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Growth Order-Dependent Strain Variations of Lateral Transition Metal Dichalcogenide Heterostructures

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Supporting Information

ABSTRACT: Understanding the heterojunction of a lateral heterostructured transition metal dichalcogenide (hTMD) is important in order to take advantage of the combined optoelectronic properties of individual TMDs for various applications but, however, is hampered by mingled effects from lattice mismatch and substrate interaction. Here, we systematically investigated the strain occurring at lateral hTMDs consisting of molybdenum disulfide (MoS₂) and molybdenum diselenide (MoSe₂) prepared by chemical vapor deposition. Comparison of homologous TMDs and hTMDs from



controlled growth order revealed systematic change in photoluminescence behavior depending on substrate interaction and relative lattice mismatch. Near the heterojunction, a TMD with a larger lattice constant (a) exhibits photoluminescence (PL) red-shift, whereas a TMD with smaller a shows an opposite trend owing to lattice-induced strain. These effects are augmented in a subtractive or additive manner by tensile strain from the substrate interaction. Moreover, comparison of PLs revealed that the shell region grown from the core edges exhibits weak substrate interaction contrasted by that of a shell region independently grown on a shell. This study provides detailed understandings of the heterojunction at a lateral hTMD for various applications. **KEYWORDS:** transition metal dichalcogenides, chemical vapor deposition, lateral heterostructure, strain, photoluminescence

INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs) with repeating MX₂ units where M is a group IV, V, or VI transition metal that is sandwiched by chalcogens X (S, Se, or Te) have drawn enormous interest because of their unique layer-dependent optoelectronic properties.¹⁻⁴ Heterostructured TMDs (hTMDs) produced by combinations of TMDs having various band gaps (1 to 2 eV) and relative band offsets⁵ are beneficial to controlling optoelectronic properties including those of the straddling bandgap type I, staggered gap type II, and broken gap type III semiconductors.^{6,7} These types of electronic configurations enable tuning of the charge carrier and the spin in a desired direction and various applications of hTMDs including field-effect transistors,^{6,8–11} sensors,¹² photodetectors,^{13–15} and spin-valleytronic devices.^{2,16,17} Therefore, the ability to control the growth of hTMDs and understanding of the heterojunction is significant in terms of their future applications.

Various hTMDs have been prepared by using either vertical^{6,18,19} or lateral^{9,19–21} configurations. Vertical hTMDs are obtained by stacking individual TMD layers via a transfer method using spin-coated¹⁸ or -dried²² polymers. While this technique is not limited by the chemical natures of respective TMD layers, optical properties of the stacked hTMDs are dominated by stacking orientation and interlayer coupling.¹⁸ As a consequence, the controlled bandgap structure created in a stacked hTMD having a type II heterostructure produces interlayer charge carrier flow, resulting in an enhanced

photovoltaic effect.⁶ However, this method results in an interstitial void or adsorbents trapped at the interface, leading to spatially heterogeneous performances.²³ In contrast, lateral hTMDs with various core-shell combinations (e.g., MoS₂- $MoSe_{2}$, ²⁰ $MoSe_{2}$ – WSe_{2} – WSe_{2} – MoS_{2} , ⁹ WS_{2} – MoS_{2} , ¹⁹ and $WS_2-WSe_2^{20,24}$) can be formed by using either one- or twostep growth through chemical vapor deposition (CVD). The one-step approach involves vaporization of two chalcogen precursors at different temperatures in a batch using CVD.^{19,} Despite producing seamless in-plane hTMDs with gradient alloy interfaces, this method lacks the controllability of each TMD in terms of size owing to the coevaporation of precursors.^{19,21} Two-step growth of lateral hTMDs^{20,24} comprises separate growth steps and has no temperature restriction on the selection of M and X sources. Also, it provides lateral heterojunctions with sharp interfaces²⁴ exhibiting better device performance as compared to that with a gradual interface.9

The heterojunction of an hTMD plays an important role for determining optoelectronic properties of the resulting hTMDs such as band gap energies and offsets. Among various techniques, photoluminescence (PL) and Raman spectroscopies are powerful tools to determine the layer numbers, $^{1,3,25}_{1,3,25}$ strain, $^{26-30}$ and defects $^{31-33}$ of TMDs. Recently, Ajayan and

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Figure 1. Two-step CVD growth of lateral hTMD by using two separated chalcogen and metal precursors. (A) Schematic of two-step process via core followed by shell growths. (B) Experimental setup to grow the TMD. The corresponding OM images of (C) $MoSe_2$ alone, (D) $MoSe_2-MoS_2$ core-shell, (E) MoS_2 alone, and (F) MoS_2-MoSe_2 core-shell.



Figure 2. Various characterizations of $MoSe_2$ and MoS_2 grown by CVD. Analysis of $MoSe_2$ by (A) AFM height image and (B) TEM image and the SAED pattern of $MoSe_2$ as an inset. Dotted line in SAED pattern indicates [2110] and [1100] diffraction patterns for outer and inner dots. (C) Representative PL spectrum with Raman spectrum as an inset. Gray lines are fitted line with Lorentzian shape. (D) Spatial PL spectra obtained from the spot indicated in the PL position map as an inset. Each PL intensity was normalized with respect to peak maximum. Characterization of MoS_2 with (E to H) similar measurements.

co-workers²⁸ reported that CVD-grown single-layer (SL) MoS₂ exhibits tensile strain at the basal plane and progressive compressive stains toward edges, owing to the localized lattice distortion from the thermal expansion coefficient (TEC) difference between the TMD and substrate. Such an effect stems from the substantial interaction between the TMD and underlying substrate, leading to strain in the level of $\sim 1\%$. More recently, Li and co-workers9 demonstrated that the lateral hTMD consisting of a lattice-mismatched WSe₂-MoS₂ core-shell displays localized PL blue- and red-shifts, which were suggested to have spatially localized compressive and tensile strain. Those studies suggest that lattice mismatch and substrate interaction must be carefully considered to understand the heterojunction of a lateral hTMD. However, the systematic study on the heterojunction considering substrate interaction and lattice mismatch is still lacking.

In the investigation described below, we studied the strain heterogeneity at the heterojunction of hTMDs consisting of a MoS₂-MoSe₂ core-shell or shell-core structures fabricated by changing growth order using a two-step CVD method. Single- or two-step growths with separated metal and chalcogen precursors were utilized for the production of the TMD and hTMDs. Forward and reverse growth orders (i.e., MoSe₂-MoS₂ and MoS₂-MoSe₂ for core-shell) were devised to decipher the mingled lattice mismatch and substrate effects on an hTMD via PL and Raman mappings. Especially, PL shifts were correlated with the exerted strain of an hTMD by lattice and substrate according to core and shell positions.

RESULTS

Lateral hTMD structures were formed by using two-step growth via atmospheric pressure CVD (APCVD). Figure 1A

shows a schematic of in-plane hTMD growth involving initial core growth using MoO₃/Se and cooling, followed by secondary shell growth using MoO_3/S (see Methods for the details) according to a reported process. ^{11,34–37} Measuring the thermal profile of the furnace (Lindberg blue/M, Figure S1) enables tight control of precursor temperature with ± 5 °C in the process. The TMD core was initially grown by placing a 285 nm thick SiO₂/Si substrate facing a crucible containing MoO_3 in the center of the heating zone, as shown in Figure 1B. Chalcogen precursors were placed at upstream positions so that when the temperature of heating zone reached the growth temperature of 650 °C, the temperature of the sulfur and selenium zones simultaneously reached 150-200 and 220-250 °C, respectively. The growth temperature was maintained at 650 °C for 15 min under 5 sccm Ar for MoS₂ and under 15 sccm Ar and 1 sccm H₂ for MoSe₂ growth. Importantly, MoSe₂ growth requires the use of H₂ flow along with Ar, because in its absence, growth does not reproducibly generate a triangular single-crystalline grain.¹¹ After th heating zone was cooled down to room temperature, a second TMD growth was performed with the substrate following the first step. As shown in the optical image (OM) of Figure 1C–F, we found that the each step produces the designated TMD and its lateral heterostructured form (i.e., MoSe₂ and subsequent MoSe₂-MoS₂ core-shell, MoS₂ and MoS₂-MoSe₂ core-shell). For instance, the OM image of CVD-grown MoSe₂ (Figure 1C) shows the presence of an over 10 μ m equilateral triangle, indicating single crystallites. Occasionally, bowtie and star shapes are observed, which originated from the merged MoSe₂ triangles.³⁷ The observed color contrast is quite uniform throughout MoSe₂ grains and slightly thinner for the peripheral MoS_2 layer (Figure 1D), suggesting the formation of the lateral hTMD. Growth of MoS₂-MoSe₂ core-shell by reverse growth order was carried out in a similar manner. Initially, the synthesized MoS_2 core (Figure 1E) displayed similar triangular shapes with uniform contrast. Upon the shell growth, the contrast of the formed MoS_2-MoSe_2 core-shell (Figure 1F) was reversed as compared to that of the MoSe₂-MoS₂ grain, indicating that both forward and reverse growths are successful. These samples were subject to further optical characterizations.

MoSe₂ and MoS₂ Grown by Using the Single-Step **Method.** In the first stage, individual MoSe₂ and MoS₂ grains were characterized and prepared by using the single-step method, because the strain of the hTMDs is affected by the individual constituents.⁹ For this purpose, MoS₂ and MoSe₂ grains were further analyzed by using various techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM), and Raman and PL spectroscopies. AFM measurement of the MoSe₂ grain (Figure 2A) was conducted to determine its layer number. A height profile (black trace) showed that the average height (black trace) is ca. 0.97 nm, in accordance with that (0.67 nm) of the SL MoSe₂.^{1,8,35} Moreover, the surface analysis revealed that the root-mean-square (RMS) roughness of the MoSe₂ basal plane (Figure S2) is quite uniform (i.e., 112.8 pm) and is similar to that (i.e., 113.3 pm) of bare substrate. This observation suggests that the synthesized MoSe₂ layer conforms to the underlying SiO₂ substrate topography as a consequence of interactions between these layers.³⁵ TEM inspection of the transferred MoSe₂ (Figure 2B, see Methods for the details of transfer to the TEM grid) showed that it has a triangular shape, and their selected area electron diffraction pattern (SAED,

inset) displayed equally intense 6-fold symmetry diffraction spots, confirming the formation of the SL $MoSe_2$.^{14,37}

In order to obtain further insight on this sample, we acquired the PL and Raman spectra. The PL spectrum (Figure 2C) displays a maximum PL peak at 811 nm. This value is significantly red-shifted by ~60 meV as compared to 780 nm from mechanically exfoliated SL MoSe₂ (and 660 nm for the SL MoS₂).^{1,25} This result indicates that the lattice of the MoSe₂ sample is distorted owing to the substantial substrate interaction based on the aforementioned MoS₂ grown by the CVD process. Raman measurements of a representative grain (inset of Figure 2C) display a prominent peak at 240.7 cm^{-1} , which corresponds to an out-of-plane vibrational A1g mode of the SL MoSe₂^{25,31} and is shifted to low frequency as compared to that (241.2 cm^{-1}) of pristine MoSe₂. Spatial heterogeneity of the PL position was probed by PL raster-scanning, as shown in the inset of Figure 2D. The PL map exhibits nearly similar peak maximum at 811 nm throughout the grain, irrespective of positions numbered 1, 2, and 3. Raman measurements of 42 different grains (Figure S3A) display nearly uniform bands at 240.6 ± 0.2 cm⁻¹. This result suggests that uniform SL MoSe₂ grains with red-shifted PL were grown by the CVD method.

MoS₂ grains grown by using a similar protocol were also investigated. AFM measurement (Figure 2E) showed that the average height of the basal plane is about 0.79 nm, indicating SL MoS₂.^{1,8,35} Similar to those of the MoSe₂ grain, TEM and its corresponding SAED pattern (Figure 2F and inset) support the formation of SL MoS₂, judging by the similarly intense hexagonal diffraction pattern. PL spectrum (Figure 2G) displays a peak at 676 nm, red-shifted by ~50 meV as compared to the 660 nm peak for pristine MoS₂.¹ The corresponding Raman spectrum (inset of Figure 2G) of a single grain contains two prominent peaks at 383.5 and 405.1 cm^{-1} , which correspond to an in-plane E_{2g}^{1} vibration mode $(\omega_{\rm E})$ and the aforementioned A_{1g} mode $(\omega_{\rm A})$ of MoS₂, respectively. The difference of 21.6 $m cm^{-1}$ between $\omega_{\rm E}$ and $\omega_{\rm Av}$ which can be used to determine the layer number,^{3,10} indicates SL MoS₂. Raman measurements of 40 different grains (Figure S3B) further indicates that the average interpeak separation is 21.6 cm⁻¹ (383.1 \pm 0.17 and 404.9 \pm 0.14 cm⁻¹ for $\omega_{\rm E}$ and ω_A), which is greater than 19 cm⁻¹ for mechanically exfoliated SL MoS₂.^{3,10} Like the case of homologous MoSe₂, PL position mapping of a representative MoS₂ grain (inset of Figure 2H) displayed that the PL position from the center exhibits a redshift (679 nm) as compared to that of pristine MoS_{21} along with spatial heterogeneity.

The PL position of the TMD is quantitatively sensitive to strain.^{27,28,38,39} It was reported that the SL MoS_2 exhibits a PL red-shift per % tensile uniaxial²⁷ (biaxial)³⁹ strain (i.e., -45 (-99) meV/%), indicating that 1.0 (0.45) % tensile strength results in PL red-shift. In particular, since the CVD-grown SL MoS₂ grain is prepared at high temperature over 650 °C, this condition produces substantial strain owing to the substrate/ TMD interaction and the differences in TEC, supported by a recent report.²⁸ Similarly to the case of MoS₂, the SL MoSe₂ displayed PL shift per % strain (-42 (-90) meV/% for uniaxial²⁹ (biaxial)⁴⁰ strain). On the basis of these shifts, our SL MoSe₂ and MoS₂ exhibit a PL red-shift corresponding to 1.4 (0.65) and 1.0 (0.45)% tensile strains for uniaxial (biaxial) stretching, indicative of substantial interaction with the underlying substrate. The comparison of PL-based values with strain values (0.47 and 0.58% for $MoSe_2$ and MoS_2 , respectively) obtained from the calculation considering TEC



Figure 3. Spatial analysis of a lateral $MoSe_2-MoS_2$ core-shell grain using PL and Raman mapping. (A) The OM image and (B) the corresponding PL position map. (C) PL contour maps near the interface indicated by yellow arrow in (A), and (D) the selected PL spectra acquired at the respective position. (E) Schematic illustration of strain evolution near heterojunction.



Figure 4. Characterization of lateral MoS_2-MoSe_2 core-shell structure. (A) The OM image of several hTMD grains. (B) Spatial PL spectrum extracted from lateral MoS_2-MoSe_2 core-shell grain (indicated with white arrow in (A)). (C) PL spectrum changes across the interface whose numbers correspond to spatial positions in (B). (D) Spatial Raman spectrum of the interface indicated by white arrow in (A) and (E) its corresponding Raman spectrum changes across the interface.

differences between the TMD and SiO_2 substrate (see Supporting Information for the details)⁴¹ indicates that the strains result from biaxial stretching during the CVD cooling process. We also note that strain distributions of MoSe₂ and MoS₂ based on PL position (insets of Figure 2D,H) are different despite similar growth conditions. Typically, the interior has greater tensile strain as compared to the edge.²⁸ Currently, we speculate that this result is related to different surface energies of MoSe₂ and MoS₂ as compared to the underlying SiO₂ surface,^{42–44} leading to sliding of the TMD. Recently, the surface energy of few-layer MoS₂ via contact angle measurement⁴² was determined to be 46.5 mJ/m², whereas indirect measurement from dispersions with various solvents roughly estimates that MoSe₂ along with MoS₂ have surface energies of 70 mJ/m²,⁴³ which are markedly different from that (i.e., 130–260 mJ/m²) of SiO₂, which also highly depends on hydration.⁴⁴ The discrepancy for the surface energies in the TMDs requires more detailed study. Never-

theless, because the basal plane of the TMD is under tensile strain, the peripheral edges would have weak interactions with underlying substrate, expressing relatively compressive strain as compared to tensile strain in the basal plane. This is in accordance with PL shift of CVD-grown MoS_2 in our case. With this result in mind, the optical characterization of the produced lateral hTMD were performed.

MoSe₂-MoS₂ Core-Shell (or Forward Growth). In order to understand spatial heterogeneity of optical properties, PL and Raman maps were collected (see Methods for the mapping details) via a custom-made micro Raman setup.⁴⁵ Figure 3A displays the OM image of a MoSe₂-MoS₂ coreshell grain. The image displays distinct three parts contrasted by their colors. The resulting PL position map (Figure 3B) displays two PL positions centered at 788 and 666 nm for the inner and outer parts, respectively, indicating the core MoSe₂ and shell MoS₂ parts, respectively. Upon closer inspection of Figure 3B, a general trend exists in that the PL position of the MoS₂ shell progressively red-shifts, as its location becomes closer to the interface with the MoSe₂ core. Figure 3C illustrates a PL contour map near the interface, showing that PL positions of MoS₂ and MoSe₂ become slightly closer for each other. The PL spectra of MoS₂ and MoSe₂ near the interface (Figure 3D) display a 3 meV red-shift and 6 meV blue-shift, respectively, as compared to those away from the interface. The observed peak shift in each region originates from the compensation of the lattice mismatch between two TMDs, as portrayed by Figure 3E. For instance, in-plane lattice constants (a) of MoSe₂ and MoS₂ are 3.32 and 3.18 Å, respectively, showing 4% lattice constant difference.5,41 Near the interface of the hTMD, MoS₂ experiences tensile strain, while MoSe₂ undergoes compressive strain, leading to opposite PL shifts. We also acquired similar Raman spectra near the interface, as shown in Figure S4A-D. The band difference for MoS_2 and $MoSe_2$ is below our detection limit (<1.2 cm⁻¹), which is expected for strain below 0.1% (see Supporting Information for the detailed explanation). Although Raman spectra display little difference, the comparison of AFM height and phase images (Figure S4E,F) suggests that MoS_2 shell has larger phase drag especially for the interface as compared to that of the MoSe₂ core, indicating a different substrate interaction.

MoS₂-MoSe₂ Core-Shell (or Reverse Growth). Since the substrate interaction might be different for the core/shell position, an hTMD with opposite growth order has been conducted. Figure 4A displays an OM image of an hTMD synthesized in the reverse manner. Like the aforementioned contrast, MoS₂ core exhibits thinner contrast as compared to that of the MoSe₂ shell. In this time, MoSe₂ shell contains small triangular satellites along its triangular periphery. Across the interface (Figure 4B), the MoS₂ core exhibits a 22 meV red-shift (i.e., 693 to 702 nm), while the MoSe₂ shell displays a 3 meV blue-shift (797 to 800 nm) as it approaches the interface. According to a of the TMD, it shows a similar trend of PL shift trends observed in forward growth, suggesting that lattice mismatch plays an important role for determining relative PL behavior near the interface. In addition, while the corresponding AFM height image (Figure S5A) shows negligible height difference near the heterostructure, the AFM phase image (Figure S5B) displays that the shell region near the heterojunction has large phase deviation from the core, suggesting a different substrate interaction as shown in the forward growth.

Large PL variation indicates that vibrational variations must exist near the interfaces. For this, the Raman map for the MoSe₂ shell and MoS₂ core was presented in Figure 4D. In the MoS₂ region, both $\omega_{\rm E}$ and $\omega_{\rm A}$ peaks display downshifts by 2 cm⁻¹ near the interface with increasing peak separation, while $\omega_{\rm A}$ of the MoSe₂ region displays weak dependency. The magnitude of the change in MoS₂ and MoSe₂ is nearly proportional to the observed PL change. The corresponding spatial Raman spectra (Figure 4E) display simultaneous $\omega_{\rm E}$ and $\omega_{\rm A}$ shifts, supporting an increased tensile strain.^{27,28,30} This is in good agreement with the PL behavior.

We also witnessed a large PL red-shift of $MoSe_2$ in triangular satellites along the shell as indicated by red arrows in Figure 5.



Figure 5. Abrupt PL spectrum changes of MoSe₂ shell near satellite triangles whose numbers correspond to localized spatial positions in PL position map as inset.

As compared to that (~800 nm) of the $MoSe_2$ shell, the triangular region exhibits a red-shifted PL peak at 805 nm, which is a similar value to that observed in homologous $MoSe_2$. Since the triangular satellites are grown by independent nuclei,⁴⁶ subsequent merging with the $MoSe_2$ shell does not alter the intrinsic PL property. This result indicates that smaller red-shift in $MoSe_2$ shell originates from the hTMD.

DISCUSSION

PL shift might originate from the doping effect between chalcogen atoms near the heterojunction. Recently, Zhang et al.,⁴⁷ demonstrated that second harmonic generation was not suppressed in the heterojunction of the in-plane SL WS₂-MoS₂ heterostructure, which excludes the possibility of a doping effect near the heterojunction in the macroscopic level. Therefore, strain during CVD growth is possible reason for the different PL behavior according to core/shell location. The net effect of growth order was investigated by comparing PL shifts of respective grains (i.e., TMD vs hTMD). First, both the MoSe₂ core and shell from the controlled growth order display lesser PL red-shifts (i.e., 787 and 800 nm, respectively), and homologous MoSe₂ exhibits the greatest PL red-shift (i.e., 811 nm) as compared to that (i.e., 780 nm) of exfoliated MoSe₂ (Figure 6A). Within an hTMD grain, the interfacing region of MoSe₂ with MoS₂ always displays a lesser red-shift than that of the basal plane, indicating relieved tensile strain (or compressive) induced by lattice mismatch of adjacent MoS₂ in an hTMD. In addition, the MoSe₂ core in an hTMD exhibits a lesser PL shift by ~20 meV (i.e., 787 nm) than the MoSe₂ shell does (i.e., 800 nm), indicating that growth order plays a role. On the other hand, the MoS₂ interface in an hTMD (Figure 6B) exhibits red-shift irrespective of growth order as



Figure 6. Influence of substrate interaction and lattice mismatch according to core/shell locations as compared to those of a mechanically exfoliated TMD. (A) $MoSe_2$ and (B) MoS_2 .

compared to basal plane of MoS_2 , indicating more tensile strain exerted by interfacing $MoSe_2$. Note that tensile strain of the MoS_2 core exceeds that of individual MoS_2 (indicated by star) and exhibits the greatest red-shift.

Different PL behavior of the hTMD according to position (i.e., core and shell) displays systematic change. For instance, if a TMD with smaller a situates at the core region, the tensile strain of the TMD core is augmented by the additive contribution from tensile strains from the substrate interaction and lattice mismatch, as witnessed by the case of the MoS₂ core. In the opposite case, the TMD shell with larger a experiences both compressive strain by interfacing the TMD with smaller a and tensile strain with substrate, leading to smaller blue-shift in a subtractive manner. Overall, lattice mismatch and substrate interaction influences PL behavior in an additive manner, and the substrate interaction is different for the core and shell regions. However, the observed strain values near the heterojunction in Figure 6A,B is below 4% lattice mismatch between MoSe₂ and MoS₂. A recent scanning tunneling microscopy study revealed that strains and bandgap away from the heterojunction of WSe2 and MoS2 decrease rapidly with few tens of nanometer scale, and residual lattice relaxation occurs with a much longer range.^{48,49} Considering the pixel size (~1 μ m) in PL and Raman mapping, the strain value we observed near the heterojunction is mainly attributed to averaged residual strain extended from the lattice mismatch.

This observation provides a ramification on the energy band structure of a CVD-grown hTMD considering strain near the heterojunction. Figure 7A,B display a schematic of energy structure diagrams of the MoSe₂–MoS₂ core–shell structure obtained from ideal (left) and CVD-grown sample (right), considering localized strains induced by local lattice mismatch, respectively. The energy gap between the conduction band



Figure 7. Schematic band structures of MoSe₂-MoS₂ core-shell from (A) ideal and (B) CVD-grown hTMDs considering strains.

minimum (CBM) and the valence band maximum (VBM) of the basal plane is slightly smaller than that of the ideal case owing to the tensile strain originating from substantial substrate-TMD interaction. Lattice mismatch near the heterojunction results in MoSe₂ experiencing compressive strain and causes a slightly larger band gap as compared to that of the basal plane, whereas the interfacial MoS₂ undergoes tensile strain and exhibits a slightly smaller band gap. This scenario is further supported by a recent report that the TMD with a larger lattice constant exhibits periodic creases owing to lattice mismatch from the heterojunction of an epitaxial hTMD.⁵⁰ It is important to mention that, under external bias. band structure is further modified to fine band alignment near the immediate heterojunction, showing type II to I changes.^{48,49} This result underscores that an hTMD has different origins for the same PL red-shift.

CONCLUSION

In the investigation described above, we systematically elucidated the strain effect near the heterojunction of an hTMD decoupled from the substrate effect. Lateral MoSe₂-MoS₂ core-shell/shell-core heterostructures grown by using a CVD method via two steps revealed that although the growth conditions are similar to those used to prepare individual TMDs and hTMDs, they have significantly different optical properties. Optical phenomena originating from the mingled effect from substrate interaction and lattice mismatch were carefully categorized by growth order control. While homologous SL MoSe₂ and MoS₂ grains are strongly influenced by substrate interaction, an hTMD displays core/ shell-dependent PL behavior. Specifically, while lattice mismatch results in PL blue- and red-shifts according to relative lattice constant, the core and shell regions exhibit different degrees of substrate interaction, in which the core region displays strong interaction. The observations made in this effort should be useful for designing an hTMD structure for various applications including a field-effect transistor, photodetector, and gas sensor.

METHODS

Materials and Instrumentation. Powders of MoO_3 (ACS reagent, $\geq 99.5\%$, lot # MKBJ0251V), selenium (99.99%, lot # MKBL9088V), and sulfur ($\geq 99.5\%$, lot # BCBF3948V) were purchased from Sigma-Aldrich and were stored in a desiccator. Reagent-grade solvents were utilized for washing and cleaning purposes. SEM images were acquired using a JEOL 6701F with an acceleration voltage of 3 kV. AFM height topographies were acquired by using the tapping mode with a Nanowizard I (JPK Instrument) and an Al-coated silicon cantilever (force constant: 37 N/m, resonant frequency: 300 kHz ACTA-20, App Nano). The acquired 512 × 512 pixel images were baseline-corrected by using polynomial fitting.

CVD Growth of a Homologous TMD and hTMD. The APCVD method was used to grow TMD grains. In order to gain tight control of temperature, a temperature profile of a fused silica tube (1 in.) in a CVD oven (Lindberg/Blue M, TF55030C-1) was obtained by using a high-temperature thermometer (Traceable Total-Range Thermometer, Control Company) with a thermocouple ($-200\sim1370$ °C, all Type-K probe). A 285 nm thick SiO₂/Si substrate (lot # 7400397-601, ShinEtsu) was cleaned sequentially with deionized water, ethanol, acetone, and isopropanol after piranha cleaning and final N₂ stream drying. In order to grow a MoSe₂ film, 14 mg of MoO₃ powder and 20 mg of Se powder were placed in separated alumina crucibles. The cleaned substrate was placed in a face-down manner above the alumina boat containing MoO₃ placed at the center of the heating zone. The quartz tube was fed with 15 sccm Ar (99.9%) and 1

sccm H₂ (99.99%) throughout the growth and cooling steps. The growth of the MoSe₂ was conducted at 650 °C for 15 min and at 220–250 °C for Se. After this, the oven was cooled to room temperature in order to obtain MoSe₂ grains. MoS₂ shell growth was conducted in a similar manner. An alumina boat containing 20 mg of sulfur powder was placed at the upstream position, whereas the synthesized MoSe₂ substrates were placed on an alumina boat containing 14 mg of MoO₃ powder by aligning the evaporation mark left from the first growth with the boat. The MoS₂ growth was performed at 650 °C as the heating zone temperature and 150–200 °C for sulfur under 5 sccm Ar flow.

OM Measurement. OM measurements were conducted using either 20× (UPlanFL, Numerical Aperture (N.A.): 0.50, Olympus) or 100× (MPlanFL N, N.A.: 0.90, Olympus) objective lenses. For the OM image, a CMOS camera (3.6 μ m/pixel, 1280 × 1024, DCC1645C, Thorlabs) was utilized. For a quantitative OM image, a 14 bit Si CCD (6.45 μ m/pixel 1392 × 1040, CoolSNAP HQ², Photometrics) was used with a 550 nm filter (fwhm = 10 nm, FB550-10, Thorlabs) in the emission side.

TEM Measurement. TEM samples of TMD grains were prepared by using the poly(methyl methacrylate) (PMMA, 950 kDa in 2% anisole, Microchem)-assisted transfer technique.¹⁸ The substrate containing the TMD sample was spin-coated with PMMA at 3000 rpm for 60 s, which results in ~70 nm thickness. Solvent was removed by baking the resulting substrate at 100 °C for 4 h under 30 mTorr vacuum. After optional cutting of the substrate, the sample was immersed into 1 M KOH solution for 4-5 h to etch the underlying SiO₂/Si substrate. The substrate-removed floating sample was scooped by using a slide glass, washed twice with deionized water, and transferred to a TEM grid (200 mesh, CF200-Cu, Electron Microscopy Sciences). The TEM grid was further dried in a convection oven, and the protective PMMA was removed by immersion in an acetone bath. TEM measurement was conducted using a JEOL 2100 and JEM-F200 with an acceleration voltage of 200 kV.

Raman and PL Measurements. Raman signal was obtained by using a backscattered geometry with a home-built upright microscope setup and calibrated with a Hg lamp according to our previous report.⁴⁵ A spectrometer (Triax 320 (focal length: 320 mm, 1800 gratings/mm, resolution: 2 cm $^{-1}$), Horiba Jobin-Yvon) with a Si array CCD (26 μ m/pixel, 1024 × 256, Syncerity, Horiba Jobin-Yvon) was used to obtain a spectrum. A diode-pumped solid state laser (532 nm) was used as an excitation source, and the objective lens with 100× magnification (MPlan, N.A.: 0.90, Olympus) was used to focus and make a diffraction-limited spot. The typical laser spot size was about ~1 μ m. An additional Si peak at 520.89 cm⁻¹ was used as an internal reference. In order to obtain Raman and PL mapping of an hTMD with a reasonable time duration (1-2 days for 1800 g/mm gratings), less than 0.5 mW of laser beam power was utilized with an accumulation time of 5 to 20 s. In the meanwhile, PL images were acquired with wide-field illumination of a 4 mW laser by using a beam expander $(1-8\times$, Cat. #: 68479, Edmunds) and a convex lens (f =200 mm, doublet, AC254-200-A-ML, Thorlabs) in the excitation beam path, as previously reported in the literature.⁴⁵ For a typical measurement, accumulation of 50 or 500 s with a 100× objective lens and a 2× beam expander were utilized with less than 4 mW beam power. Band-pass filters of either 660 or 780 nm (fwhm = 10 nm, FB660-10 and FB780-10, respectively, Thorlabs) were used in the emission path to image the PL of MoS₂ and MoSe₂, respectively, using an imaging CCD (4.54 μ m/pixel 1940 × 1460, CoolSNAP MYO, Photometrics). Raman maps were acquired by scanning stage (twophase stepper motor, resolution: 0.01 μ m, SCAN 75 \times 50–2 mm, Marzhauser Wetzlar GmbH & Co.). Typical step size for rasterscanning is $1 \ \mu m$.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaelm.8b00051.

Temperature profile of the oven (Figure S1); RMS roughness comparison between $MoSe_2$ on the substrate and the substrate only (Figure S2); respective Raman spectra of over 40 grains of $MoSe_2$ and MoS_2 (Figure S3); strain calculation based on TEC differences; AFM and Raman analysis of $MoSe_2-MoS_2$ core-shell region (Figure S4); AFM height and phase images of lateral MoS_2-MoSe_2 core-shell region (Figure S5); and table of PL and Raman shifts per strain according to TMD type (Table S1) (PDF)

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Growth Order-dependent Strain Variations of Lateral Transition Metal Dichalcogenide Heterostructures

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Figure S1. Measured temperature profile of CVD oven (Lindberg/ Blue M, TF55030C-1)

according to set temperature of heating zone, and the distance from the oven center under atmospheric pressure. 650 °C line and outside of the oven is indicated as lines as guides.



Figure S2. RMS roughness comparison between MoSe₂ on SiO₂/Si substrate (orange) and substrate (green) only.



Figure S3. Raman spectra (A) MoSe₂ and (B) MoS₂ grains from over 40 different triangular grains grown by single step. Bottoms are average Raman peak positions with standard deviation.

of $MoSe_2$ and MoS_2 lattice along a axis can be expressed as following polynomial equations, according to the reference¹:

 $a(MoS_2) = 3.1621 + 0.6007 \times 10^{-5}t + 0.3479 \times 10^{-7}t^2$

$$a(MoSe_2) = 3.2910 + 0.2382 \times 10^{-4}t + 0.0118 \times 10^{-7}t^2$$

where t is temperature in Celsius. Since the thermal expansion coefficient of amorphous SiO₂ is negligible $(\sim 0.56 \times 10^{-7} / ^{\circ}C)$,¹, this value can be ignored in the calculation. For SL MoS₂, the tensile strain in MoSe₂ and MoS₂ can be calculated by:

strain (MoS₂) =
$$\frac{a_{650} - a_{20}}{a_{20}} = 0.58\%$$

strain (MoSe₂) = $\frac{a_{650} - a_{20}}{a_{20}} = 0.47\%$

Characterization of the lateral MoSe₂-MoS₂ core-shell (Figure S4). The AFM image (Figure S4A)

of the grain displays height topography corresponding to concentric equilateral triangles with different heights. The height profile (Figure S4B) shows that shell, middle, and inner triangle layers have average heights of ~1.8, 1.0, and 2.2 nm, respectively. The observed small PL variation would result in smaller Raman spectra variations near the interface. In Figure S4E and F are displayed spatial and its corresponding Raman spectra recorded across the interface (indicated with black arrow in Figure S4C). No appreciable peak shift in ω_E and ω_A of MoS₂ and ω_A of MoSe₂ is observed because the PL shift per strain, which is proportional to Raman shift per strain, is small.

The results of Raman mapping reveal the existence of localized vibrational frequency variations of hTMD. In Figure S4C and D are displayed the ($\omega_A - \omega_E$) map of MoS₂ shell, and ω_A map of hTMD. Although the interpeak difference ($\omega_E - \omega_A$) map from the MoS₂ shell (Figure S4C) exhibits a similar value (*i.e.*, ~20.1 cm⁻¹) throughout the domain, the down corner region of the MoS₂ shell (indicated by dotted circle) displays a ~0.5 cm⁻¹ downshift (*i.e.*, 405.1 cm⁻¹) in both ω_E and ω_A (Figure S4D), as compared to the average positions (*i.e.*, 405.6 cm⁻¹). Moreover, down corner region of the ω_A map of MoSe₂ (Figure S4D) display a similar behavior. Although the frequency shift is small and below our levels of spectral resolution (*i.e.*, 0.8 cm⁻¹), the simultaneous shift for both TMDs interfacing with each other is observable, indicating the presence of localized substrate-TMD interactions.



Figure S4. Characterization of the lateral MoSe₂-MoS₂ core-shell of Figure 3 in the maintext. Raman maps of (A) interpeak separation or ω_A-ω_E, and (B) ω_A. (C) Raman contour maps near the interface indicated by black arrow in (A), and (D) the selected Raman spectra acquired at the respective position. (E) AFM height image of the

representative hTMD and (F) its height profile along orange triangles in (A) with cartoons for layered structures as an inset. (G) AFM phase image of the corresponding hTMD and (H) phase profile.



Figure S5. (A) AFM height and (B) phase images of lateral MoS₂-MoSe₂ heterostructure. The

line traces originates from the dotted lines in each image.

 Table S1.
 PL and Raman shifts per strain according to TMD type.

TMD type		Energy shift for strain				
		PL (meV/%)		Raman (cm ^{-1/%})		
		Uniaxial	Biaxial	Uniaxial	Biaxial	
MoS ₂	SL	$\begin{array}{c} -45\pm7^a\\ -70^b\end{array}$	-99°	$\begin{array}{c} - \text{ and } + \text{ modes of} \\ \text{E}^{1}_{2g} \text{: } -4.5 \pm 0.3 \\ \text{ and } -1.0 \pm 1^{a} \end{array}$	E^{1}_{2g} : -5.2 ° A^{1}_{g} : -1.7 °	
	BL	$\begin{array}{c} -53\pm10^a\\ -48\pm5^b\end{array}$		$\begin{array}{l} - \text{ and } + \text{ modes of} \\ \text{E}^{1}_{2\text{g}} \text{:} -4.6 \pm 0.4 \\ \text{ and } -1.0 \pm 0.9^{a} \end{array}$		
	ML	N.A.		3~5 layer: -1.7°		
MoSe ₂	SL	-42 ^d	-90^{f}	N.A.		
	BL	-35 ^d		N.A.		

^aNano Lett. 13, 3626–3630 (2013) ^bNano Lett. 13, 2931–2936 (2013) ^cNano Lett. 13, 5361–5366 (2013) ^dChinese Phys. B 25 (7), 077802 (2016) ^eNano lett. 16, 5836-5841 (2016)

^f npj 2D Mater. Appl *1* (1), 10 (2017).

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