Epitaxial Single-Crystal Growth of Transition Metal Dichalcogenide Monolayers via the Atomic Sawtooth Au Surface

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Growth of 2D van der Waals layered single-crystal (SC) films is highly desired not only to manifest the intrinsic physical and chemical properties of materials, but also to enable the development of unprecedented devices for industrial applications. While wafer-scale SC hexagonal boron nitride film has been successfully grown, an ideal growth platform for diatomic transition metal dichalcogenide (TMDc) films has not been established to date. Here, the SC growth of TMDc monolayers on a centimeter scale via the atomic sawtooth gold surface as a universal growth template is reported. The atomic tooth-gullet surface is constructed by the one-step solidification of liquid gold, evidenced by transmission electron microscopy. The anisotropic adsorption energy of the TMDc cluster, confirmed by density-functional calculations, prevails at the periodic atomic-step edge to yield unidirectional epitaxial growth of triangular TMDc grains, eventually forming the SC film, regardless of the Miller indices. Growth using the atomic sawtooth gold surface as a universal growth template is demonstrated for several TMDc monolayer films, including WS$_2$, WSe$_2$, MoS$_2$, the MoSe$_2$/WSe$_2$ heterostructure, and W$_{1-x}$Mo$_x$S$_2$ alloys. This strategy provides a general avenue for the SC growth of diatomic van der Waals heterostructures on a wafer scale, to further facilitate the applications of TMDcs in post-silicon technology.
investigated in terms of micrometer-scale grains, its inhomogeneity in a wafer scale limits application to integration challenges associated with structural defects such as grain boundaries and disorder.\[15\] The growth of single-crystal (SC) monolayer and multilayer graphene films on SC Cu (111) and Cu–Si (111) surfaces has been demonstrated in a wafer scale,\[16,17\] whereas the growth of diatomic 2D SC film such as hBN and TMdCs remains still complicated due to their non-centrosymmetric structures.\[18\] Recently, the self-collimation of hBN grains on liquid Au substrate has been proposed for growing diatomic hBN SC film in a wafer scale but further study is required to grow other 2D vdW materials.\[19\] Moreover, step-edge guided epitaxial growth has been observed in hBN films on SC Cu (111) and (110).\[18,20\]

Our primary concern is to discover a growth platform for single-crystal TMdCs in a centimeter scale. While SC hBN and Au (111) vicinal surface have been produced for the growth of SC TMdC film,\[19,21\] evidence of seamless stitching, other Miller indices, and more importantly, a growth platform for general diatomic TMdCs still require investigation. We report a growth platform for SC TMdCs in a centimeter scale via an atomic sawtooth Au surface, which is evidenced by cross-sectional high-resolution transmission electron microscopy (HRTEM) to further verify the grain boundary (GB)-free SC TMdC film, regardless of Miller indices.

The key to achieving SC TMdC growth is to construct the atomic sawtooth Au surface, to serve as a universal growth template, consisting of periodic tooth-gullet step edges to accommodate the self-assembly of unidirectional TMdC grains (Figure 1a). The atomic sawtooth Au surface with periodic step edges and low Miller index terraces, including (100), (110), and (111) facets, was prepared through the one-step solidification of liquid Au on W substrate (see Experimental Section). The atomic sawtooth Au (533) surface with the topmost WS2 monolayer is clearly distinguishable through cross-sectional annular dark-field scanning transmission electron microscopy (ADF-STEM) (Figure 1b). A surface with an irregular atomic sawtooth periodicity still yields a robust WS2 monolayer (Figure S1, Supporting Information). The chemical inertness of Au and negligible solubility of metal and chalcogen atoms in Au film

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**Figure 1.** Growth of single-crystal WS2 on atomic sawtooth Au surface. a) Schematic illustration of WS2 film grown via an atomic sawtooth Au surface. b) Cross-sectional ADF-STEM image and the corresponding ball-and-stick model of as-grown WS2 on an atomic sawtooth Au (533) surface. c,e,g) EBSD IPF maps and d,f,h) SEM images of coherently aligned WS2 grains on Au (5,7,11), (169), and (114) with respective (111), (110), and (100) terrace facets. i) SEM image of SC WS2 film with a photograph of a centimeter-scale SC WS2 film. j) LEED pattern of WS2 film on Au (221). Each peak is assigned to WS2 hexagonal lattice, Au (111) terrace facet, and atomic sawtooth Au (221) surface. k) Spatial LEED mapping and l) stacked 25 LEED patterns over 5 × 5 mm² area.
make the epitaxial growth of monolayer TMD film possible.[22] In contrast, conventional Cu film is highly reactive with chal- cogen atoms.[23]

The electron backscatter diffraction (EBSD) inverse pole figure (IPF) maps of the solidified Au foil demonstrate the formation of diverse atomic sawtooth surfaces such as (5,7,11), (169), and (114) on respective (111), (110), and (100) terrace facets (Figure 1c,e,g). The EBSD mappings of high Miller indices are uniformly colored. We note that high-index surfaces were randomly produced after the solidification of liquid Au (Figures S2, S3, and Table S1, Supporting Information), contrary to previous study in which low-index Au (111) surface was obtained using similar preparation procedure.[21] Monolayer WS$_2$ grains were synthesized at 800 °C by injecting ammonium sulfide with a bubbler system onto the W precursor-coated atomic sawtooth Au substrate (see Experimental Section). After the initial growth stage of 5 min, WS$_2$ grains are oriented along a specific direction with coherent triangles in a centimeter scale (Figure 1d,f,h; Figure S4, Supporting Information), which is persistent with the presence of scarce coherent triangular voids near the final stage of film growth (Figure S5, Supporting Information).

These results are in stark contrast with the appearance of triangular and inverted triangular TMD grains on c-plane sapphire substrates reported by other studies.[24–26]

After a growth period of 20 min, a centimeter-scale SC WS$_2$ film is eventually obtained (Figure 1i). Low energy electron diffraction (LEED) pattern clearly indicates a supercell of WS$_2$ hexagonal lattice, Au (111) terrace facet, and atomic sawtooth Au (221) surface (Figure 1j and inset), congruent with the constructed LEED pattern (Figure S6, Supporting Information). The superposition of 25 LEED patterns in $5 \times 5 \text{ mm}^2$ area clearly confirmed the identical honeycomb lattice to assure SC WS$_2$ film (Figures 1k,l; Figure S7, Supporting Information). The perfect honeycomb WS$_2$ lattice was obtained with a lattice constant of 3.22 Å, indicating that the strain is negligible. This is distinct from previous work involving the growth of strained SC hBN on liquid Au substrate.[19]

To verify the existence of GB-free WS$_2$ film, partially merged WS$_2$ grains grown for a period of 5 min were characterized by HRTEM. After the transfer of the WS$_2$ grains onto the TEM grid, the coherent WS$_2$ grains are preserved (Figure 2a). ADF-STEM image depicts a hexagonal crystal structure with a d-spacings of the (10 – 10) and (11 – 20) planes of WS$_2$ are 0.28 and 0.16 nm, respectively. c) Stacked SAED patterns of six yellow-circled regions in (a). d) SEM image of WS$_2$ grains on TEM grid. The inset shows a TEM image of the merged region. The angle between two merged WS$_2$ grains is 60°. e) ADF-STEM image corresponding to the red-dashed square in (d). f) Three ADF-STEM images and stacked FFT patterns obtained from areas enclosed in white-dashed squares in (e). g,i) SEM and h,j) confocal Raman intensity mapping associated with the 2LA(M) mode of aligned (g,h) and misaligned (i,j) WS$_2$ grains after oxidation at 350 °C.

Figure 2. Coherent WS$_2$ grains. a) TEM image of aligned WS$_2$ grains transferred onto TEM grid. b) ADF-STEM image of WS$_2$. The d-spacings of the (10 – 10) and (11 – 20) planes of WS$_2$ are 0.28 and 0.16 nm, respectively. c) Stacked SAED patterns of six yellow-circled regions in (a). d) SEM image of WS$_2$ grains on TEM grid. The inset shows a TEM image of the merged region. The angle between two merged WS$_2$ grains is 60°. e) ADF-STEM image corresponding to the red-dashed square in (d). f) Three ADF-STEM images and stacked FFT patterns obtained from areas enclosed in white-dashed squares in (e). g,i) SEM and h,j) confocal Raman intensity mapping associated with the 2LA(M) mode of aligned (g,h) and misaligned (i,j) WS$_2$ grains after oxidation at 350 °C.
Optical and electrical properties of SC WS\textsubscript{2} film. a) Optical image of SC WS\textsubscript{2} film after the transfer onto the SiO\textsubscript{2}/Si substrate with a photograph of a centimeter-scale SC WS\textsubscript{2} film. b) Raman and c) PL mapping images for the intensities of A\textsubscript{1g} phonon mode (at 415 cm\textsuperscript{-1}) and neutral exciton (X\textsuperscript{0}) at 2.035 eV. d,e) Representative Raman spectra (d) and PL spectra (e) obtained from regions I–IV in the mapping images. f) Optical image of fabricated SC WS\textsubscript{2} FETs at random positions. The inset represents the WS\textsubscript{2} channel (a scale bar: 10 \textmu m). g) Representative I–V transfer curve obtained from SC WS\textsubscript{2} FET. h) Benchmark of carrier concentrations and i) field-effect mobility and on/off ratio of SC WS\textsubscript{2} FETs with those values from the literature.\textsuperscript{[29–38]}

d-spacings of 0.28 and 0.16 nm, corresponding to the (10-10) and (11-20) planes of 2H-WS\textsubscript{2}, consistent with previous work (Figure 2b).\textsuperscript{[22]} The stacked six selective-area-electron-diffraction (SAED) patterns (regions I–VI of Figure 2a) demonstrate the exclusive overlap of the hexagonal dots, confirming the coherent lattice orientation (Figure 2c).

The grain boundary in 60° triangular region at the junction between two merged WS\textsubscript{2} grains is carefully analyzed (Figure 2d and inset). The monolithic fringes of heavy W atoms are observed without the trace of GB lines (Figure 2e), in contrast with polycrystalline WS\textsubscript{2}, which possesses structural defects at GBs (Figure S8, Supporting Information). The higher magnification images of three regions in Figure 2e and their stacked fast Fourier transform (FFT) patterns clearly demonstrate the absence of GB lines in the merged regions (Figure 2f). Similar results are also obtained for other merged regions (Figure S9, Supporting Information). The absence of GB lines is analyzed in a macroscopic scale via oxidation in air at 350 °C.\textsuperscript{[27]} No prominent oxidized GB lines are visible between aligned WS\textsubscript{2} grains based on SEM and Raman intensity mapping, while oxidized GB lines are apparent between misaligned polycrystalline WS\textsubscript{2} grains (Figure 2g–j; Figure S10, Supporting Information).

To explore high and uniform material quality of SC WS\textsubscript{2} film in a large area, the WS\textsubscript{2} film is transferred onto the SiO\textsubscript{2}/Si substrate using a bubble transfer method (Figure 3a) and further evaluated by optical and electrical measurements. The WS\textsubscript{2} film is uniform in optical micrograph (Figure 3a). Raman and photoluminescence (PL) mapping images for the intensities for respective A\textsubscript{1g} phonon mode and neutral exciton (X\textsuperscript{0}) manifest the homogeneous optical properties (Figure 3b,c). The representative Raman and PL spectra obtained from the regions I–IV of the mapping image clearly show no noticeable shift of A\textsubscript{1g} phonon mode and constant PL intensity ratio of trion (X\textsuperscript{−}) and X\textsuperscript{0}, respectively, indicating the uniform doping concentration over the whole region (Figure 3d,e; Figure S11, Supporting Information). These results are clearly distinct from previous polycrystalline WS\textsubscript{2} that the position of A\textsubscript{1g} phonon and PL intensity ratio are significantly altered by the defect domains.\textsuperscript{[28]}

The electrical properties of SC WS\textsubscript{2} film are further characterized after fabricating the field-effect transistors (FETs) at random positions (Figure 3f). The I–V transfer curves of fabricated WS\textsubscript{2} FETs are almost overlapped (Figure S12, Supporting Information), proving the homogenous electrical properties of SC WS\textsubscript{2} film (Figure 3g). Particularly, the low carrier concentrations \textapprox 10\textsuperscript{12} cm\textsuperscript{-2} extracted from the parallel capacitor model, \( n = C_{\text{ox}}(V_{gs} - V_{th})/q \), where \( n \), \( C_{\text{ox}} \), \( V_{gs} \), \( V_{th} \), and \( q \) are carrier concentration (cm\textsuperscript{-2}), gate capacitance per unit area (F cm\textsuperscript{-2}), gate voltage (V), threshold voltage (V), and charge (C), respectively, are comparable to those of mechanically exfoliated SC monolayer WS\textsubscript{2} in the literatures (Figure 3h).\textsuperscript{[29–33]} Moreover, the FET devices in terms of field-effect mobilities (\textapprox 3 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}) and on/off ratios (\textapprox 10\textsuperscript{8}) outperform previously reported values of CVD-derived polycrystalline monolayer WS\textsubscript{2} FETs.\textsuperscript{[29–38]} More notably, such performances are comparable to those of SC monolayer WS\textsubscript{2} FETs. These indicate that SC WS\textsubscript{2} film has remarkable crystallinity over the whole region (Figure 3i).

Density-functional theory (DFT) calculations were carried out to elucidate the underlying mechanism of the coherent WS\textsubscript{2} grain growth on an atomic sawtooth Au surface. We presumed that the growth proceeds with the formation of a W\textsubscript{3}S\textsubscript{6} cluster, followed by surface migration, nucleation, and growth.\textsuperscript{[39]} We first considered the B edge as a nucleation site, where a topmost Au atom is placed between second top Au layers along the step edge (Figure 4a,b; Figure S13a, Supporting Information).\textsuperscript{[39]} A W\textsubscript{3}S\textsubscript{6} cluster adsorbed onto a flat terrace can freely migrate and anchor at B step edge rather than A step edge, owing to preferable energetics with a relatively larger adsorption energy of 1.43 eV at the Au (221) step edge of the Au (111) terrace facet (Figure S13 and Table S2, Supporting Information). The energetics rely on the rotation angle of the W\textsubscript{3}S\textsubscript{6} cluster (Figure 4a,b). Sulfur atoms energetically favor 0° at the step.
edge over other angles independent of Miller indices (Figure 4c; Table S3, Supporting Information). Another metastable angle is found at 60° with a rotational barrier height of 0.25–0.75 eV, which varies with Miller indices. Such barriers can be overcome at a growth temperature of 800 °C to rotate the W3S6 cluster from 60° to the energetically favorable 0° angle. This theory is congruent with experimental results, where unidirectional WS2 grains were grown at an elevated growth temperature of 800–880 °C. When the thermal energy is not sufficient to overcome the rotational barrier height, that is, at low growth temperature such as 750 °C, a proportion of inverted triangular WS2 grains were grown (Figure S14, Supporting Information). In addition, if the terrace facet is consistent over the entire region, the WS2 grains are unidirectionally aligned, regardless of Miller indices. Coherent triangular WS2 grains are consistently obtained, despite the possible generation of several other Miller indices in addition to the main (236) and (2, 10, 25) surfaces at fixed (111) and (100) terrace facets, respectively (Figure S13 and Table S2, Supporting Information). This is again attributed to the energetically favorable adsorption of W3S6 clusters on a specific “B step edge” of an atomic sawtooth surface confirmed by DFT calculations.

To prove the SC WS2 growth mechanism on atomic sawtooth Au surface at the atomic-scale, scanning tunneling microscopy (STM) measurement was performed. STM image of the WS2 film grown on, for example, an Au (221) surface, shows aligned hexagonal bright protrusions of sulfur atoms along its regular periodic dark linear features (Figure 4d). Such a periodicity of the dark lines coincides with a terrace width of Au (221), corresponding to the step edges of Au (221) (Figure S15, Supporting Information). The WS2 film on Au (221) substrate is reconstructed with the simulated LEED analysis in Figure 1j. The dark linear features indicated by the white dashed lines in Figure 4e are attributed to charge transfer from Au to the d orbitals of W in WS2,[40] caused by a close contact between Au step edge and topmost WS2 layer (see cross-sectional TEM image of Figure 1b; Figure S1, Supporting Information). The highly aligned WS2 along the step edge of Au (221) apparently demonstrates the step-edge assisted growth mechanism as proposed by DFT calculations. A structural model of WS2

![Figure 4. Energetics of rotation angles of WS2 clusters at the B step edge. a) Side and b) top views of W3S6 cluster on Au (221) surface with rotation angles of 0° and 60°, respectively. c) Relative binding energies of a W3S6 cluster on different atomic sawtooth Au surfaces as a function of rotation angle. d) Atomic-resolution STM image of SC WS2 film on Au (221) with applied sample bias of 0.5 V. The bright and dark sites correspond to respective S and W atoms. Au (221) step edges and aligned sulfur atoms are indicated by the white-dashed lines and the red hexagon, respectively. e) Simulated STM image and f) corresponding structural model. The coinciding supercell and doubled terrace width of the experimental and simulated results are indicated by dashed lines.](image-url)
monolayer on Au (221) surface including a supercell of WS$_2$ across the step edges for a doubled terrace width in unit cell is constructed (see Experimental Section and Figure 4f). Along the step edges ([011]), ×9 of WS$_2$ is commensurate with ×10 of Au (221), indicative of negligible strain formation.

The atomic sawtooth Au surface can serve as a universal growth template for synthesizing other SC TMdC monolayers, lateral heterostructure, and alloy such as WSe$_2$, MoS$_2$, MoSe$_2$/WSe$_2$ lateral heterostructure, and W$_{1-x}$Mo$_x$S$_2$ alloy. SC WSe$_2$ was grown with a supply of Se precursor at 780–820 °C under growth conditions similar to that used to produce SC WS$_2$ films (see Experimental Section and Figure 5a). SC MoS$_2$ was nucleated first with coherent triangular grains. At a final growth temperature of 800 °C for 10 min, native tungsten oxides on the W foil are decomposed by introducing H$_2$. The W atoms are energetically preferred to anchor to the edge of the MoSe$_2$ layer and eventually substitute Mo atoms to form MoSe$_2$/WSe$_2$ heterostructure, while retaining coherent triangular grains (Figure 5d). Consequently, WSe$_2$ domain is gradually formed, as confirmed by the confocal Raman mapping image of E$_{2g}^1$ phonon in the WSe$_2$ region and spatially resolved confocal Raman spectra (Figure 5e,f). W$_{1-x}$Mo$_x$S$_2$ alloy can be also grown by supplying H$_2$S gas at a growth temperature of 800 °C (see Experimental Section and Figure 5g). By introducing H$_2$ at the beginning, Mo precursors and vaporized WO$_x$ are mixed to form alloy and segregate into a serpentine MoS$_2$ structure in a WS$_2$ lattice, identified by distinct intensity differences

Figure 5. Synthesis of SC TMdC monolayers, heterostructure, and alloy on atomic sawtooth Au surfaces. a,b) SEM images and c) Raman spectra of as-grown coherent WSe$_2$ and MoS$_2$ grains. d) SEM image and schematic illustration of as-grown MoSe$_2$/WSe$_2$ heterostructure. e) Raman mapping image of the WSe$_2$ E$_{2g}^1$ phonon of the MoSe$_2$/WSe$_2$ heterostructure and f) spatially resolved Raman spectra along the white arrow in (e). g) Schematic illustration of serpentine MoS$_2$ in WS$_2$ (W$_{1-x}$Mo$_x$S$_2$ alloy). h) ADF-STEM image of W$_{1-x}$Mo$_x$S$_2$ alloy with FFT pattern and i) intensity profile along the yellow-rectangular line in (h). j) Representative Raman spectrum.
in the ADF-STEM image and Raman spectra (Figure 5h–j). Moreover, the absence of GB lines between merged grains indicates the single crystallinity of the alloy, confirmed by ADF-STEM and their stacked FFT patterns (Figure S17, Supporting Information).

We propose an atomic sawtooth Au surface as a universal growth platform for SC TMdC monolayers, including WS2, WSe2, MoS2, MoSe2/WSe2 heterostructure, and W1−xMoxS2 alloy in a centimeter scale, regardless of Miller indices. Energetically favorable adsorption sites at periodic gutter step edges promote the growth of coherent TMdC triangular grains to eventually form the GB-free SC TMdC film. Avenues to explore in the future include i) the control of atomic sawtooth Au surface orientation, ii) the scaling up of the fabrication process for industrial applications, and iii) the discovery of appropriate atomic sawtooth surfaces beyond Au films. Our strategy offers new insights into the synthesis of SC diatomic 2D materials in a wafer scale to further facilitate the realization of SC vdW heterostructures.

Experimental Section

Cleaning Procedure of Au and W Foils: To remove impurities on the surfaces of Au and W foils, 1.2 × 1.2 cm2 high-purity Au foils (0.2 mm thick, 99.99%, iNexus, Inc.) and 1.3 × 1.3 cm2 W foils (0.1 mm thick, 99.95%, Alfa Aesar) were respectively dipped into Au etchant (GE-8111, Transene) and Ni etchant (TFB, Transene) for 10 min. After removal of the impurities, the etchant residues were washed away with fresh deionized water. The cleaned Au and W foils were annealed at 1000 °C for 1 h under high-purity Ar and H2 atmosphere with flow rates of 390 and 100 sccm, respectively.

Preparation of the Atomic Sawtooth Au Surface via Solidification of Liquid Au: Au foil stacked on W foil was loaded into the center of a 2-inch quartz tube. The residual gases in the quartz tube were purged by high purity Ar (99.999%) with a flow rate of 500 sccm for 30 min. The temperature was then slowly reduced to 1050 °C with a cooling rate of 0.5–60 °C/min. The crystal lattice and orientation of TMdC films were characterized by field-emission scanning electron microscope (JSM7000F, JEOL) equipped with electron backscatter diffraction (EBSD) analysis.

Growth Procedures of Various Single-Crystal (SC) Transition-Metal Dichalcogenide (TMdC) Monolayers: Metal precursor coated Au substrate was loaded into the quartz tube and purged by high purity Ar (99.999%) with a flow rate of 500 sccm for 15 min. The furnace was applied to the structural model, which consisted of monolayer WS2 and WSe2: Two-zone furnace was used to evaporate Se in the zone upstream from the substrate.

MoS2: Coherent MoS2 grains were grown on Mo precursor coated Au/W substrate by supplying H2S gas at a flow rate of 5–20 sccm at 800 °C for 10 min. To eliminate any interference by W source from native tungsten oxides on W foils, the substrate was annealed at 800 °C for 5 min prior to growing monolayer MoS2. Only Ar gas was used during the entire growth procedure.

MoSe2/WSe2 Heterostructure: For the growth of MoSe2/WSe2 heterostructure, triangular MoSe2 grains were first grown on Mo precursor coated Au/W substrate by supplying Se vapors under only Ar atmosphere while the temperature was increased to 800 °C in a two-zone furnace. The MoSe2/WSe2 heterostructure was subsequently grown with a supply of W source from W foil underneath the Au foil via sublimation of native tungsten oxides by introducing of H2 10 sccm at 800 °C for 10 min.

W1−xMoxS2 Alloy: Coherent W1−xMoxS2 grains were grown on Mo precursor coated Au/W substrate by supplying H2S gas at a flow rate of 5–20 sccm at 800 °C for 10 min under a mixture of Mo and W, derived from the native tungsten oxides of the W foil under H2 and Ar atmosphere.

Transfer of SC TMdC Grown on Au: As-grown SC TMdC on Au/W substrates were coated with poly(methyl methacrylate) (AP MMMA, MicroChem) under 4000 rpm for 1 min. The PMMA layer was baked at 200 °C for 5 min. For bubble transfer, the PMMA/TMdC/Au/W sample and Pt foil were used as anode and cathode, respectively. Under a voltage of 3–7 V in 1 M NaOH aqueous solution, the PMMA/TMdC was delaminated from Au substrate by the hydrogen bubbles generated at the interface between the TMdC film and Au substrate. The PMMA/TMdC samples were cleaned by deionized water for 10 min and transferred onto target substrates such as TEM grids and SiO2/Si substrates. To reuse the Au substrates, the Au/W substrate was cleaned in a piranha solution for 3 h, 10% nitric acid for 1 h, and buffer oxide etchant for 1 h. Warning note: Piranha solution is a very reactive solution. If the concentration of H2O2 reaches more than 50%, an explosion could occur. Because of the high reactivity with organic materials, only glass or Pyrex containers can be used for Piranha solution. The solution should be handled inside a certified chemical fume hood due to its corrosive vapors.

Characterizations: A field-emission scanning electron microscope (JSM7000F, JEOL) equipped with electron backscatter diffraction (EBSD) was employed to analyze the surface orientation of atomic sawtooth Au substrates. FESEM (JSM7010F, JEOL) was used to characterize the surface morphology and orientation of TMdC grains. The optical properties of TMdC grains were characterized by Raman spectroscopy system using 532 nm wavelength (NTEGRA Spectra, NT-MDT). Scanning tunneling microscope (STM, VT-STM, Omicron, Germany) and low-energy electron diffraction (LEED, Specs, Germany), with a beam diameter of ~1 mm, were utilized to corroborate the crystallographic relationship between WS2 and atomic sawtooth Au substrates under ultrahigh vacuum conditions with a base-pressure of ~1.0 × 10−10 Torr at room temperature. The LEED map of a WS2 film for 5 × 5 mm2 area was obtained by changing the sample position with a precision of 0.01 mm. The crystal lattice and orientation of TMdC films were characterized by STEM (JEEM ARM 200F, JEOL) with an electron acceleration voltage of 80 kV. Cross-sectional STEM lamellas of WS2/Au samples were prepared using a focused ion beam (FIB, FEI Helios NanoLab 450). To visualize the grain boundaries in polycrystalline WS2, as-grown WS2 grains were oxidized in air at 350 °C for 30 min.

Simulation of STM Image: Simulation of STM images was performed by Tersoff–Hamann approximation using Vienna Ab initio Simulation Package (VASP) based on density functional theory (DFT) with a plane-wave basis set. We used projector augmented wave (PAW) formalism for the pseudopotentials with Perdew–Burke–Ernzerhof (PBE) parametrization of the general gradient approximation (GGA) as implemented in VASP. A slab geometry with a vacuum of ~13 Å was applied to the structural model, which consisted of monolayer WS2 and
six layers of Au. The supercell size of WS$_2$ on Au substrate corresponded to the doubled period of Au (221) across the step edges. The supercell size was minimized by compressing WS$_2$ along the step edges due to the doubled period of Au (221) across the step edges. The supercell resistance. For electrical measurement, the SiO$_2$ layer and highly electrode, respectively. The transfer characteristics of WS$_2$ FETs were

**Fabrication and Measurement of Field-Effect Transistors:** FETs were fabricated by e-beam lithography. SC WS$_2$ film was transferred onto a 300 nm SiO$_2$/Si substrate using the electrochemical bubbling transfer method. WS$_2$ channel (8 μm x 4 μm) was patterned using SF$_6$ plasma under a plasma power of 3 W for 30 s in a reactive ion etching system (RIE, AFS-4RT). Cr/Au (5/50 nm) electrode was deposited on the channel layer by e-beam evaporator system (TLP1001, TERALEADER).

**Computational Details:** Adsorption of W$_x$S$_y$ cluster on the various Au facets were studied by DFT calculations using VASP. The revised PBE exchange-correlation functional and PAW method were used. Periodic supercell geometries were constructed to model (100), (110), (111), (1,4,10), (169), (2,10,15), (221), and (233) Au surfaces using 5 x 5, 4 x 3, 6 x 6, 6 x 3, 2 x 1, 2 x 1, 2 x 1, 4 x 2, and 4 x 1 unit cells, respectively, and a vacuum layer larger than 15 Å was added onto each surface to eliminate interlayer interactions. The Brillouin zones were sampled using a source measure unit (SMU, Keithley 4200, Keithley Instruments) in a probe station at room temperature under vacuum condition (1.76 × 10$^{-6}$ Torr).

**Supporting Information:** Data availability on request from the authors.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data available on request from the authors.

**Keywords**

atomic-sawtooth surface, chemical vapor deposition, epitaxial growth, single-crystal, transition metal dichalcogenides
