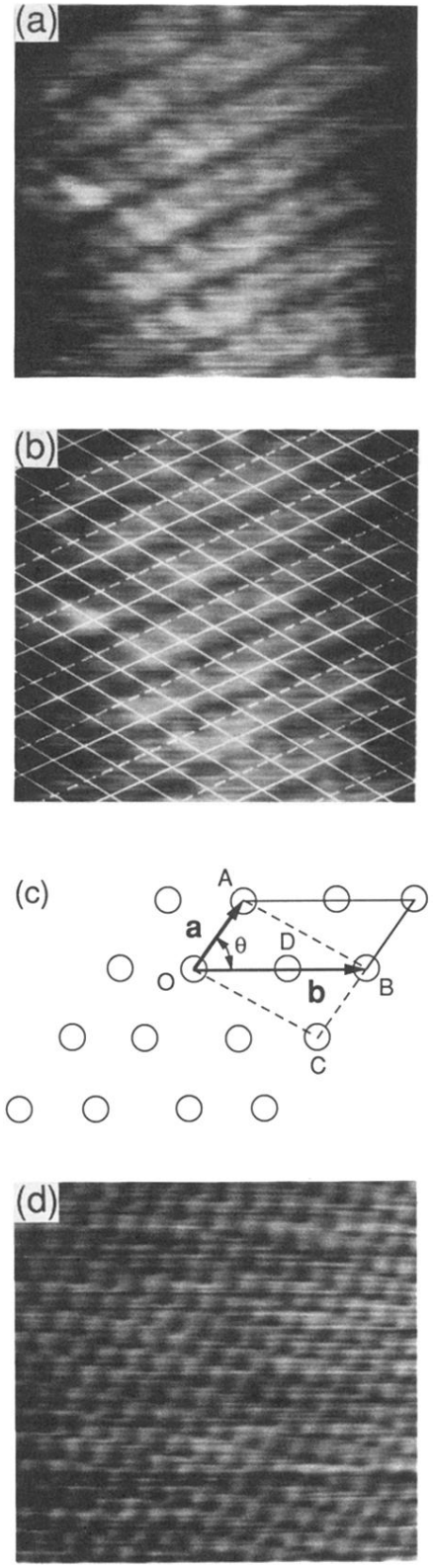

FIG. 2. (a) A constant-height image ($\sim 38 \times 30$ Å^2) of another water bilayer MoS_2 sample. (b) The same image with a grid superimposed. (c) Schematic representation of the image pattern shown in (a). The open circles represent the bright spots in the current images. The $2a_0 \times a_0$ unit cell is outlined with solid lines. The dashed lines show an alternative definition of a unit cell. (d) A constant-height image ($\sim 46 \times 41$ Å^2) of a dry restacked MoS_2 surface.