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Unveiling Three-Dimensional Stacking Sequences of 1T Phase MoS₂ Monolayers by Electron Diffraction

Ziqian Wang,†∥ Shoucong Ning,‡ Takeshi Fujita,∥ Akihiko Hirata,∥ Mingwei Chen,†∥,⊥,*

† Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8577, Japan; ∥ WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan; † Department of Mechanical and Aerospace Engineering, School of Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR; ⊥CREST, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan;

*Address correspondence to: mwchen@wpi-aimr.tohoku.ac.jp

ABSTRACT: The phase transition between semiconducting 1H to metallic 1T phases in monolayered transition metal dichalcogenides (TMDs) essentially involves three dimensional (3D) structure changes of asymmetric relocations of S atoms at top and bottom of the one-unit-cell crystals. Despite that the phase transition has profound influence on properties and applications of 2D TMDs, a viable approach to experimentally characterize the stacking sequences of vertically asymmetrical 1T phase is still not available. Here we report an electron diffraction method based on dynamic electron scattering to characterize the stacking sequences...
of 1T MoS$_2$ monolayers. This study provides an approach to unveil the 3D structure of 2D crystals and to explore the underlying mechanisms of semiconductor-to-metal transition of monolayer TMDs.

**KEYWORDS:** two-dimensional materials, transition metal dichalcogenide, phase interface, MoS$_2$, electron diffraction

Monolayer crystals, such as graphene and transition metal dichalcogenides (TMDs), are usually referred as two-dimensional (2D) materials because they are free from repeating crystal lattices in the out-of-plane direction. This feature gives rise to tremendous properties in electronics, photonics, catalysis, mechanics, so on.$^{1-5}$ Recently, three-dimensional (3D) structural features of 2D materials have attracted great attention because of a great number of functionalities from 3D heterostructures formed by stacking or stitching 2D materials$^{3,6-11}$ and, more importantly, structure transition of TMD monolayers from semiconducting 1H to metallic 1T by relocating top or bottom chalcogen atoms with vertical symmetry breaking.$^{12-16}$ The equilibrium trigonal prismatic 1H phase, such as MoS$_2$ monolayers, belongs to the $D_{3h}$ group and has reflection symmetry with the mirror plane in in-plane directions and 3-fold symmetry from the invariance of the structure after in-plane rotation by 120° (Figure 1a). In contrast, the octahedral 1T phase is a member of the $D_{3d}$ group and has no reflection symmetry but, instead, has an inversion center (Figure 1b).$^{16}$ Even though the transition from 1H to 1T phase leads to the breaking of reflection symmetry in in-plane directions, this symmetry breaking has little meaning in geometry when 1T phase is treated alone because the appearance of inversion
symmetry results in no properties change after a 60° rotation in reality, equivalent to 6-fold rotational symmetry. However, in the case of the coexistence of 1T phase with parent 1H phase, separated by a coherent metal/semiconductor interface, the breaking of reflection symmetry in 1T matters. As schematically shown in Figure 1c and d, the phase transition via top (0001) or bottom (000\bar{1}) S layer gliding along the same direction gives rise to two 1T phases with a 60° rotation angle difference and, more importantly, the resultant two 1T/1H metal-semiconductor interfaces are chiral to each other (Figure S1, Supporting Information) and expected to have distinct properties in spintronics and electromagnetics of 2D TMDs. Therefore, the interfacial structure and related 1H↔1T transition in the 2D TMDs are essentially 3D issues in terms of the stacking sequences of the three-atomic-layer crystals. Apparently, revealing 3D structure of the 2D TMD crystals is critical for understanding the underlying mechanisms of the metal-semiconductor transition and for designing 2D TMD electronic devices with 1T/1H interfaces as metal/semiconductor contacts.\textsuperscript{13,16–19}

High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) have been widely used as powerful tools to characterize the atomic structures of 2D materials.\textsuperscript{20–28} However, either HRTEM or STEM images are basically the projection of 3D structures and have poor spatial resolution in vertical direction parallel to electron beams. Although the recently developed atomic counting algorithms based on high angle annular dark field (HAADF) STEM are capable of reconstructing 3D atomic structures of crystals,\textsuperscript{29–32} it is not practical for this method to identify the stacking sequences of vertically asymmetric 1T phase because there are no superposed atoms along <0001> direction in the phase. In fact, monolayer TMDs do not require atomic counting. Alternatively, electron diffraction involves 3D information by means of electron wave interference with single-unit-cell
thick TMDs and extensive perspectives of 3D structure of 2D crystals can be expected. Particularly, the combination of selected area electron diffraction (SAED) with dark-field TEM is capable of revealing structure and crystal orientation of monolayer TMDs on a large scale by utilizing the diffraction vector variation caused by the symmetry degeneration from 6-fold of bulk phases to 3-fold of monolayers.\textsuperscript{21,26,33} In this work, we developed an electron diffraction method with the consideration of dynamic electron scattering to unveil the stacking sequences of 1T phase of monolayer MoS\textsubscript{2}.

RESULTS AND DISCUSSION

Reciprocal lattice configurations of 1H and 1T MoS\textsubscript{2} monolayers are shown schematically in Figure S2. To be specific, both reciprocal lattices have a repeating unit indicated by the green rhombus area in Figure S2, which can be explained by the kinematic diffraction theory. Accordingly, the diffraction intensity is given by $|G_{2D}(K)|^2 \cdot |F(K)|^2$, where $G_{2D}(K)$ is the Laue function and $F(K)$ is the structural factor. Since 1H and 1T monolayers have the same 2D Laue function $G_{2D}(K)$, the term determining diffraction intensity is the absolute square of structural factor of each phase $F_{1H}$ or $F_{1T}$. When the lattice vectors of 1H and 1T are defined as shown in Figure 1a and b, the absolute squares of structural factors of $(h\ k\ i\ l)$ diffraction are derived to be:

\[
|F_{1H}|^2 \approx \begin{cases} 
(f_{M0}^\prime + 2f_5^\prime)^2 + (f_{M0}^{''''} + 2f_5^{''''})^2 & h - k \equiv 0 \text{ (mod 3)} \\
(f_{M0}^\prime - f_5^\prime + \sqrt{3}f_5^{''''})^2 + (f_{M0}^{''''} - \sqrt{3}f_5^\prime - f_5^{''''})^2 & h - k \equiv 1 \text{ (mod 3)} \\
(f_{M0}^\prime - f_5^\prime - \sqrt{3}f_5^{''''})^2 + (f_{M0}^{''''} + \sqrt{3}f_5^\prime - f_5^{''''})^2 & h - k \equiv 2 \text{ (mod 3)} 
\end{cases}
\]

(1)
in 1H and 1T structure, respectively. Herein, \( f_{\text{atom}} = f_{\text{atom}}^I + i f_{\text{atom}}'' \) is the atomic shape factor containing real and imaginary parts; and “\( a \equiv b \mod c \)” means that \( b \) is the remainder of the division of \( a \) by \( c \). Distribution of the spots defined by 0, 1 or 2 (mod 3) in the reciprocal space is shown in Figure S2. However, electron diffraction is not a sample-only issue as simplified by the kinematic theory above but a dynamic process where multiple Bloch waves inside the sample are excited during an electron beam penetrating a crystal, or in equivalent real space description, electrons might be multiply scattered in the sample owing to its particle nature.\(^{34}\) Deducing the diffraction contrast of each individual diffraction beams has to resort to solving Schrodinger equation of the electron optics from incident to exit. However, the boundary conditions at the incident and exit sides of the monolayer crystals are resultantly different because of only one incident beam but multiple exit diffraction beams, which put the two S layers in different conditions with regard to the electron beam and could give rise to the possibility of resolving the difference between two S layers as vertical information of 2D crystals. Specifically, the inversion symmetry of 1T monolayer disappears (Figure 2) from the viewpoint of the whole diffraction optics containing not only the 1T monolayer sample but also the incident and exit electron beams. This symmetry breaking could cause noticeable inaccuracy of the diffraction intensities predicted by the conventional kinematic theory. Therefore, the dynamic theory of electron diffraction is required. In this study we applied “effective atomic scattering factors” to discriminate the top and bottom S layers in monolayer MoS\(_2\) by coercively combining the

\[
|F_{1T}|^2 \approx \begin{cases} 
(f_{\text{Mo}'} + 2f_{\text{S}''})^2 + (f_{\text{Mo}''} + 2f_{\text{S}''})^2 & h - k \equiv 0 \mod 3 \\
(f_{\text{Mo}'} - f_{\text{S}'})^2 + (f_{\text{Mo}''} - f_{\text{S}''})^2 & h - k \equiv 1 \mod 3 \\
(f_{\text{Mo}'} - f_{\text{S}'})^2 + (f_{\text{Mo}''} - f_{\text{S}''})^2 & h - k \equiv 2 \mod 3
\end{cases}
\]

(2)
kinematic and dynamic theories. The effective atomic scattering factors of S at incident and exit 
sides $f_{\text{Si}} = f'_{\text{Si}} + if''_{\text{Si}}$ and $f_{\text{Sx}} = f'_{\text{Sx}} + if''_{\text{Sx}}$ are not equivalent, and eq 1 and eq 2 becomes as 
follows:

$$|F_{1H}|^2 \approx \begin{cases} 
\left(f_{\text{Mo}}' + \Sigma f_{\text{S}}'\right)^2 + \left(f_{\text{Mo}}'' + \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 0 \pmod{3} \\
\left(f_{\text{Mo}}' - \frac{1}{2} \Sigma f_{\text{S}}' + \frac{\sqrt{3}}{2} \Sigma f_{\text{S}}''\right)^2 + \left(f_{\text{Mo}}'' - \frac{\sqrt{3}}{2} \Sigma f_{\text{S}}' - \frac{1}{2} \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 1 \pmod{3} \\
\left(f_{\text{Mo}}' - \frac{1}{2} \Sigma f_{\text{S}}' - \frac{\sqrt{3}}{2} \Sigma f_{\text{S}}''\right)^2 + \left(f_{\text{Mo}}'' + \frac{\sqrt{3}}{2} \Sigma f_{\text{S}}' - \frac{1}{2} \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 2 \pmod{3}
\end{cases}$$

(3)

$$|F_{1T}|^2 \approx \begin{cases} 
\left(f_{\text{Mo}}' + \Sigma f_{\text{S}}'\right)^2 + \left(f_{\text{Mo}}'' + \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 0 \pmod{3} \\
\left(f_{\text{Mo}}' - \frac{1}{2} \Sigma f_{\text{S}}' + \frac{\sqrt{3}}{2} \Delta f_{\text{S}}''\right)^2 + \left(f_{\text{Mo}}'' - \frac{\sqrt{3}}{2} \Delta f_{\text{S}}' - \frac{1}{2} \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 1 \pmod{3} \\
\left(f_{\text{Mo}}' - \frac{1}{2} \Sigma f_{\text{S}}' - \frac{\sqrt{3}}{2} \Delta f_{\text{S}}''\right)^2 + \left(f_{\text{Mo}}'' + \frac{\sqrt{3}}{2} \Delta f_{\text{S}}' - \frac{1}{2} \Sigma f_{\text{S}}''\right)^2 & h - k \equiv 2 \pmod{3}
\end{cases}$$

(4)

Here, $\Sigma f_{\text{S}}^{(r)} = f_{\text{Si}}^{(r)} + f_{\text{Sx}}^{(r)}$ and $\Delta f_{\text{S}}^{(r)} = f_{\text{Si}}^{(r)} - f_{\text{Sx}}^{(r)}$. Note that $\Delta f_{\text{S}}^{(r)}$ is non-zero since two 
S layers are not effectively equivalent in a real diffraction. Consequently, neither of diffraction 
peaks of $h - k \equiv 1, 2$ or $3 \pmod{3}$ in 1H or 1T shows the same intensity and this directly leads 
to the non-centro-symmetry of real diffraction patterns in either case. Especially for the case of 
1T MoS$_2$ monolayers, contrary to the centro-symmetric diffraction patterns deduced by the 
kinematic theory in eq 2, non-centro-symmetric diffraction patterns should be observed and 
$h - k \equiv 1 \pmod{3}$ diffractions have different intensity from $h - k \equiv 2 \pmod{3}$ diffractions 
with the same distance from [0000] peak. The symmetry-breaking electron optics of 2D crystals
in the electron diffraction mode could be utilized as a tool to resolve structural information in out-of-plane direction of 2D crystals involved in the diffraction patterns.

As a model system, two-phase MoS\(_2\) monolayers, prepared by chemical vapor deposition (CVD),\(^{35}\) were placed on holey carbon coated Cu grids for structure characterization. The TEM and STEM images of the region in vicinity of a 1H/1T interface are shown in Figure S3. Selected area electron diffraction (SAED) patterns were taken from a 200 nm diameter region containing exclusively 1H or 1T phase as illustrated in Figure 3a and 4a, respectively. The diffraction peaks in Figure 3a and 4a are indexed according to the lattice vectors shown in their corresponding HAADF-STEM images in Figure 3c and 4c and structure models in Figure 3d and 4d.

Considering the inevitable influences on the intensity profiles of diffraction peaks by actual acquisition conditions, such as focus parameters and charge coupled device (CCD) performances, we evaluated the integrated intensity of each diffraction peak rather than peak height or peak width and the analytical results are shown in Figure 3b and 4b. The peak intensity values are integrations over the areas enclosed by the squares with a constant area marked in Figure 3a and 4a and normalized by the average value of six \(<1\bar{1}20>\) diffraction peaks in either 1H or 1T case. The six \(<1\bar{1}20>\) peaks in both diffraction patterns have a nearly identical intensity (green bars in Figure 3b or 4b), verifying that the incident electron beam perfectly aligns with the \([0001]\) zone orientation of the 2D crystals. In contrast to the \(<1\bar{1}20>\) peaks, the intensities of six \(<10\bar{1}0>\) diffraction peaks in both 1H and 1T show two nonequivalent groups: the \(h - k \equiv 1 \text{ (mod 3)}\) group, including \([10\bar{1}0],[0\bar{1}10]\) and \([\bar{1}100]\), has higher intensity than the \(h - k \equiv 2 \text{ (mod 3)}\) group (\([\bar{1}000],[\bar{1}0\bar{1}0]\) and \([0\bar{1}\bar{1}0]\)) in 1H (red bars in Figure 3b) and the opposite contrast relation is observed in 1T (red bars in Figure 4b). This splitting of \(<10\bar{1}0>\) peaks intensity is consistent with previous observations in 2H TMD monolayers while no such reports
on 1T monolayer are found.\textsuperscript{21,26,33} According to our experiments, the integrated intensity ratio of brighter and dimmer $<10\bar{1}0>$ peaks is 1.22 for 1H and 1.35 for 1T phase of freestanding MoS$_2$ monolayers. Thus, the intensity splitting of 1T MoS$_2$ is more evident compared with 1H MoS$_2$.

We simulated the diffraction patterns based on multislice algorithm resorting to the dynamic diffraction theory by numerically solving Schrodinger equation. Simulated results assuming the sample ideally clean and flat are plotted as black dots in the Figure 3b and 4b which confirm the experimental observations of the intensity splitting in the 2D crystals. The brighter/dimmer ratios of $<10\bar{1}0>$ peaks predicted by the simulations are 1.08 for 1H and 1.15 for 1T at room temperature. Discrepancy in the normalized intensity values between experiments and simulations in 1T $<10\bar{1}0>$ diffraction peaks (Figure 4b) could be due to the surface rippling of the free-standing MoS$_2$ (S4, Supporting Information).\textsuperscript{21,36,37} According to the experimental and simulated results, there is a well-defined correspondence between diffraction vectors and the atomic configuration as shown in the enlarged STEM images and the atomic models (Figure 3c,d and 4c,d) in which brighter and dimmer directions are noted. Accordingly, the brighter/dimmer relation is dependent solely on the atomic configuration of the Mo and exit-side (000\bar{1}) S layers in 1H or 1T structure, \textit{i.e.} brighter diffraction vectors are parallel to the in-plane projection of (000\bar{1}) S-Mo bonds toward Mo direction whereas dimmer vectors toward S, and the relative position of (0001) S on the incident side only modifies the intensities very slightly.

Taking advantage of distinct intensity variations in $<10\bar{1}0>$ diffraction peaks in 1H and 1T phases, the two phases and corresponding interfaces can be visualized by dark-field (DF) TEM through the selection of one specific diffraction vector for imaging. Figure 5a shows a typical repeating unit in the reciprocal lattice (green rhombus) which involves four diffraction spots:
$\bar{1}100$, 01$\bar{1}$0, $\bar{1}$2$\bar{1}$0 and 11$\bar{2}$0 in either 1H or 1T phase. A bright-field (BF) TEM image by using the direct beam (0000) is shown in Figure 5b and DF-TEM images by ($\bar{1}100$), (01$\bar{1}$0), (1$\bar{2}$10) and (11$\bar{2}$0) are shown in Figure 5c-f with their corresponding diffraction vectors marked by yellow circles in the inserted SAED patterns. The same contrast of 1H and 1T regions in Figure 5b,e,f manifests the equivalence of the center and all $<1\bar{1}20>$ diffraction peaks. Visible contrast difference in Figure 5c and d confirms the intensity variation of $<10\bar{1}0>$ diffraction peaks between 1H and 1T, i.e. 1H shows higher intensity over 1T for peak $\bar{1}100$ while the 01$\bar{1}$0 peak gives an opposite contrast (Figure 3 and 4). Benefited from phase identification by DF-TEM, 1T/1H interfaces can be readily identified at microscopic scale (Figure S3c and d). Figure 5g shows the intensity profiles across the phase interface as indicated by the yellow square in Figure 5c-f for ($\bar{1}100$), (01$\bar{1}$0), (1$\bar{2}$10) and (11$\bar{2}$0) DF-TEM images. The X-axis in Figure 5g indicates the distance along the yellow arrows and Y-axis is the integrated intensity along the dot line direction. A slight dip at the interface, marked by white arrowheads, can be seen in all the profiles, which may be caused by diffuse scattering from interface defects and thereby gives a lower intensity in the diffraction images. Moreover, small hills can always be observed next to the interface at 1H sides as indicated by the black arrows. The additional elastic scattering from the semiconductor side has not been well understood.

At 1H/1T phase interfaces of monolayer MoS$_2$, the stacking order changes from AbA stacked 1H to 1T by two possible paths with different stacking sequences: gliding the top (0001) S layer to produce CbA stacked 1T or gliding bottom (000$\bar{1}$) S layer to produce AbC stacked 1T. The two stacking structures of 1T MoS$_2$ coincide with each other after a relative rotation of 60° as described in Figure 1c and d. Figure 6 schematically illustrates the diffraction pattern forming process as electron beam penetrates MoS$_2$ monolayer perpendicularly to its basal plane in a
TEM. After incident beam interacts with crystal lattices, brighter and dimmer groups of diffraction peaks arise and become signatures of 3D crystallographic orientations of both 1H and 1T phase. In the case of (0001) S glide (right and middle panel of Figure 6), brighter and dimmer peak directions are identical with respect to AbA stacked 1H and CbA stacked 1T phase. On the contrary, in the case of (0001) S glide (left and middle panel of Figure 6), the brighter/dimmer direction inversion is observable upon the phase transformation between AbA stacked 1H and CbA stacked 1T. Hence, by simply recording and analyzing changes of diffraction patterns across a phase interface, the stacking sequence change in resultant 1T phase and the chirality of the 1T/1H interface can be extracted. By using this method, the 3D structure of the 1T phase shown in Figure 5 can be determined to be CbA stacking. Thus, the transition from 1H to 1T in this domain takes place by the gliding of the (0001) S layer which directly contacts with the glass substrate during CVD growth. The same stacking sequences were observed from five 1T phase domains which were found from about 50 grains in an over $100 \times 100 \mu m^2$ sampling area without exception. This observation indicates that the 1H to 1T phase transition in the CVD grown TMD monolayers may be associated with the weak interaction between the films and substrates during growth and cooling.

“2D materials” is an ideal platform to investigate fundamental physical phenomena, including electron diffraction, of crystals. Since MoS$_2$ monolayers are only three-atomic-layer thick and the 1H or 1T phase only differs by the stacking order of the three atomic layers, 1H/1T two-phase MoS$_2$ is a good system for studying the scattering of atomic layers with high energy electron waves. As described in Figure 6, the changes of stacking order of only one atomic layer from 1H to 1T lead to the reversion of diffraction contrast. Moreover, the intensity variation of different $<10\bar{1}0>$ vectors from the mono-layer thick 1T phase crystals indicates that the
approximation of the conventional kinematic theory of electron diffraction cannot stand due to multiple scattering even down to sample thickness of the three-atom-layer regime.

HRTEM is a commonly used technique for structural analysis of TMDs in various reports.\textsuperscript{10,21,24,38–50} Distinguishing 1H and 1T regions remains difficult since the phase contrast nature of HRTEM image leads to the unintuitive structure determination for 1H and 1T phases and contrast inversion occurs easily due to small variation in defocus conditions. As an important perspective in understanding phase transformation in monolayer TMDs, Cs-corrected STEM enables the straightforward and clear view of the atomic structure or even atomic motion during 1H-to-1T phase transformation.\textsuperscript{12,13,15} However, the basic 3D information cannot be extracted directly from the atomically-resolved STEM images. For an instance, STEM nearly ignores the difference between (0001) and (000\linebreak 1) S layers, whereas this 3D information is preserved by electron wave interference in SAED patterns. Different from STEM and HRTEM, electron diffraction has no competency in resolving individual atomic positions in real space while has the irreplaceable advantage in crystal symmetry and orientation analyses. As evidenced in this work, by resolving the intensity variation of $<10\overline{1}0>$ diffraction peaks, 3D crystallographic orientation and stacking sequences of 1H and 1T phases in TMD monolayers can be experimental determined. The discrimination of different S layers in the three-atomic-layer TMDs provides the opportunity to unveiling the structure and properties of the 2D crystals and the underlying mechanisms of the semiconductor-to-metal transition. We have noticed that all the 1T phase domains in CVD grown MoS\textsubscript{2} monolayers are formed by the glide of the S layers that contact with the glass substrates, implying that the structure transition in the as-grown CVD TMD monolayers is possibly associated with the weak confinement from the glass substrate.\textsuperscript{35}
CONCLUSION

In summary, we developed an approach to irreplaceably characterize 1T and 1H phases and their stacking sequences of 2D TMD crystals on the basis of the dynamic effect of electron diffraction. The 3D stacking sequences of the 2D crystals revealed by the diffraction method provides a perspective on understanding the underlying mechanisms of semiconductor-to-metal transition of the of TMD monolayers. The finding that the phase transition takes place by the glide of the S layers contacting with the glass substrate during CVD growth unveils the possible role of substrate confinement in the structure phase transition. The chirality of 1T/1H interfaces, characterized by the electron diffraction method, may lead to properties in spintronics and electromagnetics of 2D TMDs for future explore. Technically, imaging 1T and 1H phase domains and corresponding interfaces in tens of micrometer scale by the dynamic electron diffraction method could be very important in designing and fabricating TMD based electronic devices by utilizing 1T/1H interfaces as the metal/semiconductor contacts. This work also underlines the robustness of commonly used electron diffraction techniques in exploring the structure of 2D materials as an important supplementary of HRTEM and STEM-HAADF.

METHODS

Monolayer MoS$_2$ crystal growth. The MoS$_2$ samples are synthesized using a low pressure chemical vapour deposition method.$^{35}$ MoO$_3$ (Sigma Aldrich, purity $>$99.5%) and S (Wako Pure Chemical Industry, purity 99%) powders are used as precursors, and micro slide glass (Matsunami Glass, S1214) as growth substrates. Growth chamber is pumped down to a base pressure of $5 \times 10^{-2}$ mbar before growth. Then, the growth is performed at 700°C for 1h with
ultrapure Ar as carrier gas under pumping, followed by rapidly cooling down to room
temperature in 5 minutes.

**Microstructure characterization.** TEM and STEM images and SAED patterns are captured
using a JEOL JEM-2100F TEM equipped with double spherical aberration (Cs) correctors
(CEOS) for imaging and probing lenses. Observations are performed at the acceleration voltage
of 200 kV and the spatial resolution of the STEM is ~0.1 nm. The collecting angle for HAADF-
STEM is between 100 and 267 mrad. The exposure time for SAED is 0.5 sec and all calibration
of acquisition conditions were performed on adjacent areas prior to final acquisition on the target
area, and detectable sample damage by the electron beam cannot be seen.

**Simulations of dynamic electron diffraction:** The multislice method is used to simulate
electron diffraction with the consideration of the dynamic effect. This is a more generalized
method for the simulations of electron propagation in arbitrary model compared with the Bloch
wave method.\(^5\) By separating the samples into thin slices in real space, the wave function at
each layer is solved in an analytical way from top to bottom. In our simulations, the accelerating
voltage is set as 200 kV, and 35*20 unit cells with 300 phonon configurations under ambient
temperature are used. E. J. Kirkland\(^5\) and Lobato\(^5\) potentials are both adopted in the
construction of real space potential field, albeit having negligible difference.

**ASSOCIATED CONTENT**

**Supporting Information.**

Supporting Information on experimental results and discussion (S1-S4). This material is
available free of charge *via* the Internet at http://pubs.acs.org.
AUTHOR INFORMATION

Corresponding Author

E-mail: mwchen@wpi-aimr.tohoku.ac.jp

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Figure 1 Structure and symmetry of 1H and 1T phase MoS$_2$ monolayer and their interfaces.

Symmetry elements of 1H MoS$_2$ are partially shown in (a) and 1T MoS$_2$ in (b). 1H has an in-plane mirror plane whereas 1T has an inversion center. Blue and yellow spheres indicate Mo and S atoms respectively. (c) Glide of (0001) S and (d) glide of (0001) S layer in 1H to 1T phase transition results in different interfacial structures chiral to each other. Yellow and cyan spheres indicate (0001) S and (0001) S atoms, respectively.
Figure 2 Illustration of the origin of non-centro-symmetry in the diffraction space of centro-symmetric 1T monolayer MoS$_2$. (a) 1T monolayer solely has an inversion center. (b) The inversion center disappears when 1T monolayer is viewed together with electron beam (the diffraction optics) due to the asymmetric boundary conditions on incident and exit sides. (c) Breaking of inversion symmetry by the diffraction optics leads to the non-centro-symmetry in diffraction patterns even though 1T monolayer itself is centro-symmetric.
Figure 3 Quantitative analyses of SAED of 1H phase MoS$_2$. (a) SAED pattern taken from a 1H region (200 nm in diameter) with $<10\bar{1}0>$ and $<1\bar{1}20>$ diffraction peaks noted on the image. Integrated intensity of each peak over the corresponding square regions is shown by the columns in (b) and is normalized by the average intensity of the $<1\bar{1}20>$ diffraction peaks. Black scatters and lines in (b) show the simulated values of each diffraction peak assuming the sample ideally clean and flat. Integrated intensity of $<10\bar{1}0>$ diffraction peaks shows two nonequivalent groups: the $h-k \equiv 1 \pmod{3}$ group ($10\bar{1}0$, $0\bar{1}10$ and $\bar{1}100$) which has higher intensity and the $h-k \equiv 2 \pmod{3}$ group ($\bar{1}100$, $\bar{1}010$ and $01\bar{1}0$) which has lower intensity. Almost no observable difference in the intensities of six $<1\bar{1}20>$ diffraction peaks. Associated with corresponding HAADF-STEM image (c), directions of brighter (blue solid lines and arrows)
and dimmer (red dot lines and arrows) peaks are noted in the atomic model in (d). Atomic model in the right panel of (d) is the side view of the atomic model in left panel of (d) viewed along the direction indicated by the black dot line and glasses symbol.
Figure 4 Quantitative analyses of SAED of 1T phase MoS$_2$. Notations and color stipulations are the same as Figure 3. Integrated intensity of each peak in (b) is also the normalized value by the average intensity of six $<11\bar{2}0>$ diffraction peaks. Black scatters and lines in (b) show the simulated values of each diffraction peak assuming the sample ideally clean and flat. Brighter group $h-k \equiv 2 \pmod{3}$ and dimmer group $h-k \equiv 1 \pmod{3}$ are inversed in comparison with the case of 1H shown in Figure 3.
Figure 5 Bright-field and dark-field TEM imaging taken from the co-lattice 1H/1T region.

(a) Schematic illustration of the reciprocal space of monolayer 1H/1T MoS$_2$. Red point in the middle indicates the center and green shaded area shows a representative repeating unit containing four nonequivalent points $\bar{1}100$, $01\bar{1}0$, $\bar{1}2\bar{1}0$ and $1\bar{1}20$. Bright-field and dark-field TEM micrographs of the same region imaged by selecting (b) 0000, (c) $\bar{1}100$, (d) 01$\bar{1}0$, (e) $\bar{1}2\bar{1}0$ and (f) 1$\bar{1}20$ diffraction vectors shown in the insets of the images (scale bar: 0.2 µm).

Images by 0000, $\bar{1}2\bar{1}0$ and 1$\bar{1}20$ show no difference in 1H and 1T regions corresponding to (b), (e) and (f), whereas images by $\bar{1}100$ and 01$\bar{1}0$ exhibit visible contrast difference, i.e. brighter 1H in (c) and brighter 1T in (d). (g) The profiles across the phase interface along the yellow...
arrows shown in (c-f). White arrows in (g) indicate the position of the phase interface and a small hill appeared next to the interface in 1H side indicated by the black arrows.
Figure 6 Illustration on the identification of stacking sequences of 1T phase by electron diffraction. Electron diffraction pattern appears upon electron beam penetrating MoS$_2$ monolayer perpendicularly to the basal plane. Brighter and dimmer groups of diffraction peaks become signatures of 3D crystallography of both 1H and 1T phases. Inversion of the brightness of the two groups indicates the occurrence of relative glide of bottom (000$\bar{1}$) S layer (from AbA to AbC stack, middle and left panel), whereas identical brightness distribution indicates the relative glide of top (0001) S layer (from AbA to CbA stack, middle and right panel).