Microscopic basis for the band engineering of Mo$_{1-x}$W$_x$S$_2$-based heterojunction

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Transition-metal dichalcogenide layered materials, consisting of a transition-metal atomic layer sandwiched by two chalcogen atomic layers, have been attracting considerable attention because of their desirable physical properties for semiconductor devices, and a wide variety of pn junctions, which are essential building blocks for electronic and optoelectronic devices, have been realized using these atomically thin structures. Engineering the electronic/optical properties of semiconductors by using such heterojunctions has been a central concept in semiconductor science and technology. Here, we report the first scanning tunneling microscopy/spectroscopy (STM/STS) study on the electronic structures of a monolayer WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction that provides a tunable band alignment. The atomically modulated spatial variation in such electronic structures, i.e., a microscopic basis for the band structure of a WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction, was directly observed. The macroscopic band structure of Mo$_{1-x}$W$_x$S$_2$ alloy was well reproduced by the STS spectra averaged over the surface. An electric field of as high as 80 $\times$ 10$^6$ Vm$^{-1}$ was observed at the interface for the alloy with $x=0.3$, verifying the efficient separation of photoexcited carriers at the interface.

Results
Atomically modulated electronic structures and macroscopic band structure of Mo$_{1-x}$W$_x$S$_2$ alloy. Monolayer WS$_2$/Mo$_{1-x}$W$_x$S$_2$ lateral heterojunctions for the STM measurements were prepared...
by chemical vapor deposition (CVD) on a graphite substrate (see Method). All STM/STS measurements were carried out using an Omicron low temperature-STM and a W tip at 87 K.

Figure 1a,b show a typical STM image of Mo$_{1-x}$W$_x$S$_2$ monolayer alloy with a triangular shape and the cross section along the blue line in the STM image, respectively. The low resolution of the STM image in Fig. 1a is due to the fact that it was difficult to obtain a high-quality image at a low temperature when the observed area included an island edge. As shown in the cross section, the height of the layer is ~0.7 nm over the triangular structure. Close inspection of Fig. 1a and the cross section reveals a slightly smaller triangular area inside the triangular shape, with the interface between the inner and outer triangles shown by two dark blue triangles. The two triangular structures are schematically shown below the cross section in Fig. 1b, in which the three red triangles indicate the positional relationship with Fig. 1a.

Figure 1c shows a magnification of a part of the interface indicated by two red triangles at the top and bottom in a. The gray rectangle indicates the noise level. Magnification of the spectra in (h) near the conduction band edge $E_{\text{CBM}}$. (j) High-resolution STM image of Mo-rich Mo$_{1-x}$W$_x$S$_2$ area.

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Figure 1c shows a magnification of a part of the interface between the smaller inner triangle and the larger outer triangle along the line joining the two red triangles at the top and bottom of Fig. 1a. The interface in the STM image in Fig. 1c is also indicated by two red triangles. To obtain the Mo and W distributions, the bias voltage was set at $+1.35$ V and the Mo and W atoms were imaged with a suitable contrast. As shown in Fig. 1c, small bright islands are distributed in the outer area (left side of the image), while dark lines form a netlike structure in the inner area (right side of the image), as previously observed for Mo$_{1-x}$W$_x$S$_2$ alloy exfoliated from its bulk structure$^{17}$. Namely, the inner triangular area in Fig. 1a (right side of Fig. 1c) is not a second layer but a Mo-rich Mo$_{1-x}$W$_x$S$_2$ alloy area surrounded by the W-rich alloy area corresponding to the larger triangle (left side of Fig. 1c), i.e., a heterostructure of W-rich and Mo-rich Mo$_{1-x}$W$_x$S$_2$ alloys was successfully formed, as observed for Mo$_{1-x}$W$_x$S$_2$ grown on a SiO$_2$ or sapphire substrate$^{11-15,18}$. Structural models for Fig. 1c,a are schematically shown in Fig. 1d,e, respectively.

The heterojunction interface was formed parallel to the edge of the triangular area. An atomically sharp heterojunction interface is clearly visible in the close-up view of the heterojunction interface shown in Fig. 1c. Such a sharp in-plane compositional variation is considered to be a result of the CVD growth sequence. At the initial growth stage, Mo-rich Mo$_{1-x}$W$_x$S$_2$ alloy was formed in the inner triangle by the Mo rich atmosphere around the substrate owing to the high vapor pressure of MoO$_3$ compared with that of WO$_3$. Subsequently, the W-rich structure was epitaxially grown from the edge of the Mo-rich structure because of the shortage of Mo and the reduced diffusion of Mo atoms. Similar sequential atomic growth
Spatial variation in the band structure of WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction. Finally, the band structure of the heterojunction interface was analyzed. Figure 3a shows an STM image of a Mo$_{1-x}$W$_x$S$_2$-based heterojunction interface similar to that in Fig. 1c, where the left and right regions correspond to W- and Mo-rich Mo$_{1-x}$W$_x$S$_2$ monolayers, respectively. To investigate the inner potential of the heterojunction, STS was carried out over the surface. The inset in Fig. 3a shows the STM image simultaneously obtained with the STS measurement.
Figure 3b shows a map of color scale $dI/dV$ curves calculated from the spatially resolved STS spectra measured along the white dashed line in the inset of Fig. 3a. The upper and lower edges of the band gap region, corresponding respectively to $E_{\text{CBM}}$ and $E_{\text{VBM}}$, continuously shifted as a function of the distance across the interface, whose position was determined from the STM image (Fig. 3a inset) and is indicated by the dashed black line in Fig. 3b. Figure 3b clearly demonstrates that a type-II staggered gap heterojunction with a nanoscale built-in potential distribution was formed at the interface. This is the first observation of the electronic structure of a TMD heterojunction. The spatial variation of $E_{\text{CBM}}$ over the surface in Fig. 3a was mapped in Fig. 3c to visualize the electrostatic potential landscape at the interface in more detail, which is almost flat along the direction of the interface compared with the change along the direction crossing the interface (from pink to dark blue).

To better understand the positional relationship between the interface and the electrostatic potential variation, the cross section profile of the $E_{\text{CBM}}$ map along the dashed line in Fig. 3c (white dotted line in Fig. 3a inset) was plotted (Fig. 3d top) along with the profile of $E_{\text{VBM}}$ (Fig. 3d middle) along the line at the same position. The comparison of the topographic image with the cross sections of $E_{\text{CBM}}$ and $E_{\text{VBM}}$ reveals that the variation in the potential was greater on the Mo-rich side. Namely, $E_{\text{CBM}}$ is almost constant in the W-rich area, while it gradually changes over the Mo-rich area, possibly reflecting the asymmetric carrier screening length, which may be due to the difference in the doping characteristics and/or dielectric constant between the W-rich and Mo-rich areas. In addition, the profile of the electric field $E_{\text{field}}$ was obtained from the derivative of the $E_{\text{CBM}}$ profile with respect to the lateral distance (Fig. 3d bottom). As expected from classical semiconductor theory, the electric field reached its maximum value at the interface position indicated by the dashed line in Fig. 3b,d. The strong electric field of as high as $80 \times 10^6 \text{Vm}^{-1}$ observed at the interface is consistent with the observed charge separation efficiency at the interface.

The red and blue spectra shown in Fig. 3e are the $dI/dV$ spectra obtained at the positions indicated by red and blue arrows in Fig. 3b, respectively, where neither $E_{\text{CBM}}$ nor $E_{\text{VBM}}$ is affected by the built-in potential at the interface. The spectra were averaged over the left and right edges of the inset of Fig. 3c, respectively. From these spectra, the band offsets of $E_{\text{CBM}}$ and $E_{\text{VBM}}$ between the W-rich and Mo-rich areas were determined to be 0.30 eV and 0.17 eV, and the band gaps of these areas were also determined.
to be 2.71 eV and 2.58 eV, respectively. Figure 3f shows the first ever schematic image of the band profile of a WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction. The values in (f) are those in (e). W$_{SCR}$ indicates the width of space charge region.

In conclusion, we carried out atomically resolved analysis by low-temperature STM/STS on the electronic structures of a monolayer WS$_2$/Mo$_{1-x}$W$_x$S$_2$ lateral heterojunction that provides a tunable band alignment. The formation of a WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction on a graphite substrate was confirmed for the first time. Then the atomically modulated spatial variation in the electronic structures, which is the basis for the macroscopic band structure of the WS$_2$/Mo$_{1-x}$W$_x$S$_2$ heterojunction, was directly observed. The macroscopic band structure of Mo$_{1-x}$W$_x$S$_2$ alloy was reproduced by the STS spectra averaged over the surface. An electric field of as high as 80 × 10$^6$ V m$^{-1}$ was observed at the interface for the alloy with $x = 0.3$, verifying the efficient separation of photoexcited carriers at the interface. The atomic-scale analysis of TMD heterostructures by STM/STS allows the verification of basic semiconductor physics and is expected to play an essential role in the further advancement of various applications.

**Method**

**Sample preparation.** Monolayer WS$_2$/Mo$_{1-x}$W$_x$S$_2$ lateral heterojunctions were formed on Kish graphite (Covalent Materials Co.) by high-temperature chemical vapor deposition$^{28}$. The graphite was mechanically exfoliated onto a quartz substrate using Nitto tape (SPV-224). The substrate was placed in a quartz tube (3 cm diameter, 100 cm long) with WO$_3$ powder (Aldrich, 99% purity, 100 mg), MoO$_3$ powder (Aldrich, 99% purity, 0.2 mg, reduced to 0.1 mg for the measurement of the effect of a single Mo atom shown in Fig. 2), and sulfur flakes (Aldrich, 99.99% purity, 2 g). The quartz tube was then filled with Ar gas at a flow rate of 100 cm$^3$/min. The temperature of the substrate and the WO$_3$ and MoO$_3$ was gradually increased to the growth temperature (1100 °C) over 60 min using an electrical furnace. When the substrate temperature reached the set value, the sulfur was heated at 200°C for 15–30 min to supply sulfur vapor to the substrate using another electrical furnace. After the growth, the quartz tube was immediately cooled using an electric fan.
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Author Contributions
S.Y. carried out the experiments with R.S., H.M. and T.K. Mo1−xWxS2/graphite samples were prepared by Y.M., S.M., Y.K. and O.T. provided technical assistance. H.S. supervised the project, analyzed the data with S.Y. and edited the paper with S.Y. and Y.M.

Additional Information

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