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 repeatedly 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 the nanoscale supercell dimensions, thereby enabling broad tuning 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 heterostructures, in which lattices of dissimilar materials are matched—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 the nanoscale supercell dimensions, thereby enabling broad tuning 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.

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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 with $\Delta \approx 4\%$, so these images are consistent with our superlattice forming coherent heterointerfaces.

Second, our superlattices displayed lattice constants that were uniform over the entire structure. Figure 2C shows selective-area electron diffraction (SAED) data measured from a representative superlattice (50 and 40 nm) within a region with a single epitaxy direction (denoted by the arrow). These data exhibited a single-crystal-like pattern with sharp and isotropic diffraction spots. We used their positions to measure the lattice constants along the directions parallel ($a_{//}$) or perpendicular ($a_{\perp}$) to the heterointerfaces (schematic, Fig. 1B), as well as the lattice mismatch along each direction [e.g., $\Delta_{//} = 2|a_{//} - a_{//,3}|/ (a_{//,1} + a_{//,2})$]. Diffraction data corresponding to $a_{//}$ (circles in Fig. 2C, enlarged in Fig. 2D) showed a single diffraction spot with no separation, confirming perfect lattice matching ($\delta_{//} = 0$). Diffraction data corresponding to $a_{\perp}$ (squares in Fig. 2C) also showed similar lattice constants; although two spots were observed, each originating from the WS2 and WSe2 regions (see below), the mismatch $\delta_{\perp} = 1.2\%$ was much smaller than $\Delta$. In contrast, the same diffraction spots measured from an incoherent WS2/WSe2 heterostructure displayed a 4% concentric separation, with $\delta_{//} = \Delta = 4.0\%$ (Fig. 2E; see fig. S3 for original SAED patterns).

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 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).

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from another superlattice (75 and 60 nm), each plotting a$_{||}$, a$_{⊥}$, and lattice rotation. The superlattice consists of three regions (α, β, and γ, as outlined in Fig. 2F), with heterointerface orientations rotated by 120° from each other. The orientations of a$_{||}$ and a$_{⊥}$ are different for α, β, and γ and are defined relative to the heterointerfaces in each region. The a$_{||}$ map (Fig. 2F, left) showed little contrast between WS$_2$ and WSe$_2$, generating a single histogram peak as shown in Fig. 2H, left (region α; see fig. S4 for β and γ histograms). The a$_{⊥}$ map showed a small contrast between the WS$_2$ and WSe$_2$ regions, generating two peaks (Fig. 2H, left) centered 0.4% below (corresponding to WS$_2$) and 0.8% above (corresponding to WSe$_2$) the a$_{||}$ peak, resulting in δ$_{||}$ = 1.2%, as seen in Fig. 2D. Third, the lattice rotation map resolved only one dislocation clearly (arrow) within the entire superlattice (lateral size ~32 μm), suggesting the existence of a dislocation-free, coherent lattice everywhere, including the boundary regions between the α, β, and γ regions. In contrast, incoherent heterostructures showed arrays of dislocations at heterointerfaces (fig. S5).

Figure 2 shows that δ$_{||}$ = 0 everywhere, confirming coherent heterointerfaces in our superlattice. In addition, the lattice isotropy and rotational symmetry were maintained over the entire superlattice. Our TEM and EMPAD data confirm (i) nearly identical and isotropic unit cell dimensions for both the WS$_2$ and WSe$_2$ regions; (ii) that the lattice orientation in our EMPAD map (Fig. 2G) was highly uniform (standard deviation < 1 mrad), consistent with the observed sharp and isotropic TEM diffraction spots (Fig. 2, C and D); and (iii) that the superlattice is triangular with straight edges and heterointerfaces. This result is in sharp contrast to the lattice anisotropy expected from conventional unidirectional epitaxy, where a$_{||}$ is matched for the epilayers and a$_{⊥}$ is free from any constraints, causing the superlattice to have a 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 (α, β, and γ) 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 a$_{||}$ 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$_{||}$ and a$_{⊥}$) 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$_{||}$ values for WS$_2$ and WSe$_2$, resulting in 0 < δ$_{||}$ < Δ, 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 δ$_{⊥}$ (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 (compressive) 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 $d_{WS2}$ or larger $d_{WSe2}$ (with a small ratio $\rho = d_{WS2}/d_{WSe2}$) increased the tensile strain in WS$_2$ and decreased the compressive strain in WSe$_2$ as it brought $a_\parallel$ and $a_\perp$ closer to the intrinsic values for WSe$_2$. In addition, the band structure of both WS$_2$ and WSe$_2$ 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$_2$ (blue)/WSe$_2$ (yellow) coherent superlattices I to V with different $\rho$ (dimensions plotted in Fig. 3A). The resulting photoluminescence (PL) spectra showed two peaks, one corresponding to WS$_2$ and the other to WSe$_2$ (Fig. 3C, inset). However, the WS$_2$ peak was red-shifted from the intrinsic peak energy of 1.97 eV by $\Delta_{WS2}$ whereas the WSe$_2$ peak was blue-shifted from the intrinsic value of 1.61 eV by $\Delta_{WSe2}$. The smallest $\Delta_{WSe2}$ 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) showed uniform PL intensities at their respective peak energies over the entire structure, with a similar uniformity compared with intrinsic WS$_2$ (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 superlattices and the underlying growth substrate (SiO$_2$ in our experiment), which keep the 2D superlattice flat. Figure 4A plots the theoretically calculated total energy ($E_{tot}$, circles) per WSe$_2$ of a strained WSe$_2$ monolayer on SiO$_2$ as a function of the out-of-plane ripple height ($A$, measured from peak to valley; see schematic in Fig. 4B). $E_{tot}$ consists of the elastic strain energy ($E_{el}$, 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$_2$ and SiO$_2$ ($E_{vdw}$, squares), computed using an all-atom quantum-mechanical vdW energy model (see supplementary text and fig. S11). Although the rippled state ($A \approx 3$ nm) that relieves the compressive strain is lowest in energy, the energetic profile shows another minimum at $A = 0$ nm, corresponding to the flat state. These two states have similar energies because the reduction in $E_{el}$ roughly equals the increase in $E_{vdw}$ 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$_2$), because the increase in $A$ in the regime $0 < A < 1$ nm rapidly destabilizes $E_{tot}$ without substantially stabilizing $E_{el}$. Figure 4A thus predicts that the attractive vdW force from the substrate keeps WSe$_2$ 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 SiOx) 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 δWSe2 remained relatively constant (near 30 nm, as shown in Fig. 4E), with little dependence on δWSe2 over one order of magnitude (ranging from 20 to 320 nm). This result suggests that the presence of WSe2/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 δWSe2 = 320 nm) was released through rippling. This finding also explains the smaller range of δWSe2 shown in Fig. 3D.

For superlattices with δWSe2 > 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 WSe2/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. S1D) (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 improved spatial control of nucleation (36) and superlattice orientation (37, 38).

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/359/6380/1131/suppl/DC1
Materials and Methods
Supplementary Text
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References (39–61)
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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.

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