Coherent, atomically thin transition-metal dichalcogenide superlattices with engineered strain

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Epitaxy forms the basis of modern electronics and optoelectronics. We report coherent atomically thin superlattices in which different transition metal dichalcogenide monolayers—despite large lattice mismatches—are repeated and laterally integrated without dislocations within the monolayer plane. Grown by an omnidirectional epitaxy, these superlattices display fully matched lattice constants across heterointerfaces while maintaining an isotropic lattice structure and triangular symmetry. This strong epitaxial strain is precisely engineered via periodic modulation of the optical properties and producing photoluminescence peak shifts as large as 250 millielectron volts. We present theoretical models to explain this coherent growth and the energetic interplay governing the ripple formation in these strained monolayers. Such coherent superlattices provide building blocks with targeted functionalities at the atomically thin limit.

Epitaxial structures with coherent heterointerfaces, in which lattices of dissimilar materials are repeated and laterally integrated without dislocations, enable advanced scientific and technological applications, including multifunctional oxides with engineered strain and symmetry, high-performance quantum cascade lasers, and high-efficiency light-emitting diodes. Two-dimensional (2D) coherent heterostructures and superlattices (Fig. 1, A and B) can serve as ultrathin building blocks for advanced stacking and heterointegration with other materials and provide opportunities not available with their 3D analogs. Realizing this goal would require the integration of various 2D materials whose properties can be tuned by the strain required for coherent lattice matching, as well as a method for precisely controlling the superlattice dimensions while maintaining lattice coherence over the entire structure.

Monolayer transition metal dichalcogenides (TMDs), many of which share similar crystal structures, provide an ideal material platform with diverse electrical, optical, piezoelectric, and valley properties. Recent studies on TMD heterostructure synthesis have shown only limited capabilities toward realizing coherent 2D superlattices.

We report coherent monolayer TMD superlattices with precisely controlled supercell dimensions and lattice coherence maintained over the entire structure, which result in broad tuning of their optical properties. We used WS₂ and WSe₂ as the two main TMDs for our heterostructures and superlattices (Fig. 1A, inset), where the repeat direction of the superlattice is in the growth plane of a monolayer, rather than the out-of-plane direction of conventional thin-film superlattices. These TMDs have a substantial lattice mismatch (Δ) of ~4%, with WSe₂ having the larger lattice constant. In scanning electron microscope (SEM) images of three representative WS₂/WSe₂ heterostructures with controlled supercell dimensions (Fig. 1C), dark (bright) regions correspond to WS₂ (WSe₂) monolayers. Every triangular unit of WS₂ and WSe₂ shows a highly symmetric, equilateral triangular shape of uniform width, each defined by straight, parallel heterointerfaces, that could be directly controlled with nanoscale precision. These widths could be as narrow as 20 nm (Fig. 1C, center) and periodically modulated to form superlattices with different dimensions, represented by the two widths (d_WS₂ and d_WSe₂). Two examples of superlattices are shown, one primarily composed of WS₂ (d_WS₂ >> d_WSe₂) (Fig. 1C, left) and the other by WSe₂ (d_WS₂ << d_WSe₂) (Fig. 1C, right). Heterostructures consisting of different metal and chalcogen elements could also be synthesized with a similar level of control (see fig. S1C for an example of a WSe₂/MoS₂/WS₂ heterostructure).

These crystalline TMD superlattices were synthesized by a modulated metal-organic chemical vapor deposition (MOCVD) process (see Fig. 1, supplementary materials, and fig. S1), with two distinctive features compared with previous approaches (13–21). First, the concentration of each precursor was individually controlled, allowing the direct tuning of the supercell dimensions. The composition of TMD could be switched, for example, from WS₂ to WSe₂ and vice versa, by simply changing the chalcogen precursors. The width of each component was determined by controlling the timing of the switch, according
to a simple linear dependence between the width and the growth time (see supplementary materials, table S1, and fig. S1).

Second, the growth environment was maintained constant throughout the synthesis regardless of the specific TMD composition, which was crucial for producing coherent heterointerfaces. For example, both WS2 and WSe2 were grown under constant temperature, pressure, and overall flow rate, with the only difference being the chalcogen precursors. In our experiment, different components of our superlattices were grown with a slow growth rate (ranging between 20 and 60 nm/min) near thermodynamic equilibrium, and exhibited straight heterointerfaces with the most stable W-zigzag edges (fig. S2) (23, 24).

Fig. 2. Lattice coherence of WS2/WSe2 superlattices. (A) An ADF-STEM image at the heterointerface area between WS2 and WSe2 (epitaxy direction represented by the arrow; same for all). Scale bar, 2 nm. (B) Inverse FFT of an ADF-STEM image from a larger area near the heterointerface, based on the circled spots in its FFT (inset). Scale bar, 5 nm. (C) SAED pattern of superlattices (50 and 40 nm), taken from an area with a diameter of 280 nm. (D) Enlarged diffraction spots as indicated in (C). (E) The same diffraction spots as in (D) from an incoherent WS2/WSe2 heterostructure. (F and G) Spatial maps of normalized lattice constants $a_{||}$, $a_{\perp}$ and lattice rotation angle $\gamma$. (H) Histograms of $a_{||}$ and $a_{\perp}$ from experiment (for region $a_{\perp}$ in (F)) and theory (for the superlattice depicted in (J)). (I) Schematic of the isotropic expansion of the WS2 lattice in an omnidirectional coherent WS2/WSe2 heterostructure. (J) Composite maps of $a_{||}$ (left) and $a_{\perp}$ (right) of a superlattice with ratio $d_{WS2}/d_{WSe2} = 1.25$, computed from a coarse-grained theoretical simulation (see fig. S7 and supplementary materials).

Our WS2/WSe2 superlattices maintained lattice coherence over the entire crystal (Fig. 2). First, the superlattices were free of misfit dislocations. Figure 2A shows an annular dark-field scanning transmission electron microscope (ADF-STEM) image near a heterointerface (dashed line) between WS2 (lower) and WSe2 (upper). The ADF-STEM data taken from a larger area (Fig. 2B) shows continuous lines of atoms with no misfit dislocations near the heterointerface across ~160 unit cells (shown after the inverse fast Fourier transform (FFT)). One dislocation is expected every 25 unit cells on average for incoherent heterointerfaces. In contrast, the same diffraction spots measured from an incoherent WS2/WSe2 heterostructure displayed a 4% concentric separation, with $\delta_{||} = \delta_{\perp} = 1.2\%$ was much smaller than $\Delta$. In contrast, the same diffraction spots measured from an incoherent WS2/WSe2 heterostructure displayed a 4% concentric separation, with $\delta_{||} = \delta_{\perp} = 4.0\%$.

Lattice coherence was directly confirmed with nanoscale resolution over the entire WS2/WSe2 superlattice. We used our newly developed electron microscope pixel array detector (EMPAD), which measures local diffraction maps pixel by pixel, providing structural information for imaging with nanoscale resolution (see supplementary materials) (25). Figure 2, F and G, shows three maps generated based on EMPAD data taken...
arrays of dislocations at heterointerfaces (fig. S5). In contrast, incoherent heterostructures showed different symmetry from that of the original crystal. Instead, our superlattice grew with coherent omnidirectional epitaxy (see supplementary text and fig. S6), where regions of different epitaxy directions ($\alpha$, $\beta$, and $\gamma$) coherently connect with each other while maintaining the same symmetry of the original crystal. The perfect symmetry in our coherent superlattices imposes an additional constraint that requires identical values of $\alpha$, for both WS$_2$ and WSe$_2$. This feature is further illustrated in Fig. 2f: When a triangular WSe$_2$ unit was replaced by WS$_2$, the latter needed to expand by the same amount in all directions (i.e., larger $a_\|$, $a_\perp$, and $a_t$) to coherently bridge the inner and outer triangular WSe$_2$ units. This ideal picture changes in real superlattices with finite bulk and shear moduli values, where the final structure will minimize the total elastic strain energy. In this case, the lattice would deviate from having identical $a_\perp$ values for WS$_2$ and WSe$_2$, resulting in $0 < \delta_\perp < \Delta$, as seen from our data. These observations were quantitatively predicted by coarse-grained simulations of these superlattices that account for both bond and angle interactions on an appropriate footing (Fig. 2H, right, and 2J). In this regard, it is the inclusion of angular interactions, in particular, that accounts for the shear stiffness inside the TMD superlattice and thereby introduces local frustration (analogous to the antiferromagnetic triangular-lattice Ising model) that is key to predicting coherent omnidirectional epitaxy across the entire lattice, as well as a small but nonvanishing $\delta_\perp$ (see fig. S7 and supplementary materials). The lattice coherence further allows for high-performance p-n diodes showing high rectification ratios (>10$^6$) and electroluminescence, as well as double heterostructure transistors, which we successfully fabricated using our heterostructures (see figs. S8 and S9 and supplementary text).

This lattice coherence also resulted in a tensile strain within the WS$_2$ (WSe$_2$) region in our superlattices, the magnitude of which varied depending on the supercell dimensions.
Figure 3A illustrates such strain control. For example, a smaller $d_{\text{WS2}}$ or larger $d_{\text{WSe2}}$ (with a small ratio $\rho = d_{\text{WSe2}}/d_{\text{WS2}}$) increased the tensile strain in WS\textsubscript{2} and decreased the compressive strain in WSe\textsubscript{2}, as it brought $a_{\parallel}$ and $a_{\perp}$ closer to the intrinsic values for WSe\textsubscript{2}. In addition, the band structure of both WS\textsubscript{2} and WSe\textsubscript{2} was sensitive to the applied strain; the size of the direct band gap decreased (increased) when subjected to tensile (compressive) strain (26–29).

This strain-dependent band structure allowed for broad tuning of the optical properties by superlattice design. Figure 3B shows the false-color SEM images of five representative WS\textsubscript{2} (blue)/WSe\textsubscript{2} (yellow) coherent superlattices I to V with different $\rho$ (dimensions plotted in Fig. 3A). The resulting photoluminescence (PL) spectra showed two peaks, with one corresponding to WS\textsubscript{2} and the other to WSe\textsubscript{2} (Fig. 3C, inset). However, the WS\textsubscript{2} peak was red-shifted from the intrinsic peak energy of 1.97 eV by $\Delta_{\text{WS2}}$, whereas the WSe\textsubscript{2} peak was blue-shifted from the intrinsic value of 1.61 eV by $\Delta_{\text{WSe2}}$. Figure 3C compares the normalized WS\textsubscript{2} peaks measured from superlattices I to V (each extracted from the full PL spectra) to the intrinsic WS\textsubscript{2} peak (dashed curve). Superlattices with smaller $\rho$ showed larger $\Delta_{\text{WS2}}$, as large as 250 meV (see fig. S10 for representative original PL spectra). Figure 3D further plots $\Delta_{\text{WS2}}$ versus $\Delta_{\text{WSe2}}$ for additional superlattices with different supercell dimensions.

These PL characteristics were consistent with the strain engineered by the superlattice design. The positive values for both $\Delta_{\text{WS2}}$ and $\Delta_{\text{WSe2}}$ confirmed the tensile (compressive) strain in WS\textsubscript{2} (WSe\textsubscript{2}). Their magnitudes showed a negative correlation, which is consistent with their expected negatively correlated strain magnitude (Fig. 3A). The largest $\Delta_{\text{WSe2}}$ of 250 meV, corresponding to a 3.4% uniaxial strain or a 1.4% isotropic biaxial strain (26), was consistent with the large tensile strain expected from superlattice V with a small $\rho = 0.1$. Moreover, the PL image (Fig. 3E, right; taken at 1.75 eV) confirmed that the highly red-shifted WS\textsubscript{2} PL peak indeed originated from the strained WS\textsubscript{2} region (SEM image of a similarly grown sample shown in Fig. 3E, left). In general, superlattices with supercell dimensions below the diffraction limit (Fig. 3F, left and middle) showed uniform PL intensities at their respective peak energies over the entire structure, with a similar uniformity compared with intrinsic WS\textsubscript{2} (Fig. 3F, right).

Strained thin films relax through out-of-plane deformations such as wrinkles and ripples, which makes these films nonflat and their edges curved (30–32). However, our ultrathin superlattices maintained lattice coherence and symmetry, despite being highly strained and their edges being under alternating compressive and tensile stress during growth, because of strong van der Waals (vdW) interactions between the superlattice and the underlying growth substrate (SiO\textsubscript{2} in our experiment), which keep the 2D superlattice flat. Figure 4A plots the theoretically calculated total energy ($E_{\text{tot}}$, circles) per WSe\textsubscript{2} of a strained WSe\textsubscript{2} monolayer on SiO\textsubscript{2} as a function of the out-of-plane ripple height ($\lambda$, measured from peak to valley; see schematic in Fig. 4B). $E_{\text{tot}}$ consists of the elastic strain energy ($E_{\text{el}}$, triangles), computed using a macroscopic elastic energy model (that accounts for both stretching and bending energy components in an ultrathin film), and the interlayer vdW binding energy between the WSe\textsubscript{2} and SiO\textsubscript{2} ($E_{\text{vdW}}$, squares), computed using an all-atom quantum-mechanical vdW energy model (see supplementary text and fig. S11). Although the rippled state ($\lambda \approx 3$ nm) that relaxes the compressive strain is lowest in energy, the energetic profile shows another minimum at $\lambda = 0$ nm, corresponding to the flat state. These two states have similar energies because the reduction in $E_{\text{el}}$ roughly equals the increase in $E_{\text{vdW}}$ for the rippled state.

The rippled and flat states are separated by an energetic barrier (with an activation energy of 10 to 20 meV per WSe\textsubscript{2}), because the increase in $A$ in the regime $0 < A < 1$ nm rapidly destabilizes $E_{\text{tot}}$ without substantially stabilizing $E_{\text{el}}$. Figure 4A thus predicts that the attractive vdW force from the substrate keeps WSe\textsubscript{2} flat and that the transition from the flat to rippled state can only occur in the presence of a substantial perturbation.
As a result, these theoretical findings suggest that the synthesis conditions in our experiment, which maintained a constant growth environment with no strong perturbations, allowed the superlattice to remain flat and the growth edge straight during growth.

The superlattices reported here were subjected to a cool-down process after growth, from a relatively high growth temperature (600°C) to room temperature. This process could perturb the samples (e.g., thermal expansion/contraction of the superlattice and SiO2) and induce ripples in WSe2, which is what we observed in our samples. The atomic force microscope (AFM) height image of a representative WSe2/WSe2 superlattice (Fig. 4C) shows out-of-plane ripples in WSe2 (schematically illustrated in Fig. 4B). These ripples ran continuously across the WSe2 stripes only and were periodic along the heterointerfaces, as shown in the enlarged AFM image (Fig. 4D, top). The peak-to-valley height (A) was between 1 and 2 nm (measured from the AFM profile shown in Fig. 4D, bottom). This value is surprisingly near that of A for the lowest energy state in Fig. 4A, despite the use of a simple energetic model and an idealized superlattice geometry. We also observed that the ripple wavelengths (λ) for superlattices with different ΔWS2 were nearly constant (near 30 nm, as shown in Fig. 4E), with little dependence on ΔWS2 over one order of magnitude (ranging from 20 to 320 nm). This result suggests that the presence of WS2/WSe2 interfaces had minimal effect on the energetics of the ripple formation in this regime and that the constant compressive strain in WSe2 (even up to ΔWS2 = 320 nm) was released through rippling. This finding also explains the smaller range of ΔWS2 shown in Fig. 3D.

For superlattices with ΔWS2 > 320 nm, however, the periodic ripples were no longer continuous across the WSe2 area (see Fig. S12). This difference indicates the presence of an alternative strain relaxation mechanism, including the formation of misfit dislocations and a coherence length of ~320 nm for our WS2/WSe2 superlattices. This coherence length was substantially greater than the critical thickness of 2 nm for the Si/Ge system with a similar Δ = 4% (34), as well as the critical thickness for the WS2/WSe2 system estimated using the People-Bean model (below 20 nm) (see supplementary materials and fig. S13) (35). A full explanation for such a long coherence length would require a general theory optimized for 2D, which is currently lacking. However, we expect that our stable superlattice growth conditions and a larger energetic barrier for dislocation formation in 2D systems may account for the long coherence length. For example, there are limited configurations of covalent bonding for dislocations in 2D systems and no screw dislocations. Our demonstration of omnidirectional coherent 2D superlattices not only presents a powerful framework for the epitaxial synthesis of nanomaterials and the engineering of their properties but also opens up the possibility of a new interdisciplinary research direction because our coherent superlattice is crystalline yet highly deformable. Generation of ordered arrays of coherent superlattices would further accelerate their electronic and optoelectronic applications, which may be achieved with improved spatial control during growth.

ACKNOWLEDGMENTS
We thank S. Nagel, T. Wilten, and A. Tkatchenko for helpful discussions. We thank J.-U. Lee for help with EL measurements. Funding: This work was primarily supported by the Air Force Office of Scientific Research (FA9550-16-1-0031, FA9550-16-1-0347, and FA9550-13-1-4148) and the National Science Foundation (NSF) through the Cornell Center for Materials Research with funding from the NSF Materials Research Science and Engineering Centers (MRSEC) program (DMR-1719875), the University of Chicago MRSEC (NSF DMR-1420790), and the Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM, DMR-1359588). Additional funding was provided by the Samsung Advanced Institute of Technology. Material characterizations including electron microscopy were supported by the Cornell Center for Materials Research (NSF DMR-1719875) and the MRSEC Shared User Facilities at the University of Chicago (NSF DMR-1420790). L.T., K.U.L., and R.A.D. acknowledge partial support from Cornell University through start-up funding. This research used resources of the Argonne Leadership Computing Facility at Argonne National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC02-06CH11357 and resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC02-05CH11231. Author contributions: S.X. and J.P. conceived the experiments. S.X. developed the superlattice synthesis and performed DF-TEM, electron diffraction, and optical measurements. Y.H. and D.A.M. conducted the atomic-resolution STEM imaging and EMPAD characterizations. L.T., K.U.L., and R.A.D. conducted the coarse-grained simulations and vDW calculations. S.X., K.K., and C.P. carried out AFM and SEM characterizations, and S.X., L.H., and P.P. performed the device fabrication and measurements. S.X., R.A.D., and J.P. wrote the manuscript. All authors discussed and commented on the manuscript. Competing interests: The authors declare no competing financial interests. A provisional U.S. patent has been filed based on this work. Data and materials availability: All data are reported in the main text and supplementary materials.

SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/359/6380/1131/suppl/DC1
Supplementary Text
S1 to S13
References (39–61)
9 August 2017; accepted 22 January 2018
10.1126/science.aas5380
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Science 359 (6380), 1131-1136.
DOI: 10.1126/science.aao5360

Coherent strained superlattices
Two‐dimensional superlattices represent the atomic‐thickness limit of heterostructures that enable technologies such as strain‐engineered multiferroics and quantum‐cascade lasers. Xie et al. were able to produce monolayer superlattices of transition metal dichalcogenides (WS2 and WSe2) with full lattice coherence, despite a 4% lattice mismatch. They used a modulated metal‐organic chemical vapor deposition process that precisely controlled each precursor. Furthermore, the authors could strain‐engineer the optical properties of the superlattices to observe out‐of‐plane rippling.

Science, this issue p. 1131