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Observation of a phase transition from the T phase to the H phase induced by a STM tip in $1T$-TaS$_2$

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We have fabricated an H-phase TaS$_2$ crystal in the surface layer of a T-phase TaS$_2$ single crystal using a scanning tunneling microscope (STM) tip. After applying a relatively high bias voltage to the STM tip, we observed a significant change of the surface indicating the formation of the H phase near the exposed region. The STM image shows the characteristic triangular phase boundary between the original T phase ($\sqrt{13}\times\sqrt{13}$ charge-density-wave superstructure) and the newly fabricated H phase (a triangular atomic lattice). Around the phase boundary, the local distortions of the $\sqrt{13}\times\sqrt{13}$ charge-density-wave superstructure have also been observed. The high-resolution STM image near the phase boundary suggests a sliding of the surface S atomic sheet by the STM modification procedure. [S0163-1829(97)50248-7]

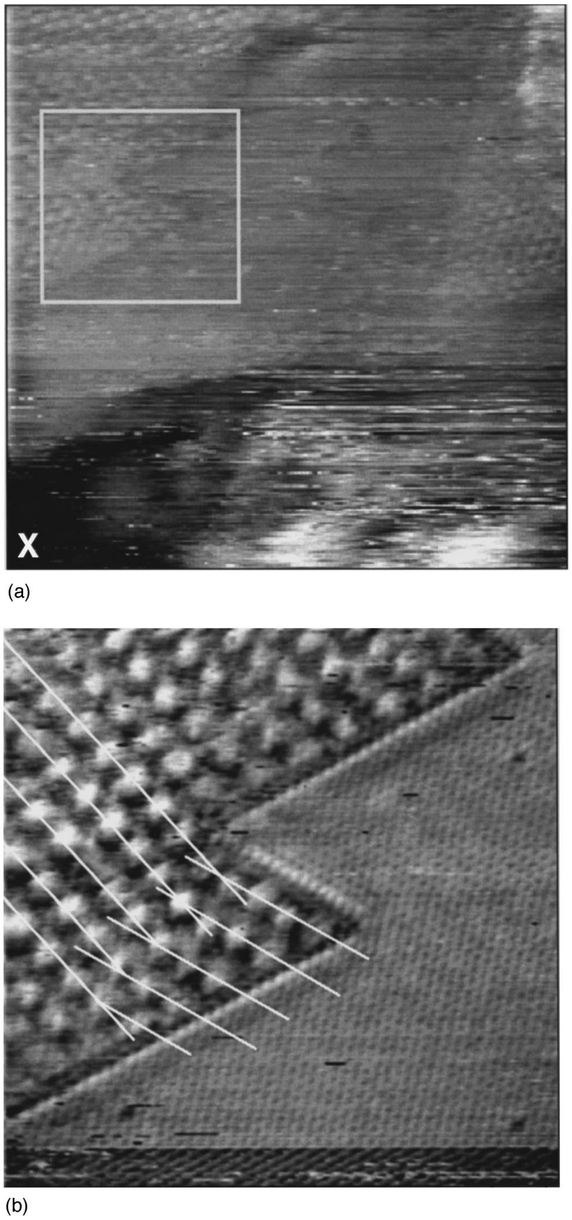
The scanning tunneling microscope (STM) represents a unique tool for controlling and modifying atomic- and nanometer-scale structures on the surface. The typical atomic-scale surface modification processes are the material transfer between tip and sample, which can extend to one-by-one removal or replacement of atoms on the surface, that can be driven by various physical and chemical mechanisms including field evaporation,[1,2] mechanical contact,[3,4] Joule heating,[5] and chemical reaction.[6,7] The STM has also been used to manipulate individual atoms and molecules into structures and to probe quantum-mechanical behaviors in nanostructures.[8]

Recently Zhang *et al.*[9] described an interesting surface modification process. They observed the well-defined crystal to crystal transformation induced by a bias voltage applied to a STM tip in the transition metal dichalcogenides (TMD's) $2H$-TaSe$_2$ crystals at liquid helium temperature. The transformation was accomplished through the collective motion of many chalcogen atoms at once, which is completely different from the surface modification mechanisms reported so far, as described above. This crystal to crystal phase transition might be closely related to the inherent layered structure of TMD's.

In this paper, we report a crystal to crystal phase transition from the T phase to the H phase induced by a STM tip in $1T$-TaS$_2$ at room temperature, which is completely the reverse of the results of Zhang *et al.*[9] After applying a high bias voltage to the STM tip, we have fabricated the H-phase TaS$_2$ crystal in the surface layer of a $1T$-TaS$_2$ single crystal. The STM image shows the characteristic triangular phase boundary along the crystallographic directions. High-resolution STM measurements near the phase boundary suggest that the H-phase crystal formation results from a coherent shift of the surface S atomic sheet. Near the triangular phase boundary, local distortions of the $\sqrt{13}\times\sqrt{13}$ charge-density-wave (CDW) superstructure have also been observed.

Single crystals of $1T$-TaS$_2$ were grown by the usual iodine transport method. The samples were cleaved in air and transferred to the UHV-STM chamber. The vacuum pressure was about 1×10^{-10} Torr. Electrochemically polished Pt/Ir tips were used. All STM images were obtained in the constant current mode at room temperature. Most areas of the cleaved surfaces are atomically flat. The STM images on this surface show the $\sqrt{13}\times\sqrt{13}$ CDW structures with a period of about 13 Å. Domain structures with a period of 80–85 Å were observed, indicating that the sample is in the nearly commensurate phase.[10]

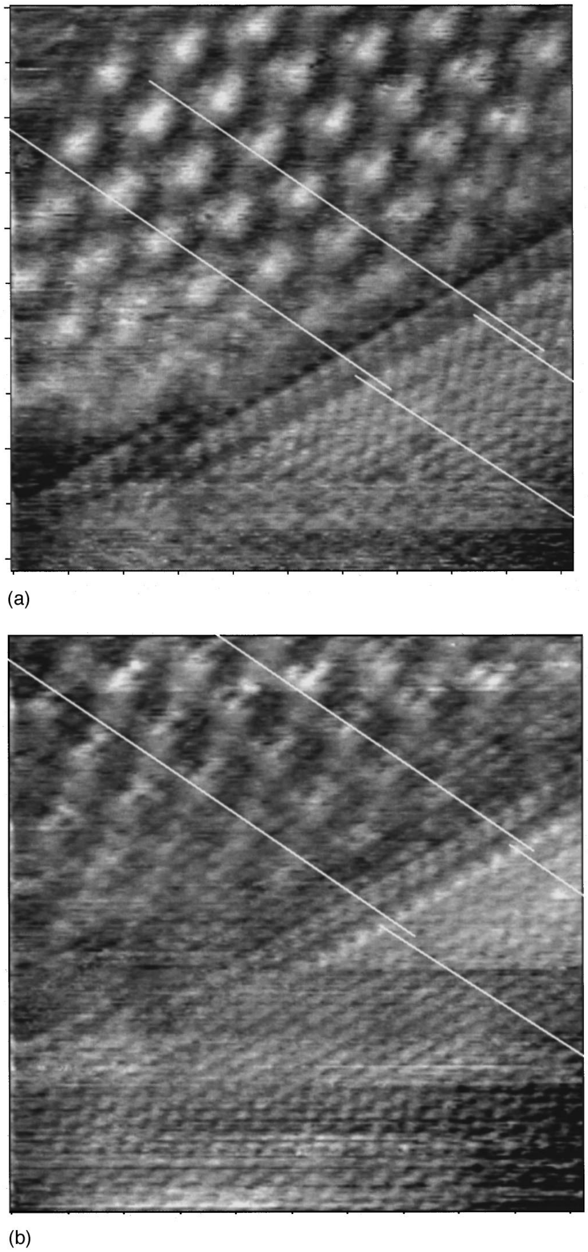
The surface modification procedure is as follows. After scanning the surface, we momentarily stopped a STM tip and suddenly raised the bias voltage up to -10 V from the imaging bias voltage (typically ~-20 mV) for 0.5–1 ms. Then, the same area was imaged to record the surface modification. Figure 1(a) is a STM image of the crystal surface after the surface modification process. Originally, this surface was atomically flat with a well-developed $\sqrt{13}\times\sqrt{13}$ CDW structure. Near the exposed region, one can see a dark region where the whole layer TaS$_2$ is removed, possibly due to the sublimation induced by an electron bombardment.[11] Around the dark region, one may notice two distinct regions in Fig. 1(a). The upper right and left regions of the picture show a strong $\sqrt{13}\times\sqrt{13}$ CDW modulation with a periodicity $\sim$13 Å, whereas rather a flat surface with no CDW structure is visible in the middle part of the figure. Figure 1(b) is a higher-resolution image recorded over the square region drawn in Fig. 1(a). In this image, we can see a triangular atomic structure with a lattice constant $\sim$3.3 Å near the exposed region and also identify a clear phase boundary with a



(a)

(b)

FIG. 1. (a) The STM image after applying a bias voltage of -10 V during 0.5 ms. The tip position was designated by the cross mark. The imaging current and bias voltage were 2 nA and -25 mV, respectively. The image size is 357×357 Å. (b) The high-resolution zoomed image designated by the square in (a). The image size is 128×128 Å.



(a)

(b)

FIG. 2. (a) The high-resolution STM image near the phase boundary. The sample current and bias voltage were 1 nA and -50 mV, respectively. (b) STM image with a bias voltage of -10 mV. The image sizes are 77×77 Å.

well-defined angle (~60° or 270°) between two regions. From the cross-sectional analysis, it was confirmed that there is no abrupt step across the boundary. These observations suggest that the $1T$-phase crystal with $\sqrt{13}\times\sqrt{13}$ CDW structure changes into the $2H$ crystal, which is known to show no CDW deformation at room temperature. The structural changes start to occur at ≈ -8–9 V and the size of the H-phase crystal at -10 V varies from 100 to 500 Å. We have observed the structural change reproducibly around the exposed region.

Figure 1(b) also shows that the CDW structure is strongly distorted near the corner region of the triangular phase boundary. The white solid lines in Fig. 1(b) are ruled along the rows of CDW maximum position. One may notice that the CDW tends to align along the phase boundary, and to rotate by the angle of 13°–15° in the corner with respect to the undistorted CDW lattice. A reasonable explanation for this distortion would be related to CDW twin structures that arise from the fact that the CDW superlattice can be oriented clockwise or counterclockwise to the atomic lattice. In room temperature, the CDW lattice in $1T$-TaS$_2$ is not commensurate with the atomic lattice as mentioned earlier so that it can be easily pinned by discontinuity at the interface. Hence CDW can rotate 14° in the corner. Near the triangular boundary, CDW lattice could rearrange to make a stable phase boundary with relatively little energy cost.

To clarify the structural change after the surface modifi-

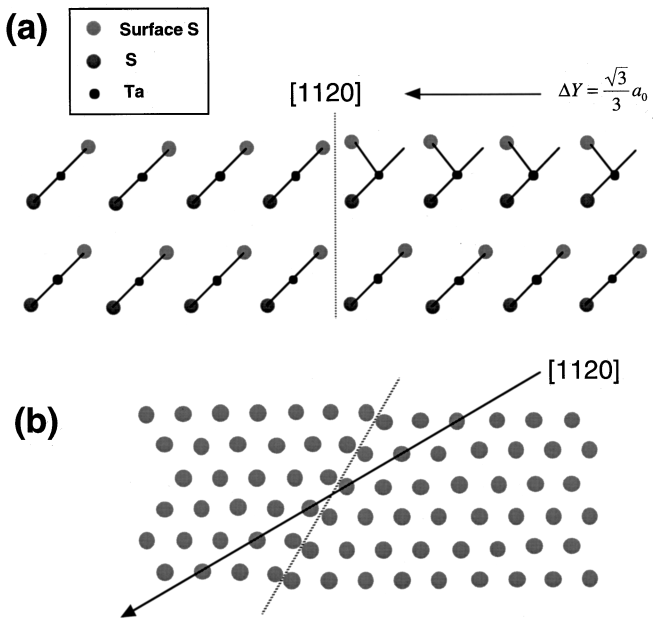


FIG. 3. (a) The schematic crystal structure near the T- and H-phase boundary along [1120] section. The surface S atom sheet slides coherently along the [1120] direction and stops to make a phase boundary. (b) The surface S atom configuration at the interface predicts that the surface S rows between the T and H phase should have a $(\sqrt{3}/6)$ fraction of a lattice constant mismatch [$\sim$1 Å at the interface (Ref. 9)]. One of the most effective ways to convert the T to the H phase is through a collective motion of S atoms by $(\sqrt{3}/3)$ of the lattice constant along the [1120] direction.

cation process, we obtained the high-resolution images near the phase boundaries. Figure 2(a) shows an example of the phase boundary images taken with a bias voltage of -50 mV and a tunneling current of 1 nA. It is well known that $1T$-TaS$_2$ exhibits a very strong $\sqrt{13}\times\sqrt{13}$ CDW which is rotated about 14° relative to the underlying atomic lattice with a lattice constant $\sim$3.3 Å. As can be seen from Fig. 2(a), the CDW superlattice in the upper left region is rotated about 14° in the lower right region. This implies that the atomic lattices in both the modified and the original T phases have almost the same spacing and orientation. The STM image obtained with a lower bias voltage of -10 mV, as shown in Fig. 2(b), clearly exhibits that both regions have the same crystal structure. Furthermore, the existence of the clear phase boundary suggests that there should be a mismatch of the surface S atom positions between two regions. From Fig. 2(b), in fact, it can be seen that the two lattice rows along the phase boundary were dislocated, and seem to act as buffer rows between the T and H regions.

Further detailed analysis of Figs. 2(a) and 2(b) shows a relative shift in the atomic lattice across the interface between the two regions. The lines drawn along the corresponding atomic lattice rows in two regions turn out to be parallel to each other, but are displaced by a fractional value with respect to the lattice constant, as shown in Fig. 2. Thus, the T-H structural phase transition is naturally understood by assuming that a surface S atomic sheet is shifted in a coherent manner by a certain distance.[9] Considering that the H-phase TaS$_2$ has the same surface structure as the T phase and that Ta atoms in the H phase are in trigonal prismatic coordination, different from octahedral coordination in the T phase, the T-phase crystal could be converted to the H-phase crystal by the slip of S sheet relative to the Ta atoms. Based on the atomic model for the T-H boundary,[9] the surface S rows between the T and H phase should have a mismatch of $\sqrt{3}/6a_0$, $\sim$1 Å, at the interface. One of the most effective ways to convert the T phase to the H phase is a collective motion of S atoms by $\sqrt{3}/3a_0$ along the [1120] direction, as shown in Fig. 3. The minimum energy paths for this phase transition also lie along this direction.

At lower negative and positive bias voltages, we could often find very weak $\sqrt{13}\times\sqrt{13}$ CDW modulations on the surface of a newly fabricated H phase, which is considered to arise from the underlying T-phase layer. This means that the structural transformation occurs only in the surface TaS$_2$ layer, supporting the coherent sliding picture discussed above. Han *et al.*[12] reported a similar weak $\sqrt{13}\times\sqrt{13}$ CDW structure appearing on the surface H-phase layer of $4Hb$-TaS$_2$, concluding that the STM senses the CDW modulation occurring in the second T-phase layer. Another interesting feature for the phase boundary is that it tends to

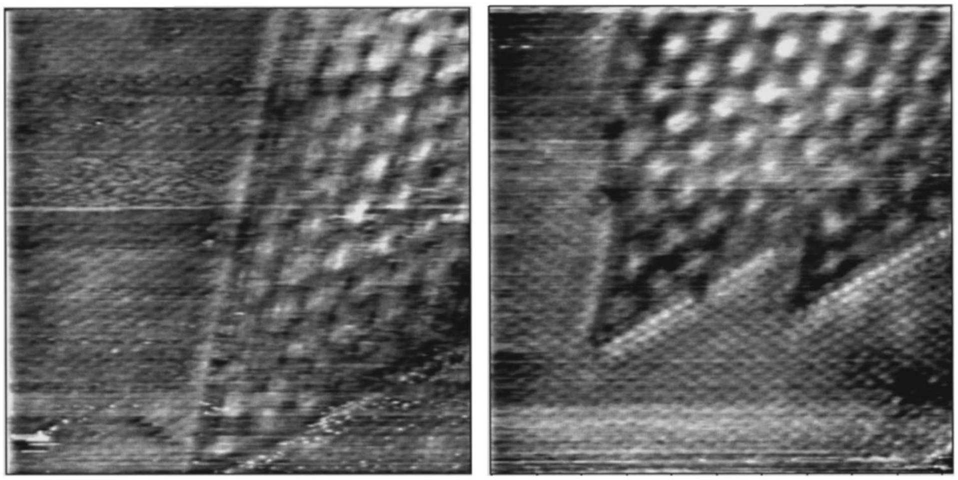


FIG. 4. The typical STM image near the exposed region after applying a high bias voltage. Most phase boundaries have the characteristic 60° angle along the crystal direction. The image sizes are 102×102 Å.

have a characteristic angle of 60°, as shown in Fig. 4, which corresponds to the lattice angle of the triangular lattice.

In summary, we have successfully fabricated the H-phase crystal sheet on the surface of a T-phase TaS_2 crystal by applying a high bias voltage to a STM tip. The high-resolution STM image near the phase boundary shows a mismatch of S atomic rows at the interface, suggesting a sliding of the surface S sheet in a collective way. The phase boundary turns out to have a characteristic angle of 60°. Near the triangular phase boundary we have also observed the local distortions of the CDW superlattice originating from CDW twins.

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