Heteroepitaxial van der Waals semiconductor superlattices

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Abstract

We report atomic layer-by-layer epitaxial growth of van der Waals (vdW) semiconductor superlattices (SLs) with programmable stacking periodicities, composed of more than two kinds of dissimilar transition-metal dichalcogenide monolayers (MLs), such as MoS$_2$, WS$_2$ and WSe$_2$. The kinetics-controlled vdW epitaxy in the near equilibrium limit by metalorganic chemical vapour depositions enables to achieve accurate ML-by-ML stacking, free of interlayer atomic mixing, resulting in the tunable two-dimensional (2D) vdW electronic systems. We identified coherent atomic stacking orders at the vdW heterointerfaces, and present scaling valley polarized optical excitations that only pertain to a series of 2D type II band alignments.

Main Text

For decades, semiconductor superlattices (SLs), periodically layered structures of two alternating semiconductors in the atomic thickness regime, have served as the material platform of various heterojunction devices in modern electronics, photonics and display technology$^{1,2}$. Such prominent SL examples can be listed as III-V compound semiconductor SLs (i.e., GaAs/AlGaAs and GaInAs/AlInAs) for high electron mobility transistors$^{3,4}$ and quantum cascade lasers$^{5,6}$, GaN/AlGaN SLs for light emitting diodes$^{7,8}$ and Si/Ge SLs for strained Si CMOS$^9$. Therein, the constituent semiconductors are “covalent-bonded” across the heterointerfaces with the lattice-matching coherences$^{10-12}$, where the two-dimensional (2D) charge carriers form diverse quantum well (QW) structures, depending on the degrees of interlayer coupling strengths$^{13}$. Meanwhile van der Waals (vdW) semiconductors, which often stemmed from transition-metal dichalcogenides (TMDCs, $M X_2$, where $M$ and $X$ represent transition-metal ions and chalcogen ions), naturally ensue the inherent 2D confinements within the unit monolayer (ML) across the chemical-bond free vdW gaps$^{14-16}$. As a broad range of TMDC semiconductors are available as a ML crystal with diverse electronic structures, precise integration of each kind into vdW-SLs can generate another category of the QW structures for unexplored functionalities$^{17-19}$. Despite extensive research on the bilayer stacks of dissimilar vdW-MLs to investigate new types of interlayer excitations, such as interlayer excitons$^{20-23}$ and twist-angle dependent strong correlations$^{24,25}$, little is known for the QW states of vdW-MLs$^{26,27}$, mainly due to fact that they are not synthetically available to date$^{28}$. Otherwise, they can be prepared by manual transfer-based stacking with some atmospheric impurities, which may not be unavoidable for the scalable integrations$^{29-31}$. In this work, we report direct growth of vdW-MLs, heteroepitaxially stacked with MoS$_2$, WS$_2$ and WSe$_2$ MLs, by metalorganic chemical vapour depositions (MOCVD)$^{32,33}$. We have achieved precise ML-by-ML sequential stacking with atomically clean and sharp heterointerfaces by kinetic control of heteronucleation in the near-equilibrium limit$^{32,34,35}$. This ML-by-ML stacking epitaxy also enables to realize the tunable vdW SL electronic structures in ML precision. We identified several atomic stacking orders at the vdW heterointerfaces, and present scalable valley polarized optical excitations that only pertain to a series of 2D type II band alignments.

Heteroepitaxial growth of vdW semiconductor superlattices
Elemental variation in the $MX_2$ SLs can be achieved either in $M$-alteration ($MX_2/M'X_2$) or $X$-alteration series ($MX_2/MX'_2$). We demonstrated both series in MoS$_2$/WS$_2$ and WS$_2$/WSe$_2$ SLs with time-lapse precursor modulations by MOCVD. The first example of MoS$_2$/WS$_2$ SLs was discussed in Fig. 1. The predetermined flow rates of Mo(CO)$_6$ and W(CO)$_6$ precursors for each MoS$_2$ and WS$_2$ ML were set to 4 sccm and 3 sccm on the (C$_2$H$_5$)$_2$S background flow of 2 sccm in a given growth sequence. A series of cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images in Fig. 1a, taken in each growth step up to 7 ML stacks, demonstrate the precise ML-by-ML stacking of WS$_2$ and MoS$_2$. We have successfully achieved such \( vdW \) stacking epitaxy by the kinetics-controlled growth in the near-equilibrium limit, \( i.e. \), the lateral growth rate, \( n_{growth} \), in each ML was \( \sim 0.15 \text{ nm/min} \) to guarantee the full lateral coverage, which is far slower than the cases of \( \sim 1500 \text{ nm/min} \) in the usual thermal CVD growth\(^{33}\), by setting the lower growth temperatures (550 °C) and precursor partial pressures (\( \sim 10^{-7} \text{ torr} \)) of MO precursors. This optimized growth condition essentially suppresses the unwanted overgrowth and interlayer mixing\(^{36,37}\) - also see Supplementary Figs. 1-4 for the detailed growth optimizations. Here we stress that the basal planes of the first MLs with the highly preferred in-plane orientations are the prerequisite for the ML-by-ML growth. For that, we have grown the first ML films on the step-and-terrace terrains of $c$-sapphire substrates, which were then mechanically transferred on SiO$_2$/Si substrates as the growth templates for the subsequent stacking growth. We fully discuss these features in Fig. 3. The layered structures of MoS$_2$/WS$_2$ SLs in greater details were presented in Fig. 1b, where the total 9 MLs (1:1 alternation of 5 WS$_2$ MLs and 4 MoS$_2$ MLs) were captured by the Z-contrast in HAADF-STEM image and energy dispersive X-ray spectroscopy (EDX) spectra. One can clearly identify the distinct intensity contrast between WS$_2$ and MoS$_2$ MLs, arising from the atomic number (Z) difference of $Z_{Mo} = 42$ and $Z_W = 74$, where the brighter MLs are WS$_2$ and the darker MLs are MoS$_2$. In addition, the periodically alternating W-$L_\alpha$ and Mo-$K_\alpha$ peak intensity across each \( vdW \) gap, assures such SL modulations. Although the image in Fig. 1b cannot be atomically resolved with a fixed TEM zone axis in the entire area, due to finite in-plane orientation variants of each ML, when the zone axis is aligned to <11 0> of the lowest ML, the local atomic structures can be identified in the bright-field (BF) STEM images. For example, we observed either \( AC \) (translation) or \( AA' \) (180° rotation) stacking sequences between WS$_2$ and MoS$_2$ MLs with the > 90 % area coverage (Fig. 1c) – we call these stacking polytypes “coherent stacks” as classified in Supplementary Fig. 5. We also found local areas with some mixtures of random rotation stacks with the < 10 % area coverage (Fig. 1d) – we call these random orientation stacking polytypes “incoherent stacks”. Interestingly, we found different values of the interlayer distances for coherent and incoherent stacks to be 0.606 nm and 0.647 nm, arising from different \( vdW \) gap sizes, consistent with the calculations\(^{38}\): we also note that the value at the coherent stack, where individual atoms tend to reside at the thermodynamically stable coordinates, is notably smaller than the average value from mechanical stacking cases\(^{39}\). The synchrotron grazing incidence wide-angle X-ray diffraction (GI-WAXD) was employed to obtain larger-scale crystallographic coherence in both out-of-plane (\( i.e., q_z \)) and in-plane (\( i.e., q_{xy} \)) directions of our SLs, as in Fig. 1e. The 2D pattern of GIWAXS at the incidence angle of 0.12° in Fig. 1f shows a series of sharp Bragg spots in reciprocal space, indicating the highly ordered P6$_3$/mmc
structures of our MoS\textsubscript{2}/WS\textsubscript{2} SLs (9 ML stacks). For a reference, we compared GI-WAXD patterns from homoepitaxial MoS\textsubscript{2} 9L, which possesses smaller grain sizes of \(~80\) to \(100\) nm in Supplementary Fig. 6. The 1D line-cut profiles were analyzed in both out-of-plane \((q_z)\) and in-plane \((q_{xy})\) directions, as shown in Fig. 1g,h. The \(q_z\) line-cut profile at \(q_{xy} = 2.3\ \text{Å}^{-1}\) clearly shows 4 diffraction peaks from heteroepitaxial MoS\textsubscript{2}/WS\textsubscript{2} SLs (purple) and homoepitaxial MoS\textsubscript{2} 9Ls (grey), verifying the highly ordered stacking textures – more pronounced peaks from MoS\textsubscript{2}/WS\textsubscript{2} SLs indicate the higher degree of ordering, due to larger grain sizes. The interlayer distances are extracted from the (103) diffractions to be 0.616 nm, consistent with the value at the coherent stack regions measured from STEM images. Similarly we find it to be 0.617 nm from MoS\textsubscript{2} 9Ls - see also Supplementary Table 1 for the complete diffraction analyses. The vertical coherence length, \(L_{c(103)}\), which strictly quantifies the number of coherently repeating layers along the \(q_z\) direction, can be also extracted to 1.87 nm by Scherrer equation – it is 1.49 nm in MoS\textsubscript{2} 9Ls. The in-plane diffraction peaks of (100), (110), and (200) are also distinct, and much pronounced in MoS\textsubscript{2}/WS\textsubscript{2} SLs, suggesting the highly ordered in-plane textures with preferred orientations. Therein we extracted the (100) interplanar distance to be 0.273 nm from the (100) diffractions in the \(q_{xy}\) line-cut profiles at \(q_z = 0\ \text{Å}^{-1}\) - see also Supplementary Table 2. Overall, we define the crystalline textures of our \(vdW\) SLs as largely coherent \(vdW\) vertical stacks, composed of in-plane oriented polycrystalline MLs.

**Designer growth of \(vdW\) semiconductor superlattices with tunable periodicities**

The established heteroepitaxial stacks of MoS\textsubscript{2}/WS\textsubscript{2} SLs by a ML-by-ML mode enables to achieve designed SLs with arbitrary periodicities. Figure 2a,b demonstrate 1:2 MoS\textsubscript{2}/WS\textsubscript{2} SLs and 2:2 MoS\textsubscript{2}/WS\textsubscript{2} SLs. This growth tunability in our \(vdW\) SL heteroepitaxy is markedly contrasted from previous covalent-bonded SLs, which intrinsically suffer from the strict requirements of lattice matching heteroepitaxy upon stacking. We also show an example of \(X\)-alteration SLs in \(MX_2\), i.e., WSe\textsubscript{2}/WS\textsubscript{2} SLs in Fig. 2c, where we employed (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}S and (C\textsubscript{2}H\textsubscript{5})\textsubscript{2}Se precursors in each time-lapse on the continuous W(CO)\textsubscript{6} background flow for the WS\textsubscript{2} and WSe\textsubscript{2} MLs (see also Supplementary Fig. 1 and 7 for the growth optimizations). Although the intensity contrast between WS\textsubscript{2} and WSe\textsubscript{2} MLs was less obvious in the \(Z\)-contrast in HAADF-STEM image, due to smaller \(Z\)-sensitivity, compared to MoS\textsubscript{2}/WS\textsubscript{2} SLs, the periodic oscillation of S-\(K\alpha\) and Se-\(K\alpha\) peaks in the EDX spectra clearly validates SL modulations. Then, we have successfully established both \(M\)- and \(X\)-modulated SLs, heteroepitaxial WSe\textsubscript{2}/MoS\textsubscript{2}/WS\textsubscript{2} trilayers, as shown in Fig. 2d. In addition, our heteroepitaxial growth can be extended to include graphene, which was intermittently inserted by an \(ex-situ\) dry-transfer method (Fig. 2E and Supplementary Fig. 8).

**In-plane crystalline textures of \(vdW\) semiconductor superlattices**

Heteroepitaxial evolution of in-plane crystal textures of our \(vdW\) SLs are investigated in WSe\textsubscript{2}/WS\textsubscript{2}/MoS\textsubscript{2} trilayers, where the chemical compositions vary for both \(M\) and \(X\), and the in-plane lattice constants also vary - they are known as 0.315 nm for bulk WS\textsubscript{2} and MoS\textsubscript{2}, and 0.328 nm for bulk WSe\textsubscript{2}. Figure 3a-c are the schematic descriptions of each stacking during the successive growth, in which the initially formed
multiple triangular facet crystals merge to form continuous MLs. Statistical variation in the in-plane crystal orientations can be verified in six-fold periodic clustering of (10 0) diffraction patterns with some degree of angular spreads (inset of Fig. 3d). The first bottom MoS$_2$ ML was formed by multiple nucleation on the regular step and terrace terrains of c-sapphire substrates to initiate the preferred in-plane crystal orientations with a typical grain size of ~0.1 to 1 μm, which are either 0° or 60° rotated with respect to each other, as captured by a series of atomic force microscopy (AFM) images in Fig. 3d (see also Supplementary Figs. 9 and 10). This ML-by-ML growth proceeded upon the successive stacking growth for the second (WS$_2$) (Fig. 3e) and third (WSe$_2$) (Fig. 3f) MLs with smaller grains of 90 - 100 nm – see also in-plane TEM images in Supplementary Fig. 11 and grain size distribution in Supplementary Fig. 12. The larger lattice parameter of 0.331 nm in the third WSe$_2$ ML was also verified from the (11 0) diffraction patterns, where we also measured those of underlying MoS$_2$ and WS$_2$ to be 0.322 nm (inset of Fig. 3f).

Atomic scale images of such in-plane crystalline textures were directly captured by in-plane HAADF-STEM observations of partially covered bilayers, WS$_2$/MoS$_2$, as in Fig 3g-k. We verified that the top MLs are preferentially oriented with the basal planes of the bottom MLs, and the stacking polytypes are mostly either AA' (Fig. 3g and Supplementary Fig. 13) or AC coherent stacking (Fig. 3h). Such textures introduce grain boundaries (GBs), mainly identified as 0° or 60° GBs, which were interfaced between either AC-AC domains (Fig. 3k) or AC-AA’ domains (Fig. 3j and Supplementary Fig. 14). We also observed random interlayer twists, showing Moiré interference patterns (Fig. 3i). According to first-principles calculations,$^41$ the formation energies of small angle (< 5°) and 60° GBs are relatively smaller than those of random angle GBs, suppressing the unwanted local overgrowth of the second MLs – for example, the second ML preferentially nucleates at the random angle GBs (other than 0° or 60° GBs), leading to non ML-by-ML growth. Whereas on the first MLs with 0° or 60° GBs, the nucleation is not locally concentrated leading to the ML-by-ML growth. We indeed observed such growth patterns, where on the smaller grained MoS$_2$ ML templates with random GBs, the initial nuclei of the second WS$_2$ are predominantly populated at such GBs (Supplementary Fig. 3). However, on the larger grained first ML with 0° or 60° GBs, the initial nuclei are uniformly distributed on the entire surfaces. It suggests that the preferred orientation growth in our work is critical to maintain the coherent ML-by-ML growth.

Valley-polarized interlayer excitations in type-II vdW superlattices

As for the electronic structures of our vdW SLs, we estimate them to be a series of type-II band alignments across the vdW gaps to a lowest order. Optical absorption spectra, collected from a series of SLs and each individual MLs in Fig. 4a, one can identify additive features of optical absorption with increasing ML stacks – the spectra of $(MoS_2/WS_2)_n$ SLs, where $n$ is the bilayer stack numbers, are linear sums of WS$_2$ and MoS$_2$ MLs, according to Voigt fitting (Supplementary Fig. 15) – see also Supplementary Fig. 16 for a series of Raman scattering spectra, obtained from the same SL batches. One of the most distinctive electronic features that only pertain in TMDC ML heterostructures is the large and long-lived spin-valley polarization of charge carriers as observed earlier in (mechanically transferred) WS$_2$/WSe$_2$ and WSe$_2$/MoS$_2$ bilayers by pump-probe spectroscopy$^42$. The ultrafast interlayer charge transfer process across the type-II alignment dramatically suppresses the exciton exchange interaction which is the major
relaxation channel of valley polarization in TMDC MLs. We indeed observed scaling of such temporal population of the valley-polarized carriers, arising from a series of type-II band alignments in our MoS$_2$/WS$_2$ SLs. Figure 4b,c illustrate such valley-polarized excitations in real and momentum space with optical circular dichroism (CD), using time-resolved pump-probe spectroscopy. First, the pump pulses with the right-handed circular polarization ($\sigma^+$) (blue arrows in Fig. 4b,c) creates the valley-polarized excitons on $K$ valleys in MoS$_2$ MLs. Then, the immediate interlayer hole transfer occurs across the type-II alignments from the MoS$_2$ ML valence bands to that of WS$_2$ MLs within the ultrafast timescale less than 50 fs$^{43}$. Initially, we verified such interlayer charge separation from the substantially extended lifetime of the CD dynamics in our MoS$_2$/WS$_2$ bilayers, compared to that of MoS$_2$ MLs (see Supplementary Fig. 17). Note that our SL series show shorter lifetime of valley polarization (~nsec), presumably due to higher defect densities, compared to mechanically exfoliated cases. Nevertheless, the valley-polarized electron selectively remains on the $K$ valley of MoS$_2$ MLs (see the upper panel of Fig. 4c). After the pump excitation, the delayed probe pulse (red arrows) was focused on the SLs, and by measuring the pump-induced differential reflectance $\Delta R$ with both $\sigma^+$ and left-handed ($\sigma^-$) circular polarization of the probe beam, we can evaluate CD = $\frac{(\Delta R_{\sigma^+} - \Delta R_{\sigma^-})}{R_0}$, where $R_0$ is probe reflectance without the pump. Such valley-polarized electron gives rise to a helicity-dependent absorption difference ($i.e.$, CD). Then, the transient CD response must scale to the amount of the residual valley-polarized electrons in MoS$_2$ MLs. Figure 4d displays such time-resolved CD responses from a series of (MoS$_2$/WS$_2$)$_n$ SLs at 77 K, when the pump and probe photon energy were set to $A$-exciton resonance of MoS$_2$ MLs with the pump fluence of 5.7 $\mu$J/cm$^2$. We observed the linearly proportional CD signals with increasing $n$ in (MoS$_2$/WS$_2$)$_n$ SLs, as in Fig. 4d.

**Methods**

**Growth of the first ML templates with preferred in-plane crystal orientations**

$MS_2$ ($M$: Mo, W) ML templates were epitaxially grown on $c$-plane sapphire substrates. Prior to the MOCVD growth, sapphire substrates were annealed in ambient air at the temperature of 1150 °C for 12 hours in a box furnace, then loaded into our MOCVD system. Pretreatment of $c$-plane sapphire substrates with chalcogen precursors is known to play a role in enhancing the vdW epitaxy$^{44,45}$. Thus before the growth, the 2-inch hot-walled quartz tube furnace was ramped up to 650 °C for 40 min, and pretreated for 1 hour with $(C_2H_5)_2S$ under the constant partial pressure of $3.3 \times 10^{-4}$ torr, and the carrier gas flow of 150 standard cubic centimeters per minutes (sccm) for Ar (99.9999 %) and 1 sccm for $H_2$ (99.9999 %) at total pressure of 4 torr. After the sulfur treatment, the furnace was ramped up to the growth temperature of 750 °C for 10 min. The total pressure was kept at 1.9 torr under the carrier gas flow of 250 sccm for Ar and 5 sccm for $H_2$. Eutectic salts of KCl and KI was placed at the upstream region of the quartz tube. The growth of MoS$_2$ on sapphire substrates was conducted for 32 hours. During the growth, Mo(CO)$_6$ and $(C_2H_5)_2S$ were supplied under the constant partial pressure of $1 \times 10^{-6}$ torr and $1 \times 10^{-4}$ torr respectively. Both precursors were kept in bubbler-typed canisters at a constant pressure of 1050 torr with Ar, and
maintained at a constant temperature of 10 °C for Mo(CO)$_6$ and room temperature (RT) for (C$_2$H$_5$)$_2$S. In the growth of WS$_2$ on c-sapphire substrates (growth time ~ 21 hours), W(CO)$_6$ and (C$_2$H$_5$)$_2$S were supplied under the constant partial pressure of 4×10$^{-8}$ torr and 1×10$^{-4}$ torr, respectively. Both precursors were kept in canisters at a constant pressure of 1200 torr with Ar and maintained at a constant temperature of 0 °C for both W(CO)$_6$ and (C$_2$H$_5$)$_2$S. Epitaxial MoS$_2$ and WS$_2$ ML templates on c-sapphire were spin-coated by poly(methyl methacrylate) (PMMA), then transferred onto fresh SiO$_2$/p$^+$-Si substrates using 5% HF solution. PMMA layer was removed by thermal annealing at 350 °C for 2 hours in an ultra-high vacuum chamber (base pressure < 1×10$^{-5}$ torr).

**Heteroepitaxy of MoS$_2$/WS$_2$ and WS$_2$/WSe$_2$ vdW SLs**

Epitaxial MoS$_2$/WS$_2$ SLs were grown on either MoS$_2$ or MoS$_2$ ML templates. The 2-inch hot-walled quartz tube furnace was ramped up to 550 °C for 30 min and the total pressure was kept at 1.9 torr under the carrier gas flow of 150 sccm for Ar and 2 sccm for H$_2$. KCl/KI crucible was placed at the upstream region of the quartz tube. The growth time of MoS$_2$/WS$_2$ SLs was determined by the number of layers and sequences, i.e., 70 hours (2L), 48 hours (4L), 47 hours (6L), and 46 hours (8L) for MoS$_2$, 24 hours (3L), 23 hours (5L), 22 hours (7L), and 21 hours (9L) for WS$_2$. During the given growth time, (C$_2$H$_5$)$_2$S was constantly supplied under the constant partial pressure of 1.5×10$^{-3}$ torr. Meanwhile, Mo(CO)$_6$ (partial pressure of ~ 1×10$^{-6}$ torr) and W(CO)$_6$ (partial pressure of ~ 5.8×10$^{-8}$ torr) were alternated for a given growth time per 1L with breaks for 20 minutes to purge out the residual precursors in the chambers and to adjust the temperature of precursors between each alternation (10 °C for Mo(CO)$_6$ and 0 °C for W(CO)$_6$). Epitaxial WSe$_2$/WS$_2$ SLs were also grown on the ML templates. The 2-inch hot-walled quartz tube furnace was ramped up to 550 °C for 30 min and the total pressure was kept at 1.9 torr under the carrier gas flow of 200 sccm for Ar 7.5 sccm for H$_2$. KCl/KI was placed at the upstream region of the quartz tube. The growth time of WSe$_2$/WS$_2$ SLs was determined by the number of layers and sequences, i.e., 38 hours (2L), 27 hours (4L), and 26 hours (6L) for WSe$_2$ and 25 hours (3L) and 24 hours (5L) for WS$_2$. During the given growth time, W(CO)$_6$ was constantly supplied under the constant partial pressure of 3×10$^{-8}$ torr. Meanwhile, (C$_2$H$_5$)$_2$S (partial pressure of 1.3×10$^{-3}$ torr) and (CH$_3$)$_2$Se (partial pressure of 2.4×10$^{-3}$ torr) were alternated for a given growth time per 1L with long breaks that conducted by ramping down the furnace temperature to room temperature and ramping up the furnace up to 550 °C for 1 hour. All precursors were kept in bubbler-typed canisters at a constant pressure of 1100 torr with Ar and maintained at a constant temperature of -1 °C for W(CO)$_6$ and RT for (C$_2$H$_5$)$_2$S and (CH$_3$)$_2$Se.

**Synchrotron grazing incidence wide angle X-ray diffraction (GI-WAXD)**

The synchrotron GI-WAXD measurements were performed at the 9A U-SAXS beamline of the Pohang Light Source-II. The X-ray from the in-vacuum undulator is monochromated using Si (111) double crystals and focused at the detector position using K-B type mirror. The 2D GI-WAXD patterns were recorded on a 2D CCD (Rayonix MX170-HS). The incidence angles, wavelength of X-ray, sample-to-detector distance, and
exposure time were set to be 0.12°, 0.623 Å (energy = 19.795 keV), 220.242 mm, and 3s, respectively. To denote the index \((hkl)\) and the interplanar distance \((d)\) of the specific plane, we assumed that the space group of our \(vdW\) SLs is \(P6_3/mmc\), which corresponds to 2H-phase TMDCs (AA’ stacks).

**Optical absorption measurements**

Optical absorption measurements of MoS\(_2/WS_2\) SLs were conducted by PerkinElmer-LAMBDA 950 UV-Vis-NIR spectrophotometer with transmission mode. A series of \((MoS_2/WS_2)_n\) SLs \((n\) is the bilayer stack numbers\) and each individual MLs are transferred on double-side polished sapphire wafers using PMMA-supported wet-transfer methods, and PMMA is removed by high vacuum annealing at 350 °C for 3 hours. The absorption was calculated from the following equations under thin film approximation.

\[
A = \frac{n_{\text{substrate}} + 1}{2} \times \frac{T_{\text{substrate}} - T_{\text{SLs}}}{T_{\text{substrate}}}
\]

, where \(A\) is the absorption of the sample, \(n_{\text{substrate}}\) is the refractive index of sapphire substrate, \(T\) is the transmittance of the bare sapphire substrate and the SLs\(^{46}\).

**Transmission electronic microscope (TEM) analyses**

For plan-view TEM observations, TMDC SLs are transferred on Cu TEM grids (holey carbon film grids for DF-TEM imaging and quantifoil grids for STEM analyses) using PMMA assisted wet-transfer methods. Specimens for the cross-section TEM observations were prepared by a focus ion beam (Helios Nanolab 650, FEI). For the protection, 50-nm thickness amorphous carbon layer was deposited on top of the specimen using a carbon evaporator. In the Fig. 1d, 1e, and 3d-h, imaging was conducted by JEOL JEM-ARM 200F with a \(C_s\)-corrected probe operated at 80 kV. The rest of STEM imaging, DF-TEM imaging, and SAED patterns were performed by using a JEOL 2100F with the \(C_s\)-corrected probe operated at 200 kV. EDX was conducted by X-Max EDX systems (Oxford Instrument). Characteristic Mo-\(K\alpha\), W-\(L\alpha\), S-\(K\alpha\), Se-\(K\alpha\) and C-\(K\alpha\) X-ray signals were used in the EDX line-profiles.

**Time-resolved pump-probe spectroscopy for valley polarized carrier dynamics study**

As-grown MoS\(_2/WS_2\) SLs on SiO\(_2/p^+\)-Si substrates were spin-coated by PMMA, then transferred onto fresh sapphire substrates using water-assisted transfer. PMMA layer was removed by thermal annealing at 350 °C for 2 hours in an ultra-high vacuum chamber (base pressure \(< 1 \times 10^{-5} \) torr). To investigate ultrafast valley-polarized carrier dynamics in our \((MoS_2/WS_2)_n\) SLs, time-resolved pump-probe spectroscopy was employed. The output of femtosecond laser source (PHAROS, Light Conversion) and optical parametric amplifier (ORPHEUS) serves wavelength-tunable pump and probe pulses with a repetition rate of 100 kHz and a pulse duration of 50 fs and spectral bandwidth of 50 meV. Both pulses were simultaneously focused on the samples using an objective lens (X40, NA = 0.5), whose relative delay was controlled by a motorized translational stage. The pump pulses were modulated by the optical
chopper, and the change in the probe reflection is recorded by a photomultiplier tube connected to the current amplifier and lock-in amplifier. The optical polarization of both pulses was manipulated independently by quarter wave plates.

**Declarations**

**Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

**Contributions:**

G.J., C.-S.L., and M.-H.J. conceived and designed the project. G.J., C.-S.L., S.-H.L., and M.Y.P. conducted MOCVD growth experiments and material characterizations. O.F.N.O., D.H.Y., and S.-Y.C. performed the TEM measurements and analyzed the data. S.-Y.S and G.M. fabricated the devices and performed optical measurements. S.C., C.H., J.L., J.K., and H.C. carried out ultrafast laser spectroscopy. G.J., C.-S.L., S.C., and M.-H.J. wrote the paper. M.-H.J. supervised the project. All the authors discussed the results and commented on the manuscript.

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**Competing interests:**

The authors declare no competing interests.

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