

Template-guided stacking regulation and morphology evolution of multilayer 2H- and 3R-WS₂ during layer-by-layer epitaxy

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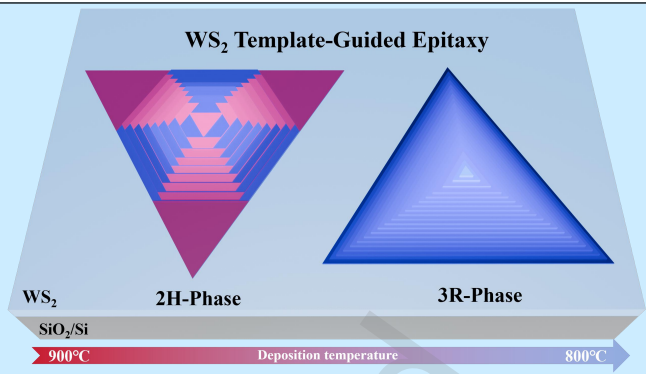
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Yuefan Peng^{1,§}, Buqian Zhao^{1,§}, Zengqi Chen¹, Junsheng Bao¹, Haomiao Wang¹, Yifan Liu^{1✉}, Weihao Zheng^{2✉}, Xiaopeng Fan^{1✉}	In this work, we adopt a template-guided van der Waals epitaxy strategy to realize the controllable growth of multilayer 2H- and 3R-phase WS₂. Combined with atomic force microscopy (AFM) and second harmonic generation (SHG) characterizations, we further reveal the intrinsic correlations among stacking evolution, layer growth, morphological evolution and optical symmetry response in multilayer WS₂.
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Template-guided stacking regulation and morphology evolution of multilayer 2H- and 3R-WS₂ during layer-by-layer epitaxy

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ABSTRACT: Two-dimensional layered materials have attracted extensive interest owing to their highly tunable electronic and optoelectronic properties associated with layer number and interlayer stacking. Tungsten disulfide (WS₂), a representative transition metal dichalcogenide, mainly adopts 2H and 3R stacking configurations in multilayer form, which exhibit distinct crystal symmetries and nonlinear optical responses. However, how template-guided stacking evolution influences the layer and morphology evolution of multilayer WS₂ during layer-by-layer epitaxy remains insufficiently understood. Herein, we demonstrate a WS₂-template-guided van der Waals epitaxial strategy to regulate the stacking propagation pathways and morphology evolution of multilayer WS₂. Under the combined effects of template-guided epitaxial regulation and deposition-temperature-dependent stacking evolution, distinct stacking propagation pathways preferentially lead to AB-stacked 2H-WS₂ and ABC-stacked 3R-WS₂. Notably, multilayer 2H-WS₂ exhibits asynchronous layer-dependent morphology evolution from triangular to hexagonal tower-like structures, whereas 3R-WS₂ maintains a self-similar pyramidal growth pathway with highly ordered stacking propagation. Atomic force microscopy (AFM) and second harmonic generation (SHG) mapping further establish the intrinsic correlation among stacking evolution, layer evolution, morphology evolution, and symmetry response in multilayer WS₂, including odd-even SHG oscillation in 2H-WS₂ and progressively enhanced SHG response in multilayer 3R-WS₂. These findings provide new insights into template-guided stacking regulation during multilayer van der Waals epitaxy, offering a potential strategy for the controllable structural engineering of layered transition metal dichalcogenide materials.

KEYWORDS: WS₂; template-guided epitaxy; stacking evolution; morphology evolution; second harmonic generation

1 Introduction

In recent years, two-dimensional (2D) materials have emerged as leading candidates for next-generation semiconductors that break the performance limits of conventional silicon-based materials, owing to their high electron mobility and unique physical properties[1-3]. Among the diverse library of 2D materials, transition metal dichalcogenides (TMDCs) with the chemical formula MX₂ (e.g., WS₂, WSe₂, and MoS₂) stand out prominently. Their band structures and interlayer coupling behaviors can be readily tailored by interlayer stacking configurations during multilayer van der Waals epitaxy[4], endowing them with unparalleled application potential in practical semiconductor devices such as electronics[5, 6], optoelectronics[7, 8], solar cells[9], and sensors[10].

Of all TMDCs, tungsten disulfide (WS₂) has garnered intense research attention for high-performance field-effect

transistors, photodetectors, and flexible electronic devices. This stems from its sizable direct bandgap in the monolayer form[11], excellent environmental stability[10, 12], and strong light-matter interaction[10, 11, 13]. However, monolayer WS₂ still suffers from limited property tunability and insufficient light-matter interaction, which restrict its use in high-performance devices[10, 11, 14, 15]. Beyond the monolayer regime, tuning the layer number and interlayer stacking order of WS₂ directly modulates its electronic, optical, and ferroelectric properties[15-17], while also influencing edge propagation and morphology evolution during multilayer epitaxial growth.

Multilayer WS₂ crystallizes predominantly in two polymorphs: the thermodynamically stable 2H phase (AB stacking) and the metastable 3R phase (ABC stacking)[18]. The core distinction between these two phases lies in their atomic stacking sequences and crystal symmetries, which give rise to profound differences in electronic, optical, and

nonlinear optical properties. The divergent interlayer symmetries of 2H and 3R WS_2 not only govern their electronic and nonlinear optical responses[19-21], but also strongly influence their multilayer growth behavior and morphology evolution pathways. Notably, 2H- WS_2 undergoes a direct-to-indirect bandgap transition with increasing layer number, whereas 3R- WS_2 exhibits a linearly enhanced second harmonic generation (SHG) response owing to its non-centrosymmetric stacking symmetry[8].

Despite remarkable progress in WS_2 synthesis, the controllable growth of multilayer WS_2 with regulated stacking configurations and layer-dependent morphology evolution pathways remains a critical challenge[22-24]. Conventional mechanical exfoliation[25] and manual assembly methods[26] introduce unavoidable surface contamination and high cost, rendering them unsuitable for practical device fabrication. Owing to the absence of epitaxial control and the complex interplay of various growth parameters[27-32], traditional CVD often produces randomly oriented 2H and 3R WS_2 phase mixtures[33]. Furthermore, the stacking-dependent layer evolution behaviors and morphology evolution pathways of multilayer 2H and 3R WS_2 remain insufficiently understood, hindering the rational design and development of WS_2 -based semiconductor devices. To address these bottlenecks, the development of a facile and robust strategy for the high-quality synthesis of highly ordered 2H and 3R WS_2 is urgently required. Previous studies have suggested that substrate interaction and deposition conditions jointly influence the stacking-selective growth behavior of multilayer WS_2 [34]. However, the role of template-guided epitaxy in regulating stacking-dependent layer evolution and morphology evolution during multilayer growth remains largely unexplored.

In this work, we achieve high-quality van der Waals epitaxial growth of multilayer 2H- WS_2 and 3R- WS_2 using WS_2 as an epitaxial template, and systematically elucidate the intrinsic correlations among template-guided stacking regulation, layer evolution behavior, and morphology

evolution of multilayer WS_2 . Under the guidance of the WS_2 epitaxial template, it's found that the high-temperature deposition region favors the thermodynamically stable AB-stacked 2H- WS_2 , which exhibits a unique layer-dependent morphological evolution from triangular to hexagonal shapes. In contrast, the low-temperature region promotes the growth of twist-free ABC-stacked 3R- WS_2 , characterized by uniform pyramidal geometry and ordered stacking. High-resolution atomic force microscopy (AFM) and SHG measurements further validate the distinct symmetries of these two phases.

Collectively, our work establishes template-guided stacking regulation as a key determinant of layer and morphology evolution in multilayer WS_2 . The underlying concept may be extendable to other isostructural TMDCs [35, 36], providing new insights for the controllable epitaxial growth and structural engineering of layered TMDC materials.

2 Materials and methods

2.1 Experimental Conditions

To investigate the phase selectivity of WS_2 in response to the deposition temperature gradient, we prepared layer-stacked multilayer WS_2 via the CVD method based on a layer-by-layer growth mechanism[37], under experimental conditions of high supersaturation and long growth time (> 10 min), as shown in Fig. S1. WS_2 powder was loaded into a quartz boat placed at the heating center of a quartz tube, and the deposition substrate was positioned 5–7 cm downstream (800–900°C) from the heating center. High-purity argon (Ar) gas was introduced into the sealed tube at a flow rate of 80 sccm to purge residual air before heating. The CVD system was heated to 1150°C over 25 minutes, and held at this temperature for 15 minutes with a constant Ar flow rate. This experimental design ensures that WS_2 first forms a continuous and uniform film on the SiO_2/Si substrate. Subsequent vertical layer stacking occurs on the pre-grown film, and the obtained samples possess large lateral dimensions. Multilayer WS_2 with well-defined layered stacking structures can be finally synthesized.

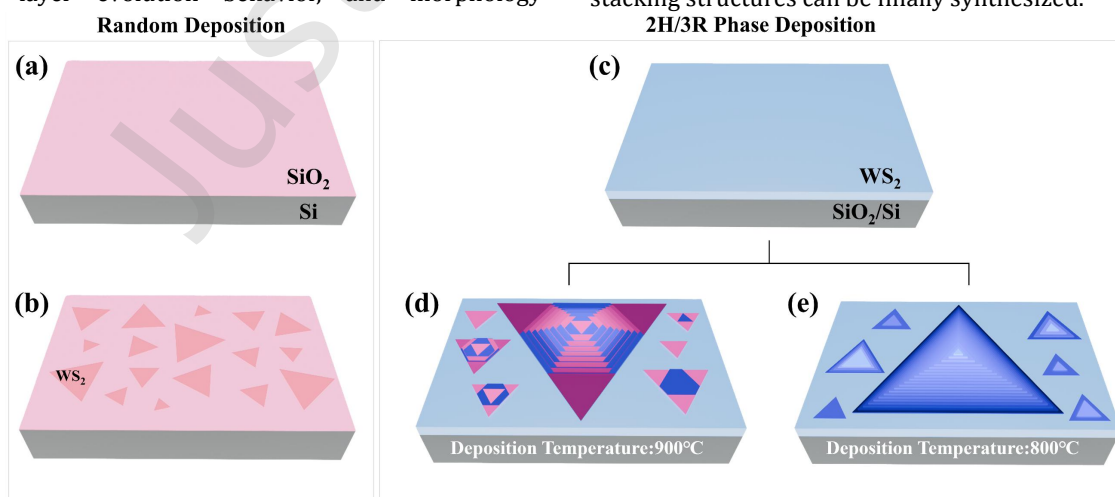


Fig. 1 Deposition of WS_2 via CVD method. (a) WS_2 is directly deposited on SiO_2/Si substrates. (b) Random-angle epitaxial growth of WS_2 . (c) WS_2 is deposited on WS_2 substrates. (d) H-phase stacking forms at a deposition temperature of 900 °C. (e) R-phase stacking forms at a deposition temperature of 800 °C.

2.2 Experimental Results

When a SiO_2/Si substrate was directly placed in the

downstream deposition region (Fig. 1(a)), the as-deposited WS_2 interacted weakly with the SiO_2 surface via van der

Waals forces, providing no effective epitaxial guidance over the lateral growth of WS₂. As confirmed by control experiments (Fig. S2), the synthesized WS₂ domains exhibited completely random orientation (Fig. 1(b))[18].

To overcome this limitation, we optimized the CVD growth strategy by employing a continuous, uniform, and flat WS₂ film as a new epitaxial substrate (Fig. 1(c)), yielding well-controlled and distinct experimental phenomena. Using WS₂ as an epitaxial template suppresses randomly oriented nucleation, standardizes the growth orientation and stacking mode of the upper WS₂ layers, and facilitates the analysis of phase-selective growth at different temperature zones[38-40]. For clarity, the WS₂ template substrate is referred to as the first layer in the following discussion. During the deposition of the second layer, the upper WS₂ layer adsorbs onto the first-layer template via van der Waals interactions. At the initial stage of second-layer growth, the small lateral size of WS₂ domains allows in-plane rotation. These distinct stacking configurations are inherited and amplified during subsequent layer-by-layer epitaxy, evolving into different multilayer stacking phases.

Notably, under the guidance of the WS₂ epitaxial template, distinct deposition conditions preferentially favor different stacking evolution pathways: in the high-temperature deposition region ($\approx 900^\circ\text{C}$), WS₂ grows in the AB stacking mode to form high-layer-count structures, resulting in an ordered array of 2H-stacked WS₂ (Fig. 1(d)); in contrast, a 3R-stacked WS₂ array forms at a deposition temperature of $\approx 800^\circ\text{C}$ (Fig. 1(e)). Our schematic models reveal the strong correlation between deposition temperature and phase-selective stacking, providing a framework for understanding stacking-dependent layer evolution and morphology evolution during multilayer van der Waals epitaxy of WS₂[18]. To further examine the proposed growth mechanism, we performed time-segmented interruption experiments during CVD. The experimental observations are consistent with the proposed growth pathway, as shown in Fig. S3. Ten independent growth batches under each deposition condition further demonstrated the reproducibility of the observed 2H- and 3R-WS₂ growth behaviors (Fig. S4).

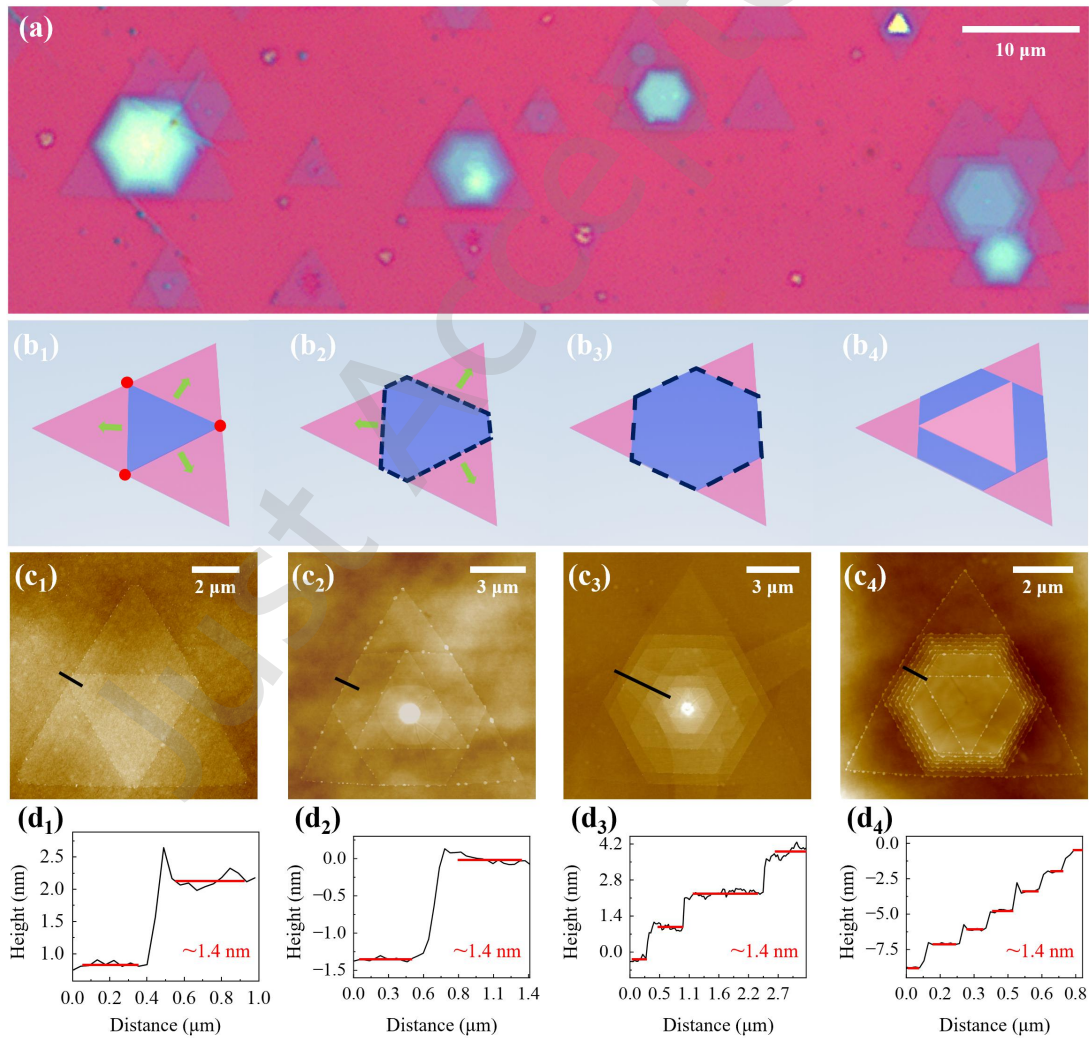


Fig. 2 Representative H-phase stacked WS₂. (a) Optical images of H-phase WS₂ arrays with different layer numbers. (b) Mechanism diagram of the morphological evolution of WS₂ induced by epitaxial growth. (c) The atomic force microscope (AFM) images of 2-, 3-, 9-, and 14-layer H-phase WS₂. (d) The black solid line-marked height profile in (c) indicates that all stacked layers exhibit monolayer characteristics.

Optical images of the as-prepared 2H-WS₂ arrays with varying layer numbers are presented in Fig. 2(a). Larger-area

2H-WS₂ with diverse and clearly distinguishable layer numbers are presented in Fig. S5. The results demonstrate

that the morphology of 2H-WS₂ evolves systematically from triangular, to truncated triangular, and finally to hexagonal shapes with increasing layer number, indicating pronounced layer-dependent morphology evolution during multilayer growth. Bilayer or few-layer 2H-WS₂ gradually develops truncated triangular edges, and the morphology transitions to a regular hexagonal shape with further layer accumulation. This confirms that layer number strongly modulates the layer evolution behavior and edge propagation pathway of 2H-WS₂ during growth.

We propose a growth pathway to explain this morphological evolution: during layer-by-layer epitaxy, the lateral expansion of the upper WS₂ layer is constrained by the boundary of the underlying layer and the local growth space, altering its edge growth behavior and driving a gradual transition from the initial triangular shape to the thermodynamically more stable truncated triangular and hexagonal morphologies.

To clarify the morphological evolution mechanism of WS₂, we schematically illustrate the transformation from triangular to regular hexagonal shapes in Fig. 2(b₁)–2(b₃). As shown in Fig. 2(b₁), the second layer (blue) epitaxially grows on the first-layer template (pink), initially nucleating and growing preferentially along specific crystal facets to retain the triangular morphology of the underlying layer. As its lateral size increases and contacts the boundary of the first layer, the atomic steps at the edge of the first layer impose spatial confinement and an energy barrier for further epitaxy of the second layer (marked by red dots)[41, 42]. With unconsumed WS₂ precursors in the central region, the second layer cannot maintain its original growth mode; the blocked edges morphology gradually transforms to form a transient truncated triangular structure (dashed line in Fig. 2(b₂)). With continued growth, the growth rate of the second layer stabilizes in all directions, terminating in the thermodynamically stable regular hexagonal morphology (dashed line in Fig. 2(b₃)). This growth regulation mechanism is preserved in subsequent multilayer growth (Fig. 2(b₄)). This simulated growth process reveals the morphological regulation of 2H-WS₂ driven by the interaction between the upper growth front and the underlying layer boundary, providing a mechanistic understanding of layer-dependent morphological evolution.

To validate this growth mechanism, we fabricated 2H-WS₂ with varying layer numbers and characterized their morphologies using high-resolution AFM. Edge morphologies of 2-, 3-, 9-, and 14-layer 2H-WS₂ are shown in Fig. 2(c₁)–2(c₄). Clearly, the bilayer structure (Fig. 2(c₁)) exhibits a truncated triangular profile, confirming spatial confinement by the underlying layer boundary. In the trilayer structure (Fig. 2(c₂)), the second layer approximates a hexagonal shape, while the third layer remains triangular due to the shorter growth time. In 9- and 14-layer 2H-WS₂, the morphology varies with layer height: lower layers adopt a nearly regular hexagonal shape, while upper layers near the top retain truncated triangular or even triangular features. This indicates that the morphological evolution of multilayer 2H-WS₂ during layer-by-layer epitaxy is not synchronous, but depends on the boundary confinement and effective lateral growth extent of each layer. This is

consistent with the shorter effective growth time of upper layers, which prevents full evolution to the stable hexagonal morphology.

The corresponding AFM height profiles are displayed in Fig. 2(d₁)–2(d₄). Fig. 2(c₁)–(c₃) reveal the characteristic bilayer step thickness of ≈ 1.4 nm, match with the reported thickness of monolayer WS₂ (0.7 nm). The visual height discrepancy between monolayer and bilayer steps is shown in Fig. S6. The step width decreases with progressive growth, compressing the monolayer step width to an extremely small value in Fig. 2(d₄). These experimental results align well with our simulated growth mechanism, further verifying the morphological evolution of 2H-WS₂ driven by the interaction between the upper growth front and the underlying layer boundary.

In sharp contrast to 2H-WS₂ with distinct layer-dependent morphological evolution, multilayer 3R-WS₂ maintains consistent interlayer orientation during layer-by-layer growth, resulting in uniform layer boundary profiles and a regular pyramidal stacking morphology. This morphological uniformity originates from the well-defined ABC stacking of the 3R phase, which endows 3R-WS₂ with exceptional structural homogeneity and well-defined interlayer stacking.

Optical images of the as-prepared 3R-WS₂ arrays with varying layer numbers are presented in Fig. 3(a), intuitively demonstrating consistent interlayer stacking without observable interlayer rotation—a key feature distinguishing 3R-WS₂ from morphologically evolving 2H-WS₂. The brightness contrast in the optical images corresponds to the layer number variation of 3R-WS₂.

To gain deeper insight into the formation pathway of the regular pyramidal morphology of multilayer 3R-WS₂ induced by thermodynamics, we schematically reconstruct its growth process in Fig. 3(b₁)–3(b₃). Specifically, in the initial growth stage (Fig. 3(b₁)), the first-layer WS₂ grows preferentially along low-energy crystal facets to form a regular triangular morphology, providing a uniform van der Waals epitaxial substrate for subsequent layers. The second layer nucleates and rapidly epitaxially grows on the first layer in a uniform twist-free stacking mode. With continued epitaxial growth (Fig. 3(b₂)–3(b₃)), strong interlayer van der Waals interactions and the thermodynamic stability of ABC stacking favor relatively uniform growth along all edge orientations. Sustained precursor supply and temperature regulation drive the formation of the pyramidal 3R-WS₂ structure shown in Fig. 3(b₄). This schematic clarifies the intrinsic correlation between the stacking characteristics and growth morphology of the 3R phase, and provides a theoretical foundation for the thermodynamically driven controlled epitaxial growth of high-quality multilayer 3R-WS₂.

To validate the proposed growth mechanism and structural homogeneity of 3R-WS₂, we characterized the as-prepared samples using AFM. Fig. 3(c₁)–3(c₄) display 2- to 5-layer 3R-WS₂, and the AFM structural characteristics of 3R-WS₂ with more layers are presented in Fig. S7. The AFM results reveal clear triangular edge profiles for each layer, with uniform, twist-free stacking between adjacent layers. Importantly, the height profiles extracted from the AFM

images (Fig. 3(d₁)–(d₄)) show a consistent interlayer step height of 0.7 nm, matching the theoretical monolayer thickness of 3R-WS₂ and confirming the high-quality uniform epitaxial growth of the 3R phase. These AFM characterizations are in excellent agreement with our growth mechanism model, further verifying the controllable synthesis of high-quality multilayer 3R-WS₂ with regular pyramidal morphology.

With continuous multilayer epitaxy, the lateral growth space at the apex of WS₂ gradually diminishes with

increasing layer number, leading to pronounced spatial confinement during layer-by-layer growth. Under the combined effects of template-guided epitaxial regulation and deposition-temperature-dependent stacking evolution, distinct stacking propagation pathways are established during multilayer growth, ultimately resulting in the formation of well-defined 2H and 3R stacking configurations with fundamentally different layer evolution and morphology evolution behaviors.

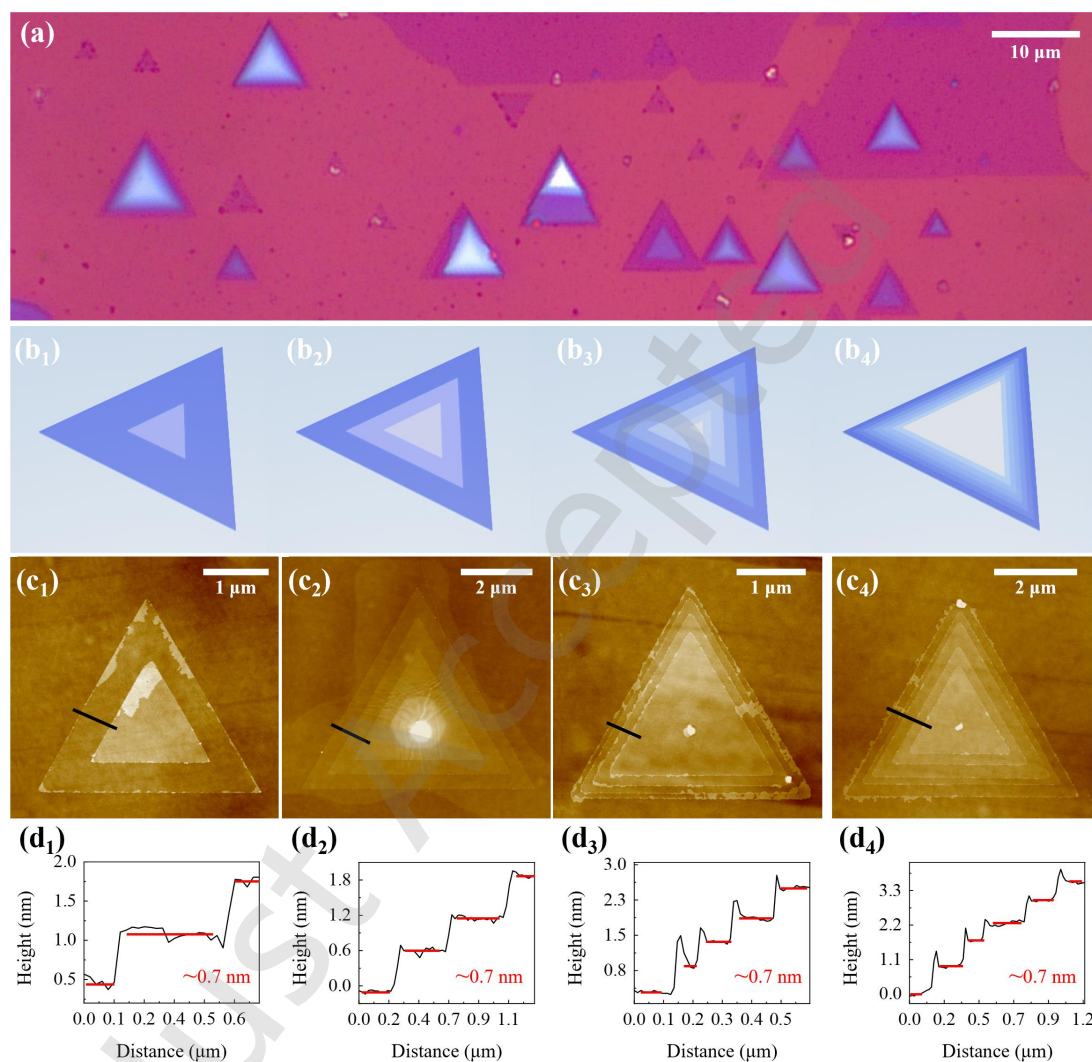


Fig. 3 Representative R-phase stacked WS₂. (a) Optical images of R-phase WS₂ arrays with different layer numbers. (b) Mechanism of R-phase WS₂ growth. (c) AFM results of 2-, 3-, 4-, and 5-layer R-phase WS₂. (d) The black solid line-marked height profile in (c) indicates that all stacked layers exhibit monolayer characteristics.

For 2H-WS₂, the lateral growth of upper layers is constrained by both limited growth space and underlying layer boundary obstruction as the layer number increases. Under the combined effects of spatial confinement and alternating interlayer rotational orientation, the edge growth behavior of multilayer 2H-WS₂ gradually evolves during layer-by-layer epitaxy, ultimately forming a morphology with a triangular base and a hexagonal tower-like upper structure, as clearly revealed by the AFM topography. (Fig. 4(a)). To further elucidate the unique stacking characteristics of 2H-WS₂, we present a magnified AFM image of the central region in Fig. 4(b); the red and blue lines reveal rotational stacking

configuration of the 2H phase, a fundamental structural signature distinguishing it from the 3R phase. To verify the layer-stacking quality of the as-prepared 2H-WS₂, we acquired a symmetric overall morphological profile along the black and red arrows in Fig. 4(a) (Fig. 4(c)). Magnified views reveal distinct height differences between monolayer and bilayer steps in different orientations of the sample, consistent with our previous conclusions and confirming the high-quality layer-by-layer epitaxial growth of 2H-WS₂ induced by template-guided epitaxial growth. ΔL represents the lateral step width, ΔH represents the step height, and the step slope is defined as $K = \Delta H / \Delta L$. Statistical analysis of the

step slope ($\Delta H/\Delta L$) reveals that the step slope remains stable up to the seventh layer, and gradually decreases from lower layers to upper layers beyond this layer (Fig. S8). This trend reflects layer-dependent evolution of step geometry and edge morphology, further supporting the layer-dependent morphology evolution of multilayer 2H-WS₂.

In contrast to 2H-WS₂ with interlayer rotation, 3R-WS₂ forms a well-defined pyramidal morphology, as shown in the AFM image (Fig. 4(d)). A magnified view of the central region of the 3R-WS₂ pyramid (Fig. 4(e)) displays distinct stacking boundaries between adjacent layers (blue dashed lines) with no observable structural disorder, intuitively reflecting the

clear layer-by-layer stacking nature of 3R-WS₂. Measurements reveal that the top-layer triangular side length is ≈ 280 nm, and the interlayer edge spacing is ≈ 90 nm; the uniform interlayer spacing further confirms the controllability and homogeneity of the epitaxial growth enabled by template-guided multilayer epitaxy. The overall height profile of 3R-WS₂ acquired along the black arrow in Fig. 4(d) (Fig. 4(f)) and its magnified view show uniform monolayer thickness in the stacked structure, verifying the exceptional layer-by-layer epitaxial quality of 3R-WS₂ prepared via template-guided epitaxial growth.

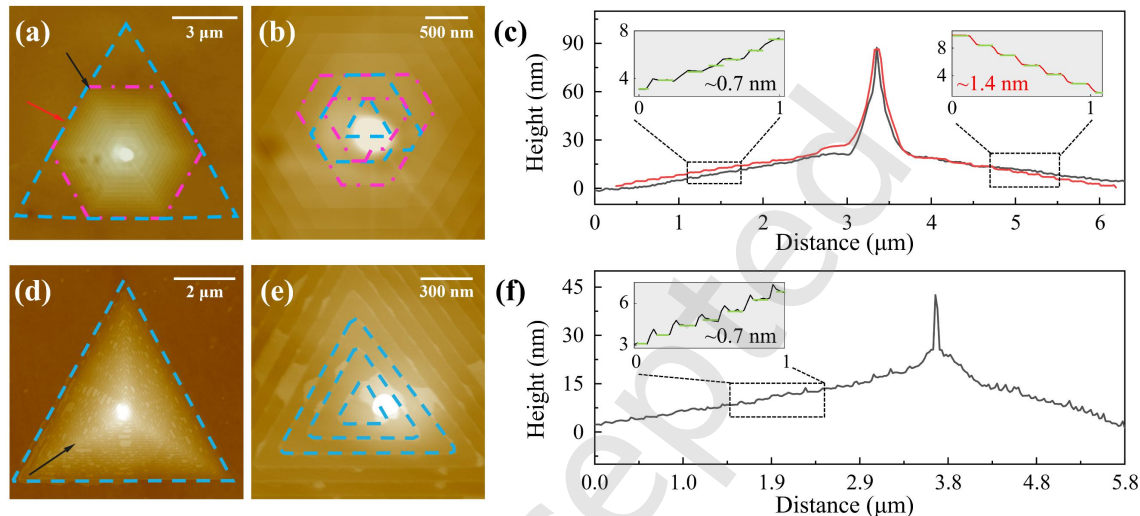


Fig. 4 AFM test results of the final structural morphology of multilayer H-phase and R-phase WS₂ limited by the top growth space. (a) AFM images of multilayer H-phase WS₂ and its locally magnified central region (b). (c) The overall height profile and the locally magnified profile acquired along the black and red arrows in (a) unambiguously resolve the monolayer and bilayer step configurations along different orientations. (d) AFM images of multilayer R-phase WS₂ and its locally magnified central region (e). (f) The overall height profile and locally magnified profile extracted along the black arrow in panel (d) clearly show a single-layer stacking structure with a thickness of ≈ 0.7 nm.

To further validate the stacking characteristics and interlayer symmetry responses of the as-prepared WS₂, we performed SHG mapping measurements on 2H and 3R phase WS₂. As a second-order nonlinear optical response, SHG is forbidden in centrosymmetric 2H-WS₂ but is efficiently generated in non-centrosymmetric 3R-WS₂, making SHG a powerful tool to verify the interlayer stacking sequence of WS₂ [18, 43, 44]. The original experimental SHG spectral data are presented in Fig. S9.

Top and side views of the atomic arrangement of bilayer 2H-WS₂ are shown in Fig. 5(a), with the first and second layers marked by blue and pink lines, respectively. The overlapping region of the two layers exhibits effective centrosymmetry, with the upper-layer atoms arranged in a mirror-image configuration relative to the lower layer; this symmetry nearly quenches the SHG signal in the overlapping region. 2H-WS₂ exhibits a typical odd-even layer-dependent SHG response: the SHG signal is significantly suppressed in the overlapping region of even layers, while it recovers in odd layers due to the restoration of net non-centrosymmetry. Fig. 5(b) shows the SHG mapping image of bilayer 2H-WS₂, where the SHG intensity scale confirms the near-complete annihilation of the SHG signal in the central overlapping region, supporting the stacking-dependent symmetry evolution proposed above. For trilayer 2H-WS₂, the overlapping region of the bottom and middle layers

produces no SHG signal, while the third layer breaks the centrosymmetry of the overlapping region, restoring the SHG signal (Fig. 5(c)). In multilayer 2H-WS₂, the central SHG response is governed by layer evolution, geometric coverage and interlayer symmetry, resulting in a distribution with a dark center and bright edges or locally attenuated signals, ultimately forming a hexagonal structure with a central signal-annihilated region (Fig. 5(e)).

In striking contrast, 3R-WS₂ exhibits a pronounced layer-dependent SHG response. SHG mapping measurements of Fig. 3(c₁), 3(c₃), and 4(e) are presented in Fig. 5(f)–5(h). For bilayer 3R-WS₂, clear layer-resolved SHG signals are observed, originating from the non-centrosymmetry of the ABC stacking. For 4-layer 3R-WS₂, the SHG signal is further enhanced; although layer resolution is limited by the laser spot size, the top and bottom layers remain distinguishable. For thicker multilayer 3R-WS₂ (Fig. 5(h)), the SHG signal is significantly intensified, forming a characteristic distribution with weak edge signals and strong central signals, consistent with the pyramidal morphology observed in AFM measurements.

These SHG results are fully consistent with the AFM characterizations and the expected stacking symmetries, collectively confirming the well-defined 2H/3R stacking characteristics of our as-prepared samples.

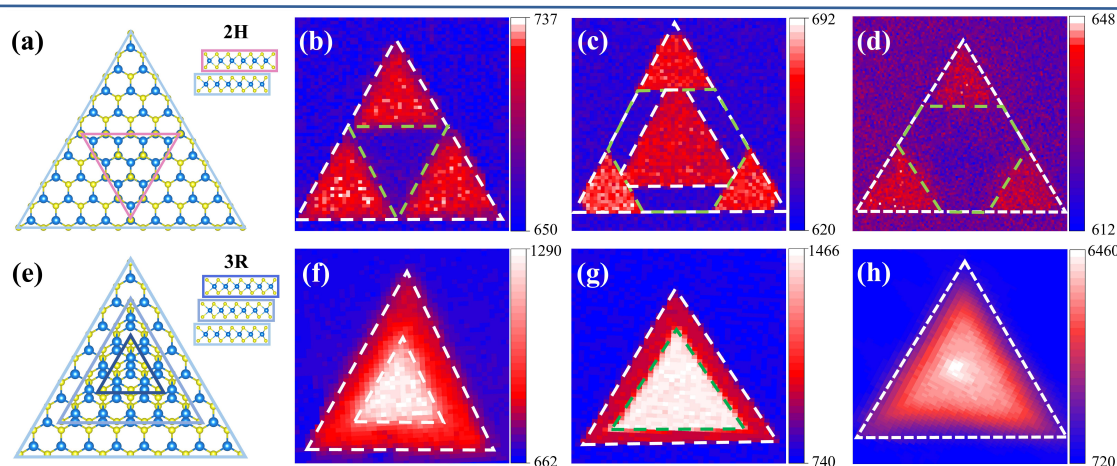


Figure 5 Layer-dependent second harmonic generation (SHG) characteristics of H-phase and R-phase WS₂ with different layers under the excitation of a femtosecond laser at a wavelength of 780 nm. The same power density was maintained throughout all measurements. (a) Atomic structure schematic of H-phase WS₂. (b-d) Layer dependence affects the SHG-mapping evolution of H-phase WS₂. (e) Atomic structure schematic of R-phase WS₂. (f-h) Layer dependence affects the SHG-mapping evolution of R-phase WS₂.

3 Conclusions

In this work, we report the controllable growth of multilayer 2H- and 3R-phase WS₂ with distinct stacking evolution behaviors via a template-guided van der Waals epitaxial strategy. By systematically investigating the influence of template-guided epitaxy under different deposition conditions on multilayer WS₂ evolution, we successfully obtain WS₂ with well-defined 2H and 3R stacking configurations and distinct layer evolution pathways. With continuous multilayer epitaxy, the lateral growth space at the apex of WS₂ gradually diminishes with increasing layer number, leading to pronounced spatial confinement during layer-by-layer growth. Under the combined effects of template-guided epitaxial regulation and deposition-temperature-dependent stacking evolution, distinct stacking propagation pathways are established during multilayer growth, ultimately resulting in the formation of well-defined 2H and 3R stacking configurations with fundamentally different layer evolution and morphology evolution behaviors. Specifically, multilayer 2H-WS₂ undergoes asynchronous morphology evolution from triangular to hexagonal tower-like structures during layer-by-layer epitaxy, whereas 3R-WS₂ maintains a self-similar pyramidal morphology with highly ordered stacking propagation. Atomic force microscopy (AFM) and second harmonic generation (SHG) measurements further establish the intrinsic correlation among stacking evolution, layer evolution, morphology evolution, and symmetry response in multilayer WS₂, providing optical verification for the proposed evolution pathways. Collectively, our work provides new insights into template-guided stacking regulation and evolution behavior during multilayer van der Waals epitaxy, offering a potential strategy for the controllable structural engineering of layered TMDC materials.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interest in this work.

Author contribution statement

The project was designed and managed by X. P. F. The samples were synthesized and characterized by Y. F. P., Z. Q. C., and J. S. B. AFM measurements were provided by B. Q. Z. and Z. Q. C. SHG measurements were obtained by Y. F. P. and B. Q. Z. Interpretation of data was provided by Y. F. P., B. Q. Z., Z. Q. C., J. S. B. and H. M. W. Y. F. L., W. H. Z., and X. P. F. revised the manuscript. All authors reviewed and contributed to the revision of the manuscript.

Use of AI statement

None.

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Supplemental File for Review

Template-guided stacking regulation and morphology evolution of multilayer 2H- and 3R-WS₂ during layer-by-layer epitaxy

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Supplementary Information: 10 pages and 9 figures

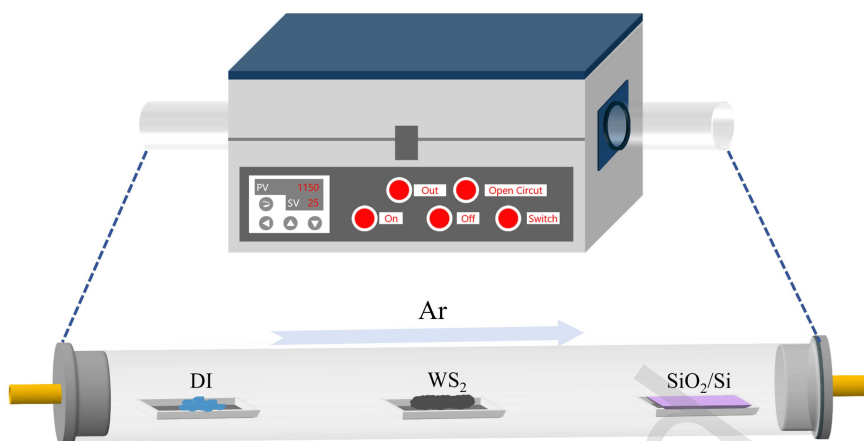


Fig. S1 Chemical Vapor Deposition Reaction System.

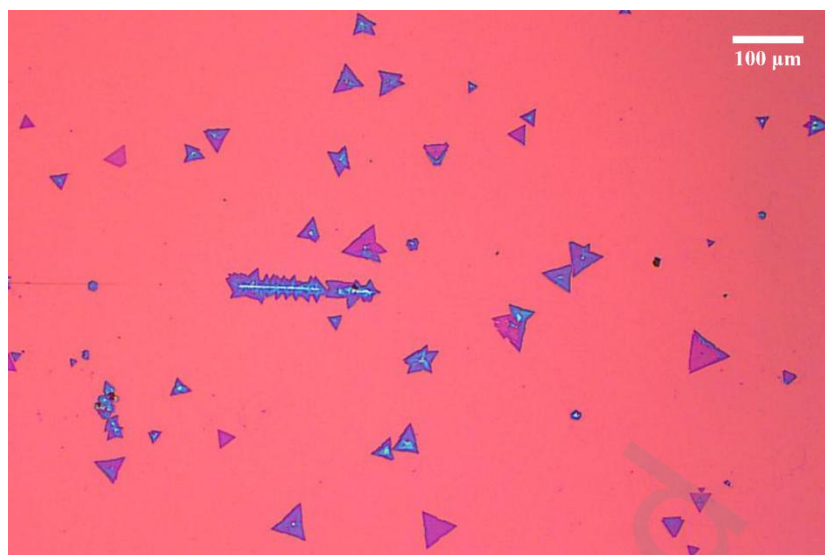


Fig. S2 Random angular distribution of WS₂ directly grown on SiO₂/Si substrate.

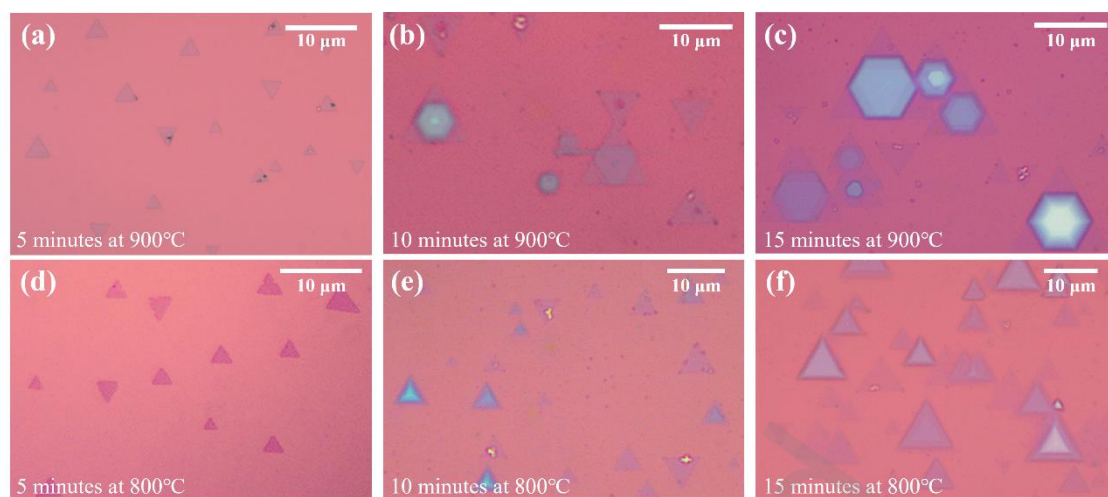


Fig. S3 The experimental results of the time segment interruption during the CVD process. (a) Initial epitaxial growth stage of WS₂ on the WS₂ template, showing a regular 0°/180° alignment; (b–c) In the higher-deposition-temperature region, the 2H phase continues to grow epitaxially along its original growth mode, while the oppositely oriented monolayers cease growth; (d–f) In the lower-deposition-temperature region, 3R-WS₂ structures begin to grow, whereas WS₂ with the opposite orientation does not continue to grow epitaxially.

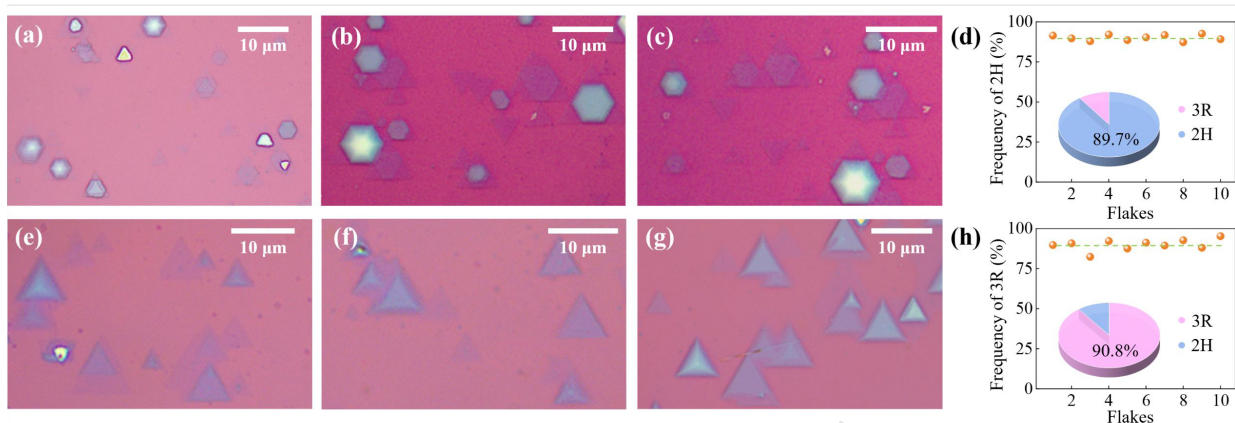


Fig. S4 Representative optical images of the sampled regions and the corresponding statistical results. (a–c) Representative optical images of 2H-WS₂ at different growth stages. (d) Statistical results for 2H-WS₂ across ten independent growth batches; the inset pie chart shows the results from the second independent batch. (e–g) Representative optical images of 3R-WS₂ at different growth stages. (h) Statistical results for 3R-WS₂ across ten independent growth batches; the inset pie chart shows the results from the second independent batch.

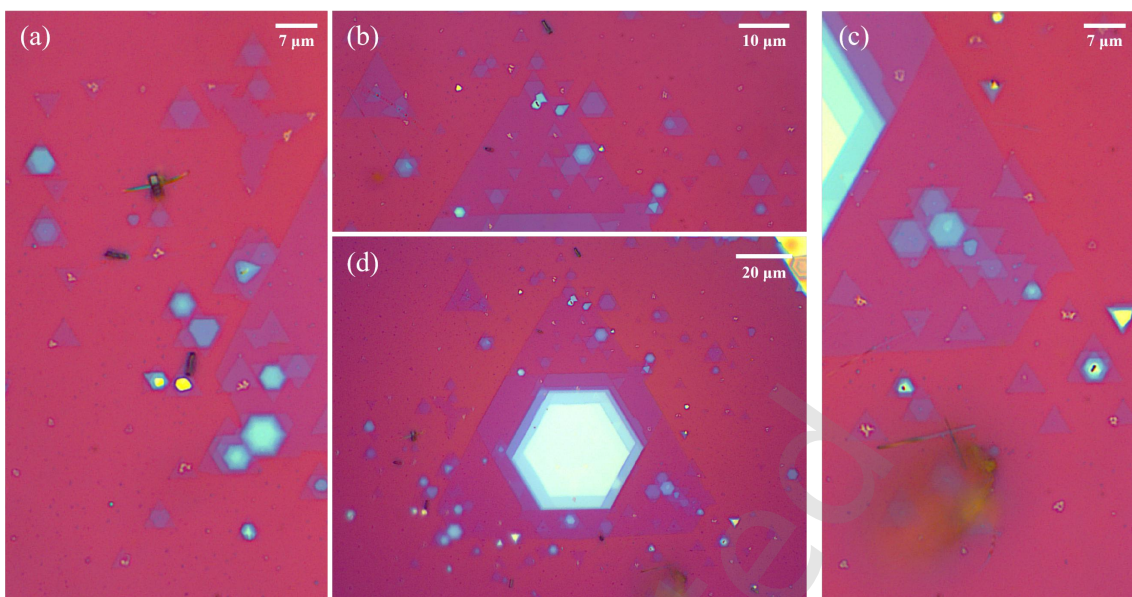


Fig. S5 Optical images of larger-scale 2H-WS₂ array regions. (a-c) are the magnified view of the local region in (d). (d) The wide-range optical images of the 2H-WS₂ arrays obtained through the experiment.

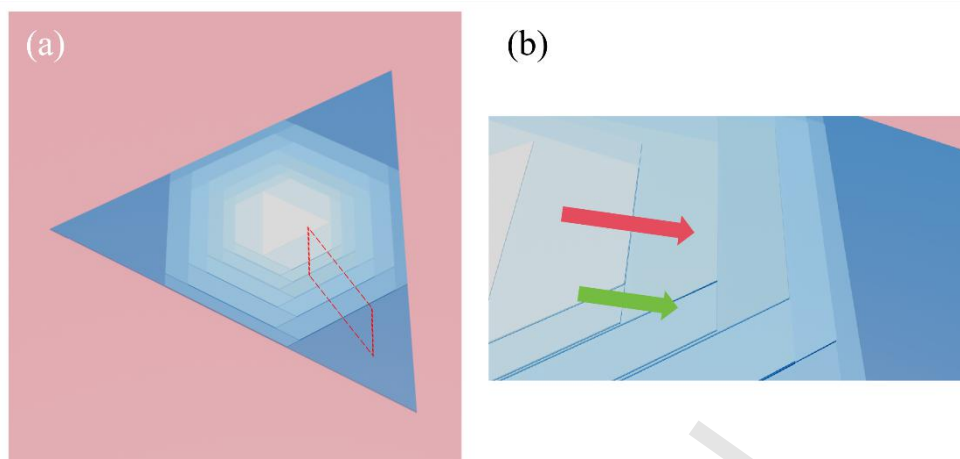


Fig. S6 Schematic illustration of monolayer–bilayer step changes along the transverse direction. (b) shows a magnified view of the red-boxed region in (a). A bilayer step structure can be identified along the red line, whereas the region along the green arrow exhibits a monolayer configuration with a Z-shaped edge.

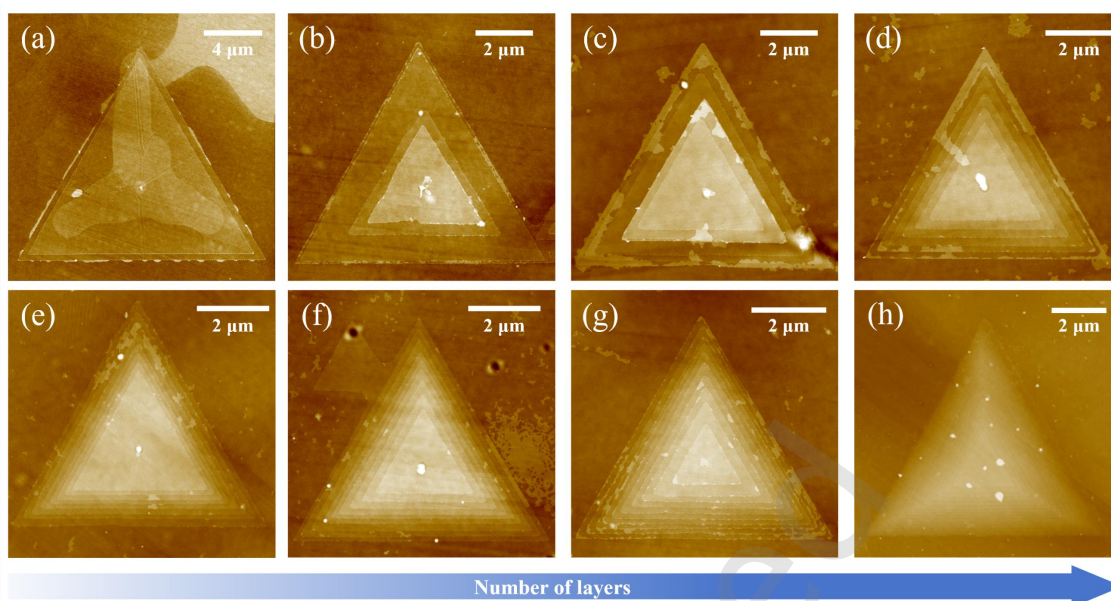


Fig. S7 AFM results of 3R-WS₂ with richer layer numbers all reveal a uniform monolayer structure.

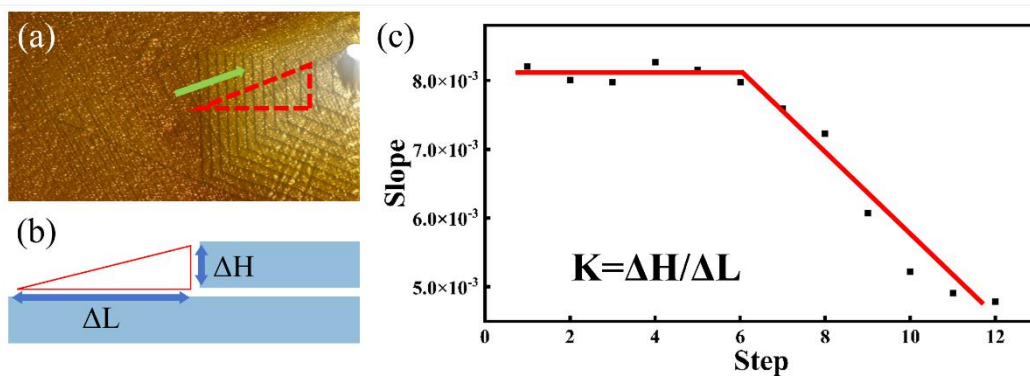


Fig. S8 Variation of step slope induced by layer-dependent growth evolution. (a) The red box indicates the selected direction for characterizing the transverse step morphology. (b) Schematic illustration of the step-slope calculation method, where ΔL denotes the step width and ΔH represents the step height. (c) Statistical analysis of the step slope ($\Delta H / \Delta L$) as a function of layer number, counted from the bottom layer upward for statistical analysis. The slope of bottom steps becomes nearly stable before the sixth layer, whereas the step slope gradually declines from lower layers toward upper layers in thicker regions. This demonstrates that adequate growth time for basal layers during the layered growth of multilayer 2H-WS₂ enables enhanced lateral expansion and steady morphological evolution.

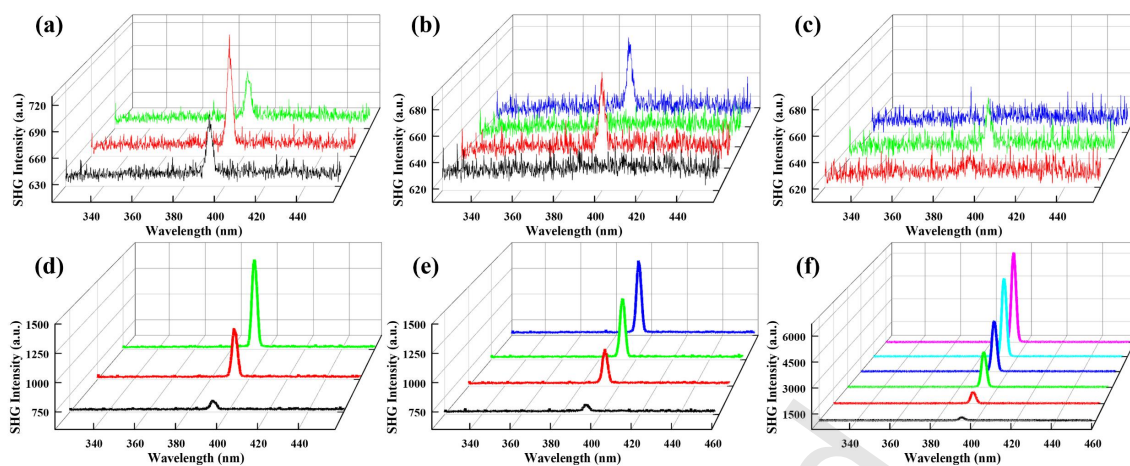


Fig. S9 Original spectral data of SHG mapping. (a-c) SHG results of 2H-WS₂ clearly reveal the SHG oscillation characteristics induced by layer-number variation. (d-f) SHG results of 3R-WS₂ clearly demonstrate the linear enhancement of local SHG signals with increasing layer number.