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A Facile Space-Confined Solid-Phase Sulfurization Strategy for Growth of High- Quality Ultrathin Molybdenum Disulfide Single Crystals

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ABSTRACT: Single-crystal transition metal dichalcogenides (TMDs) and TMD-based heterojunctions have recently attracted significant research and industrial interest owing to their intriguing optical and electrical properties. However, the lack of a simple, low-cost, environmentally friendly, synthetic method and a poor understanding of the growth mechanism pose a huge challenge to implementing TMDs in practical applications. In this work, we developed a novel approach for direct formation of high-quality, monolayer and few-layer MoS₂ single crystal domains via a single-step rapid thermal processing of a sandwiched reactor with sulfur and molybdenum (Mo) film in a confined reaction space. An all-solid-phase growth mechanism was proposed and experimentally/theoretically evidenced by analyzing the surface potential and morphology mapping. Compared with the conventional chemical vapor deposition approaches, our method involves no complicated gas-phase reactant transfer or reactions, and requires very small amount of solid precursors [e.g., Mo (~3 μg)], no carrier gas, no pretreatment of the precursor, no complex equipment design, thereby facilitating a simple, low-cost, and environmentally friendly growth. Moreover, we examined the symmetry, defects, and stacking phase in as-grown MoS₂ samples using simultaneous second-harmonic-/sum-frequency-generation (SHG/SFG) imaging. For the first time, we observed that the SFG (peak intensity/position) polarization can be used as a sensitive probe to identify the orientation of TMDs' crystallographic axes. Furthermore, we fabricated ferroelectric programmable Schottky junction devices via local domain patterning using the as-grown, single-crystal monolayer MoS₂, revealing their great potential in logic and optoelectronic applications. Our strategy thus provides a simple, low-cost, and scalable path toward a wide variety of TMD single crystal growth and novel functional device design.

Atomically thin semiconducting transition metal dichalcogenides (TMDs), MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}, \text{Te}$), represent a new family of two-dimensional (2D) materials with remarkable electrical and optical properties that have attracted great scientific and industrial interests. For instance, TMD monolayers have direct/sizable semiconducting bandgaps and exhibit strong photoluminescence (PL) emissions in the visible and near-infrared spectral range.^{1,2} In addition, inversion symmetry is broken for monolayer TMDs, which results in novel valley-dependent selection rules,³⁻⁵ as well as strong nonlinear optical responses.⁶⁻⁹ These unusual properties have motivated the development of monolayer TMDs for use in next-generation nano/optoelectronic devices, such as high-performance field-effect transistors (FETs),¹⁰⁻¹² logic circuits,^{13,14} photovoltaics and photodetectors,¹⁵⁻¹⁷ sensors,^{18,19} nonlinear optical devices,^{20,21} spintronic devices,^{4,5,22} and memristors.^{23,24} Recently, considerable interest has focused on the structural phase engineering in TMDs,²⁵⁻³⁰ which may provide a means of controlling TMD properties, leading to potential applications in novel electronic devices,^{26,31} energy storage devices,²⁷ and catalysts.²⁹ Furthermore, interest in creating ultrathin semiconductor homogenous junctions and heterojunctions based on these monolayer TMDs has also been rapidly increasing since these junctions offer unique size scaling opportunities and potential for multifunctional integration compared to conventional semiconductor devices.³²⁻³⁷ Despite these highly promising features, a major challenge that limits the development of practical applications of semiconducting TMDs is the lack of a simple, low cost, environmentally friendly, and large-scale synthetic method of creating high-quality single-crystalline TMDs with controlled atomic layers.

Recently, several methods have been developed to produce atomically thin 2D TMDs, including mechanical exfoliation, liquid exfoliation, chemical vapor deposition (CVD), molecular beam epitaxy, etc.³⁸⁻⁴⁰ While the highest quality MoS_2 samples can be obtained via mechanical

exfoliation from the bulk materials, which exhibit room-temperature charge mobility of $> 200 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ and a high on/off current ratio (of order 10^8),¹⁰ they are only suitable for the exploration of diverse potential as a proof of concept due to the poor yield, uncontrolled layer thickness and irregular sample geometry. In contrast, CVD has become the predominant method for cost-effective and scalable growth of TMD monolayers.⁴¹⁻⁴⁴ Although significant advances have been made, the fabrication of uniform and high-quality TMDs using CVD requires precise control of a series of parameters, e.g., the choice of precursors, the precursor amount, the ratio of transition metal/chalcogenide reactants, the gas flow rate, the growth temperature and time, and the source-substrate configuration. Additionally, conventional CVD methods require complex processes and hardware designs of gas-phase reactant transport and chemical reactions, which make CVD process must be separately optimized for each TMD material. More specifically, the CVD growth of single-crystalline TMDs (such as MoS_2) has primarily been achieved by using vapor-phase sulfurization of transition metal oxide powders (MoO_3 ⁴⁴⁻⁴⁶ or MoO_2 ⁴⁷), represented by the equation: MoO_3 (MoO_2) + $3\text{S} \rightarrow \text{MoS}_2 + \text{SO}_2$, where the oxygen atoms removed from MoO_3 (MoO_2) participate in forming the undesirable SO_2 gas which is extremely toxic and corrosive. In addition, if CVD chamber conditions are not properly controlled, incomplete reactions may result in uncontrolled amounts of $\text{MoS}_{2-x}\text{O}_x$ impurities in the as-grown MoS_2 crystals.⁴⁸ Furthermore, atomic oxygen is a well-known etchant for 2D materials, especially at high temperatures,^{9,49} indicating that any nascent oxygen could potentially create defects/vacancies during 2D MoS_2 growth. Therefore, the use of oxygen-free molybdenum (Mo) and pure sulfur as the initial precursors could avoid the above issues and lead to rapid growth of samples with higher quality.⁵⁰ To the best of our knowledge, using ultrathin Mo film as a solid metal precursor for single crystalline MoS_2 growth has never been successfully achieved.⁵⁰⁻⁵³ For example, some research

groups have developed the methods to directly prepare polycrystalline MoS₂ layers on SiO₂ substrate using a predeposition of Mo (or MoO₃) films followed by CVD.^{50,51,53} Additionally, sulfurizing Mo foil in sulfur vapor has been reported by Tai *et al.* to controllably grow monolayer MoS₂ at 600 °C for 1 min,⁵² while the formed MoS₂ layers are not single-crystal structure and also need tedious post-growth transfer process for fabricating MoS₂-based devices. Nevertheless, the direct sulfurization of Mo film for high-quality single-crystal MoS₂ growth remains challenging.

Recently, Chen *et al.* demonstrated a convenient method of preparing high-quality, single crystal graphene through the design of a CVD reactor with a confined reaction space.⁵⁴ The space-confined configuration in their work provides multiple advantages, including suppressing the substrate roughness, establishing a uniform distribution of reactant concentration, and shifting the growth kinetics toward a diffusion-controlled reaction. Building on this new concept, in this work, we report a novel approach to the direct formation of single crystal MoS₂ atomic layers via a single-step rapid thermal processing of a sandwich reactor with sulfur (S) and Mo film in a confined reaction space. Meanwhile, an all-solid-phase growth mechanism is proposed, as evidenced by a coupled combination of experimental measurements and first-principles calculations. In contrast to conventional CVD methods, the proposed space-confined solid-phase sulfurization strategy involves no complicated gas-phase reactant transfer or reaction, and is not restricted by multiple process constrains, such as the choice of precursors, a proper vapor ratio of the Mo and S reactants, or a precise gas flow control. More importantly, contamination-free single-crystal MoS₂ can be obtained over the most of the substrate surface with very small amount of solid precursors [Mo (~3 μg) and S (~50 mg)], which is much less than those widely used for conventional CVD methods.^{41,44,45,55} In addition, multiple 2D TMDs could be synthesized simultaneously in the same RTP furnace using the proposed space-confined sandwich reactor design (Figure 1a), which is

difficult for the conventional CVD methods. Therefore, our method not only simplifies the precursor, process, and hardware design, but also is less material costed and more environmentally friendly because of minimizing the produced gas and preventing potential environmental contamination and poisonous gas leakage.

Additionally, monolayer and few-layer MoS₂ grains can be controllably grown through variations in the reactor design and conditions, thus, we were able to control the layer-thickness and stacking order of MoS₂ so as to control properties such as nonlinear optical response. We examined the symmetry, grain boundary, and stacking order of as-grown samples using simultaneous second-harmonic generation (SHG) and sum-frequency generation (SFG) imaging, which enabled fast and reliable detection of structural information. More importantly, we first observed that polarized SFG (not only peak intensity but also peak position) can also be used to determine the crystalline orientation of TMDs. Moreover, we fabricated ferroelectric programmable Schottky junction devices via local domain patterning using the as-grown monolayer MoS₂, revealing their high potential in logic and optoelectronic applications.

RESULTS AND DISCUSSION

Highly crystalline monolayer and few-layer MoS₂ samples were fabricated in a space-confined reactor using solid-phase sulfurization of ultrathin Mo film as a precursor, instead of the previously used MoO₃ and MoO₂ powders (Figure 1a). As illustrated in Figure 1a, two different space-confined reactors were designed and placed in the central heating zone of the rapid thermal processing (RTP) system for MoS₂ growth. For Reactor Type 1, the Mo-film-coated S plate was sandwiched in the gaps between two catalytic inactive oxides substrates (such as SiO₂/Si) (Figure S1a, Supporting Information), while for Reactor Type 2, a 0.5-mm-thick S plate was sandwiched

between a pair of Mo-film-coated SiO₂/Si substrates (Figure S1b, Supporting Information) (See the *Methods* for details). In this straightforward, one-step, solid-phase growth strategy, the creation of a space-confined configuration is capable of suppressing the sublimation of sulfur in the RTP system and increasing the nucleation probability for solid-phase growth of single crystal MoS₂ under an excessive sulfur supply.

Figure 1b shows a low-magnification optical microscope image of MoS₂ flakes grown using Reactor Type 1. By combining optical contrast and atomic force microscope (AFM) measurements, most of the as-grown MoS₂ crystals are determined to be composed of strictly a single layer. Typically, the isolated single MoS₂ crystals grown display a symmetric triangular geometry with a hexagonal nucleation site at the center (top inset in Figure 1b). The nucleus exhibits the characteristic Raman signal of thick MoS₂, E_{2g}^1 at 382.2 cm⁻¹ and A_{1g} at 407.1 cm⁻¹ (Figure S2, Supporting Information). This result is similar to a recent report on CVD growth of monolayer MoSe₂,⁵⁶ indicating that the growth of MoS₂ using Reactor Type 1 could be a solid-vapor reaction involving (1) direct co-condensation and nucleation of MoS_x ($0 < x < 2$) on the substrate by Mo-S interactions and (2) sulfurization of MoS_x with local vapor-phase S to form MoS₂. Sometimes, the coalescences occur between adjacent single-crystal MoS₂ grains, resulting in the formation of monolayer MoS₂ crystals in polygonal shapes (Figure 1b and Figure S3, Supporting Information). Additionally, a large MoS₂ grain with polycrystalline geometry and an edge size of approximately 44 μm was also obtained (middle inset in Figure 1b) and confirmed to be a monolayer characteristic by AFM measurements (bottom inset in Figure 1b).

Figure 1c shows typical optical images of MoS₂ samples formed using Reactor Type 2, which exhibit several types of shapes, mainly including triangle-shaped monolayers and few-layers (Figures S4 and S5, Supporting Information), and monolayer and few-layer polygonal shapes

(Figure S6, Supporting Information). In some cases, we also observed the growth of multilayer MoS₂ with various shapes and morphologies. The well-defined shapes of those polygons indicate good crystallinity for the as-grown MoS₂ samples. It is interesting to note that no nucleation sites are visible at the center of any MoS₂ crystal, which suggests that the solid-vapor-phase growth mechanism, as mentioned above, seems unsuitable for the growth of layered MoS₂ using Reactor Type 2. The growth mechanism (solid-phase sulfurization) will be discussed later. To the best of our knowledge, this is the first time anyone has observed that solid-phase sulfurization (SPS) of ultrathin Mo film can lead to the formation of monolayer and few-layer MoS₂ single crystals.

On the basis of the above experimental observation and analysis, we can conclude that, with Type 1 reactor design (substrate/Mo-S/substrate), most of the MoS₂ samples formed on the substrate are epitaxial single layer, while Type 2 reactor design (substrate-Mo/S/Mo-substrate) offers a better yield of few-layer MoS₂ flakes, which indicates that monolayer and few-layer MoS₂ can be controllably synthesized through variations in the reactor design. More interestingly, the nucleation and growth of single crystal MoS₂ was observed to occur on both the top and bottom surfaces of the silicon substrates (Figure S7, Supporting Information). A comparison of the MoS₂ on the top and bottom surfaces indicates that, for the same reactor, MoS₂ can grow from both substrate surfaces through the same mechanism. To demonstrate the important roles of space-confined configuration, the top silicon substrate in Reactor Type 1 (or the top Mo-film-coated silicon substrate in Reactor Type 2) was removed and then annealed at 750 °C under the same conditions. The subsequent optical image and Raman analyses show the formation of continuous polycrystalline MoS₂ thin films (Figure S8, Supporting Information), while no single crystals were obtained. This outcome is attributed to the rapid sulfur evaporation and the reduced probability of nucleation for growing single-crystal MoS₂.

To study the structural phase (semiconducting 2H or metallic 1T) of the as-grown MoS₂, Raman, photoluminescence (PL), and SHG spectroscopic analyses were carried out (Figure S9, Supporting Information). Figure S9a shows the Raman spectrum taken from a monolayer MoS₂ grown via Reactor Type 1, where only two main Raman peaks of the in-plane E^{1}_{2g} mode and the out-of-plane A_{1g} mode, but no additional Raman signals of the J_1 , J_2 , and J_3 originated from the 1T phase MoS₂, can be seen.^{57,58} This Raman feature indicates that the as-grown monolayer MoS₂ via Reactor Type 1 is semiconducting 2H phase. PL analysis in Figure S9b reveals that this monolayer MoS₂ is highly photoluminescent, with a PL energy of about 1.85 eV, which is consistent with a direct band gap structure of monolayer 2H phase MoS₂ (1.8-1.9 eV).^{1,2} SHG spectroscopy imaging can also be used to distinguish 2H and 1T phase in monolayer TMDs, because the inversion symmetry is broken in the 2H phase but present in the 1T phase.³¹ As expected, a strong SHG signal was observed over the entire monolayer MoS₂ (Figure S9c), further confirming the formation of 2H structural phase. In addition, we found that the MoS₂ samples grown using Reactor Type 2 behavior almost the same in Raman, PL, and SHG optical properties compared to the MoS₂ grown using Reactor Type 1 (Figures S9d-f). Taken together, the above analyses indicate that the space-confined SPS strategy favors the formation of high-quality, thermodynamically stable 2H phase MoS₂ single crystals.

As is known that the ability to control the physical properties of the as-grown MoS₂ layers via phase engineering is very important for next generation novel device applications,^{25,26,59} which has been so far realized by lithium intercalation,^{28,29,59} electron beam irradiation,⁶⁰ and plasmonic hot electrons⁵⁸. In particular, Chang et al. realized the selective synthesis of 2H- and 1T-phase MoS₂ monolayers at different annealing temperature by employing lithium molten salts (e.g. LiOH).²⁹ Building on this work, it is also possible for us to control the different phases of MoS₂ single

crystals by rapid thermal processing of a sandwich reactor with LiOH, S, and Mo films in a confined reaction space, which needs an in-depth study in the future. It is expected that 2H phase MoS₂ could be obtained at a relatively low temperature (≤ 750 °C), while a phase transition in MoS₂ from 2H to 1T by lithium intercalation will occur when the processing temperature is over 1000 °C, leading to the formation of 1T-phase MoS₂.

To further study the phase purity and crystal quality of the as-grown MoS₂ crystals, high-resolution transmission electron microscopy (HR-TEM) characterization was performed to obtain a direct observation of their atomic structures. Figure 2a shows a typical high-resolution TEM image of the as-grown MoS₂ single crystal with a schematic of the atomic positions, where the uniformly distributed bright spots correspond to Mo atoms but S atoms are not evident due to their smaller electron cross section.^{45,61} The lateral intensity profile along the green line in Figure 2a reveals a Mo-Mo (or S-S) bond distance of 3.13 Å for the MoS₂ crystals. One can also see that the as-grown MoS₂ has a hexagonal phase structure with measured lattice distances of 2.75 and 1.60 Å, which correspond to those of (100) and (110) planes of 2H-MoS₂ monolayers.⁶² Additionally, no obvious defects, such as dislocations, interstitials or vacancies, are observed over the whole sample region, demonstrating that the grown MoS₂ single crystals via all-solid state reaction method have very high 2H phase purity and crystallinity. The selected-area electron diffraction (SAED) pattern displayed in Figure 2b clearly shows a single set of diffraction peaks with the hexagonal symmetry, which is consistent with the result obtained from fast Fourier transform (FFT) pattern analysis (Figure S10, Supporting Information), further confirming that it is a single crystal with 2H phase structure in the as-grown sample. In addition, energy-dispersive X-ray spectrometry (EDS) and elemental mapping analyses were performed to identify the chemical composition and uniformity of the as-grown 2D crystals (Figure 2c), which reveals that the as-grown MoS₂ is only

composed of Mo and S with a Mo:S atomic ratio of about 1:2.03, without the presence of any other impurities, indicating that the as-grown 2H phase MoS₂ has good stoichiometry.

To improve the preparation of high-quality layered MoS₂, we will learn more about the single crystalline grain growth process. As has been mentioned above, monolayer and few-layer MoS₂ crystals grown using Reactor Type 2 were realized by direct sulfurization of solid-phase Mo film deposited on silicon substrate in a space-confined configuration, which is different from the generally accepted vapor-phase^{41,44,51,63} or solid-vapor phase⁵⁶ reaction mechanism for CVD growth of monolayer TMDs. To better understand its growth mechanism, the intermediate phases in quenched MoS₂ samples at the initial stage were analyzed via AFM and KPFM. Figures 3a₁-3d₁ show optical images of the triangular-shaped MoS₂ formed with four different degrees of sulfurization. Initially, small triangular-shaped MoS₂ grains are appreciated and nucleated from Mo film by sulfurization, leading to the formation of holes on silicon substrate, as shown in Figures 3a₂-3d₂. It is surprising that the hole is much deeper (in the range 8 nm to 25 nm) than the thickness of the Mo film (2 nm to 5 nm), indicating that a thick sulfur coating layer is deposited on the Mo film surface at the initial growth stage. As the sulfurization evolves over time, the depths and sizes of the holes continue to increase, resulting in larger single-crystal MoS₂. More interestingly, it is observed that the crystalline edges of MoS₂ grains in the hole are surrounded by a triangular border with a gradient thickness (increasing from the inner to the outer edge) approximately from 300 nm to 500 nm in width (see insets in Figures 3a₂-3d₂), which is consistent with a TEM observation of the crystal boundary (Figure S11, Supporting Information). We surmise that the gradual height changing profiles of the triangular ring that were observed are correlated with the in-plane “feedstock” condition of the sulfur source, where the inner edge provides more sulfur for single-crystal MoS₂ growth, which results in the surrounding ring edge being “etched away”.

From the corresponding KPFM imaging, as shown in Figures 3a₃-3d₃, the surface potential or the potential difference (ΔPD) between the as-grown MoS₂ and the substrate are also found to strongly depend on the sulfurization degree, namely, MoS₂ with the different degrees of sulfurization corresponds to different work functions. We find that the more the amount of MoS_x ($0 < x \leq 2$) (or the higher crystallinity), the larger the surface potential values for MoS₂ nucleations. The work function of MoS_x can be calculated using the following equations:⁶⁴

$$\phi_{MoS_2} = \phi_{tip} - e \cdot (CPD_{tip} - CPD_{MoS_2}), \quad (1)$$

$$\phi_{Substrate} = \phi_{tip} - e \cdot (CPD_{tip} - CPD_{Substrate}), \quad (2)$$

$$\phi_{MoS_2} = \phi_{Substrate} + e \cdot (CPD_{MoS_2} - CPD_{Substrate}) = \phi_{Substrate} + e \cdot \Delta PD, \quad (3)$$

where ϕ_{MoS_2} , ϕ_{tip} , and $\phi_{Substrate}$ represent the work functions of the MoS₂, Pt-Ir tip, and substrate; CPD_{MoS_2} , CPD_{tip} , and $CPD_{Substrate}$ are the corresponding surface potentials. From Eq. (3) and the above observed surface potential variation, we can conclude that the work function of MoS₂ increases with the increment (or decrement) in the sulfurization degree (or S-vacancy concentration). The work function of monolayer MoS₂ as a function of S-vacancy concentration has been further validated using *ab initio* calculations (Figure S12, Supporting Information). Consistent with the experimental results, the work function of monolayer MoS₂ decreases with S-vacancy concentration (Figure 3e).

Considering the above AFM and KPFM analyses, the growth of single-crystal MoS₂ under these conditions could be an all-solid-phase reaction, where the solid Mo film and solid S film served as reactants. We, therefore, propose a multistep growth model for monolayer MoS₂, depicted in Figure S13, based on the space-confined solid-phase sulfurization reaction mechanism (Figure 3f). The first step is physical adsorption of a thick layer of sulfur coating on the Mo-film-coated

substrate during the ramp up to the reaction temperature to provide the excess of sulfur precursor. The second step is the nucleation by sulfurization of Mo film, involving Mo-S bond formation, lattice reorganization, and triangular island formation. During the nucleation (second step) and epitaxial growth (third step) processes, the top cover in sandwich reactor plays important roles of 1) increasing the interaction between Mo and S atoms, and 2) physically confining the sulfur precursor in the spaces between the top structure and the bottom substrate to suppress the sulfur sublimation, thereby keeping the excessive amounts of sulfur, which are beneficial for the nucleation and epitaxial growth of MoS₂ (Figure 3f). However, for reactor design without the top cover (Figure 3f), it may lead to the reduced concentration of sulfur precursor and the decreased interaction between Mo and S atoms, thereby resulting in the formation of polycrystalline or amorphous MoS₂ films (Figure S8, Supporting Information). With the growth time increased (third step), the small-grain MoS₂ expands outward from the nucleation sites to form large crystals by in-plane diffusion of the Mo and S feedstocks from the surrounding Mo film/S coating. Different from conventional CVD growth, the Mo film not only serves as the local Mo source but also serves as the nucleation site for the in situ sulfurization, which determines the final MoS₂ growth position. Finally, the growth stops when the precursor sources, including Mo and S, are completely evaporated and exhausted.⁶⁵ The formation of isolated MoS₂ crystals but not continuous highly crystalline films is likely due to the multi nucleation, but no epitaxy to line up the crystals.

It is known that 2D materials show strong layer-thickness- and stacking-phase-dependent optical properties. Therefore, the as-grown monolayer and few-layer MoS₂ samples enables us to observe the unique layer-thickness- and stacking-phase-dependent nonlinear optical responses that have not been previously reported in mechanically exfoliated MoS₂ samples.⁶ Figure 4a shows a representative optical image of as-grown MoS₂ grains with different layer thicknesses transferred

onto a fused silica wafer. The number of atomic layers is first verified via AFM analysis (Figures S14a and S14b, Supporting Information), where the two triangular MoS₂ flakes, marked by dashed lines in red and blue, correspond to one atomic layer (monolayer sample) and roughly 10 monolayers (few-layer sample), respectively. Moreover, by combining the examination of the Raman frequency difference between the E_{2g}^1 (in-plane vibration) and A_{1g} (out-of-plane vibration) modes and the PL peak intensity, we further confirm their monolayer and few-layer characteristics (Figures S14c and S14d, Supporting Information). In addition, Raman and PL mappings are performed to examine the spatial uniformity. As shown in Figure 4b, the excellent uniformity of the Raman A_{1g} peak intensity mapping reflects the high degree of uniformity within both monolayer and few-layer MoS₂ samples. A similar degree of uniformity could also be observed from the PL mapping of the A^o exciton, as shown in Figure 4c. It should be noted that significant variations in PL intensity are observed close to the grain edges of few-layer MoS₂, indicating structural defects (e.g., sulfur vacancies)⁶⁶ or thickness variations at the edge regime. In general, all of the characterizations based on Raman and PL spectroscopy suggest the uniformity and high optical quality of the as-grown samples.

We next investigate more structural information about these samples using multimodal nonlinear microscopy, as described in the Experimental section.⁹ Figures 4d and 4e show the simultaneous SHG and SFG imaging of the same region shown in (a), including monolayer and few-layer (up to 10 layers) MoS₂ crystals. The contrasts of both SHG and SFG are similar, as both modalities are sensitive to the elements of second-order nonlinearity $\chi^{(2)}$. Features seen in the SHG image are reproduced in the SFG image. For example, both the SHG and SFG images for monolayer MoS₂ show a suppressed nonlinear optical signal intensity at the points indicated by three yellow arrows (Figures 4d and 4e), revealing its polycrystalline nature and opposite

orientation between adjacent grains (top inset in Figure 4e). The suppressed SHG and SFG at the grain boundaries is attributed to the destructive interference and annihilation of the nonlinear waves generated from the neighboring grains with opposite orientation.⁶⁷ These grain boundaries, however, cannot be identified using Raman and PL mapping or AFM (Figure S14a, Supporting Information), demonstrating the capability of direct visualization of the grain structures in MoS₂ via not only the SHG⁶⁷ but also the SFG imaging techniques.

Second-order optical nonlinearity, which is responsible for both SHG and SFG, is very sensitive to the thickness of TMDs due to their inversion symmetry variation. It is known that the lack of an inversion center in monolayer or few-layer TMD samples with an odd number of layers leads to strong second-order optical responses, while TMDs with an even number of layers produce no second-order signals.^{6,9} Here, the enhanced SHG and SFG signals from few-layer MoS₂ are observed, which are substantially more than a magnitude stronger than those from the monolayer MoS₂ (insets in Figures 4d and 4e). This is surprising, since one normally expects the intensities of nonlinear SHG and SFG signals to exponentially decrease with the number of layers.^{6,9} The stronger SHG and SFG responses in few-layer MoS₂ can be attributed to the absence of an inversion center, namely, the results of the AA (the in-plane Mo-S bond is the same for the adjacent layers) stacking configuration in this few-layer sample, which is different from the naturally few-layer MoS₂ with AB (the in-plane Mo-S bond is opposite for the adjacent layers) stacking. Quantitatively, similar to the artificially stacked TMD bilayers,⁶⁸ the SHG and SFG fields in the as-grown few-layer MoS₂ can be modeled as a coherent superposition of the SHG and SFG fields from the individual layers. Then, the SHG and SFG intensities in the AA stacking, few-layer MoS₂

$$\text{can be expressed as } I_{SHG}^n = \left| \sum_{k=1}^n \vec{E}_k(2\omega_{probe}) \right|^2 = n^2 I_{SHG}^1 \quad \text{and} \quad I_{SFG}^n = \left| \sum_{k=1}^n \vec{E}_k(\omega_{probe} + \omega_{pump}) \right|^2 = n^2 I_{SFG}^1,$$

where I_{SHG}^n , I_{SFG}^n , I_{SHG}^1 , I_{SFG}^1 , and n represent SHG and SFG intensities in few-layer MoS₂, SHG and SFG intensities in monolayer MoS₂, and layer number, respectively. However, both the measured SHG and SFG intensities were somewhat lower than the above model prediction, which might be due to the inconsideration of the propagating effects of electromagnetic waves through the MoS₂ layers and the substrate. In some cases, we also observed the growth of AB stacking, few-layer MoS₂, which is easily identified via SHG and SFG imaging (Figure S15, Supporting Information). Nonetheless, both SHG and SFG imaging are reliable in rapidly distinguishing the AA, AB, and even more complex stacking orders in the as-grown few-layer MoS₂.

Moreover, the crystal orientation of monolayer and few-layer MoS₂ crystals is investigated using polarization-resolved SHG and SFG. The incident laser beam is labeled with a green arrow (Figures 4d and 4e). The parallel polarization of SHG intensity is found to exhibit a six-fold rotational symmetry in both monolayer and few-layer MoS₂, which reflects the three-fold rotational symmetry of these crystals (Figure 4f).⁶ The orientation of each SHG intensity maximum (or minimum) pointed to the armchair (or zigzag) direction in monolayer and few-layer MoS₂ samples (Figure S16, Supporting Information).⁶⁹ Figure 4g presents a polar plot of SFG peak intensity from monolayer and few-layer MoS₂, where a clear, coherent, and six-fold symmetry is observed in both monolayer and few-layer regions. This result is consistent with SHG polarization dependence measurement, suggesting that SFG polarization can also be used to determine TMD structural symmetry.

Figures 4h and 4i compare the polar plots of the parallel polarization (h) SHG and (i) SFG peak position as a function of monolayer and few-layer MoS₂ rotation angle. Interestingly, the polarized SFG peak position also shows a characteristic six-fold pattern (Figure 4i), similar to that of SHG

and SFG intensity polarization dependence (Figure 4f and 4g). A similar phenomenon is also observed in the mechanically exfoliated few-layer MoS₂ samples (Figure S17, Supporting Information). In contrast, the peak position of polarized SHG emission is independent of crystal orientation (Figure 4h). By rotating the sample, the SFG peak position blue shifts and a minimum wavelength is obtained when the zigzag direction is parallel to the incident polarization. It then rapidly red shifts and reaches a constant position when the bisector of the triangular is roughly parallel to the incident polarization, which indicates that the SFG peak position is tunable and more sensitive to the MoS₂ zigzag configuration. Such tunability may arise from the selective absorption and coupling of fundamental beams with different wavelengths, demonstrating a new platform for frequency converters (or optical switches) based on 2D TMDs. To the best of our knowledge, this is the first observation that SFG (not only peak intensity but also peak position) polarization can also be established as a precise optical method of determining the orientation of crystallographic axes of TMDs.

In order to demonstrate the great potential of the as-grown SPS monolayer MoS₂ for use in logic and optoelectronic applications, we designed a programmable MoS₂-metal Schottky junction device by contact engineering via local ferroelectric domain patterning (Figure 5a). We deposited a thin layer ferroelectric polymer, Poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), on a MoS₂ device (Figure 5b), using its out of polarization to control the Fermi level in MoS₂, which in turn can modulate the contact potential between MoS₂ and the metal contact (Ti/Au). Figure 5c compares the source-drain current-voltage (I_{DS} - V_{DS}) of the sample (Figure 5b) in the initial unpoled state of PVDF-TrFE, and after poling the ferroelectric top-layer via a conductive AFM tip with either a positive (+10 V) or negative (-10 V) bias voltage, resulting in the polarization down (P_{down}) or polarization up (P_{up}) states, respectively. In Figure 5e, we poled the entire device area

with a tip bias of +10 V. Compared with the un-poled state (Figure 5d), the channel conduction increases significantly, as the P_{down} state accumulates electrons into MoS₂, raising the Fermi level of MoS₂ towards the conduction band edge. We then poled the two contact areas with -10 V tip bias, while keeping the ferroelectric polymer above the MoS₂ remaining in the P_{down} state (Figure 5f). Surprisingly, the two-point conduction decreases drastically, which is attributed to an enhanced contact potential between MoS₂ and metal electrodes. We have thus achieved a nonvolatile current switching ratio of approximately 150 between the P_{down} and P_{up} states of contact doping. In all three states, we observed linear, Ohmic $I_{\text{DS}}-V_{\text{DS}}$ characteristics, indicating the symmetric configuration of the MoS₂ device.

On the basis of the above experimental results, we created the monolayer MoS₂ heterojunction by asymmetric contact doping, poling the upper electrode to the P_{down} state and the lower electrode to the P_{up} state (Figure 5g inset). The device then exhibits a rectified $I_{\text{DS}}-V_{\text{DS}}$ relation with a forward to reverse current ratio in excess of approximately 20 at ± 0.3 V. The diode-like $I_{\text{DS}}-V_{\text{DS}}$ relationship can be well described by the thermionic emission model:⁷⁰

$$J_{\text{DS}} = J_0 \exp\left(\frac{qV_{\text{DS}}}{\eta k_B T}\right) \left[1 - \exp\left(-\frac{qV_{\text{DS}}}{k_B T}\right)\right], \quad (4)$$

where q is the electron charge, k_B is the Boltzmann constant, η is the ideality factor which is normally between 1 and 2, and J_0 is the saturation current density, given as

$$J_0 = A_{2D}^* T^{3/2} \exp\left(-\frac{q\phi_B^{\text{eff}}}{k_B T}\right) \quad (5)$$

with $A_{2D}^* = \left[\left(qm_c k_B^{3/2}\right) / \left(\pi\hbar^2\right)\right] \left(m_t^* / 2\pi\right)^{1/2}$, where A_{2D}^* is the 2D effective Richardson constant, m_c is the number of equivalent conduction band minima, m_t^* is the transverse electron effective

mass for MoS₂, and ϕ_B^{eff} is the effective Schottky barrier height. An ideality factor $\eta = 1.40$ at room temperature is extracted from Eq. (4). From Eq. (5), the Schottky barrier height ϕ_B^{eff} corresponding to the difference in Fermi level between the two poling states is obtained, approximately 530 meV, that is much larger than other 2D MoS₂-based homojunction devices.^{36,71}

More interestingly, if we reverse the poling configuration between two contacts, that is, poling the upper electrode to be P_{up} and the lower electrode to be P_{down} (Figure 5h), we observed a rectified I_{DS} - V_{DS} behavior with an opposite rectified polarity. We interpreted this phenomenon as the contact modulation. When one electrode is poled down, more electrons are doped into the Ti-MoS₂ contact which makes the contact to be an Ohmic type, while if the other electrode is configured to be P_{up} state, a depletion happened in the contact region, thus forming a Ti-MoS₂ (Metal-Semiconductor) Schottky junction. This mechanism naturally explains the rectified I_{DS} - V_{DS} behavior formation and its polarity reversal phenomenon after changing it from Ti-MoS₂ junction to MoS₂-Ti junction. This experiment provides an example for well-controlled, reconfigurable modulation of the contact type in 2D materials electronics through the ferroelectric domain patterning.³⁷ Overall, the successful creation of novel functional devices using the as-grown, high-quality single-crystalline MoS₂ will enable ultrathin, high-performance advanced electronics and optoelectronics.

CONCLUSIONS

In summary, we have demonstrated a facial single-step strategy for synthesizing high-quality monolayer and few-layer crystals of the transition-metal dichalcogenide MoS₂ by solid-phase sulfurization of Mo film in a 2D confined reaction space. Using this unique method, single-crystalline MoS₂ can be obtained without the added cost, time, and complexity (in precursor, process, and hardware designs) typically required for growth by chemical vapor deposition. We

followed evolution of MoS₂ crystal growth through imaging by atomic force microscopy and Kelvin-probe force microscopy and found an unusual dependence between sulfurization degree and surface morphology or potential, based on which an all-solid-phase synthesis mechanism was proposed. In addition, we examined the symmetry, grain boundary, and stacking orders of as-grown samples using second-harmonic generation and sum-frequency generation nonlinear optical imaging, and report for the first time that the dependence of the SFG peak intensity and position on optical polarization direction can be used for a reliable, simple, and noninvasive determination of crystal orientation. Moreover, monolayer SPS MoS₂-based ferroelectric programmable Schottky junction devices via local domain patterning were successfully fabricated, and shown to have excellent nonvolatile modulation characteristics, and thus demonstrating their high potential in 2D logic and optoelectronic applications. Our strategy might be universal and readily applicable to a large class of 2D TMD single crystals, which is a big step toward both fundamental research and practical applications in novel nanoelectronics and optoelectronics.

METHODS

MoS₂ single crystal growth. The growth of single-crystal MoS₂ was carried out using an rapid thermal processing (RTP) system (MTI, OTF-1200X-4-RTP) within a specially designed, sandwiched reactor with a sulfur plate and Mo film in a confined reaction space (Figure S1, Supporting Information). Two sandwich-structured reactors were designed and fabricated. [Reactor Type 1 (Figure S1a): A thick plate of sulfur (10 mm × 5 mm × 0.5 mm) (Aldrich, 99.998%) was deposited with a Mo film of approximately 3 nm by direct current (DC) magnetron sputtering using a Mo target at room temperature. The Mo-coated S plate was then embedded between two 300-nm-thick silicon substrates to form a substrate/Mo-S/substrate sandwiched structure. Reactor Type 2 (Figure S1b): both the top and bottom silicon substrates (area: ~1 cm²)

were deposited with Mo by DC sputtering to a thickness in the range 3 nm to 5 nm. Then, a sulfur plate approximately 0.5 mm was placed between two Mo-coated silicon substrates to form a substrate-Mo/S/Mo-substrate sandwiched structure.] The weight of the deposited Mo film was calculated to be $\sim 3 \mu\text{g}$, and the sulfur plate used was $\sim 50 \text{ mg}$. The sandwich-structure reactors were loaded into the central heating zone of an RTP system, and then the RTP tube was purged with Ar gas to remove the air from the tube. Next, the RTP tube was pumped down and maintained at approximately 2 Torr. The temperature of the RTP tube was rapidly increased from room temperature to $750 \text{ }^\circ\text{C}$ at a rate of $500 \text{ }^\circ\text{C min}^{-1}$, kept at $750 \text{ }^\circ\text{C}$ for 5 to 10 min, and then cooled down to room temperature. The growth temperature and time used in this work are comparable with those generally required for conventional CVD methods.^{41,55,72,73}

The fabrication of programmable monolayer MoS₂-metal heterojunctions. First, monolayer MoS₂ device with two-probe geometry was fabricated via standard photolithography and e-beam evaporation using the Ti/Au (5/50 nm) as the contacts. Second, a thin layer ferroelectric polymer, PVDF-TrFE with a thickness of approximately 20 nm, was coated on the monolayer MoS₂ device by horizontal Langmuir-Blodgett (LB) deposition technique.^{74,75} Finally, the ferroelectric domain patterns were written via the conductive AFM. Note that bipolar polarization patterns can be prepared on the sample with very stable polarization state up to 7 weeks, with no significant decay of polarization.⁷⁶

Micro-Raman and PL measurements. Raman and PL spectroscopy was performed in a micro-Raman spectrometer (InVia plus, Renishaw, Gloucestershire, UK) using a 50 \times objective lens. The excitation source used was an Ar⁺ laser with a wavelength of 514.5 nm, a power of approximately 1.5 mW, and a spot size of approximately $1 \mu\text{m}^2$.

Multiphoton nonlinear optical spectroscopy measurements. The nonlinear optical properties of as-grown MoS₂ samples were investigated using a previously described multiphoton nonlinear optical microscopy system.^{9,77} A commercial Ti:Sapphire femtosecond laser (MaiTai DeepSee HP, SpectraPhysics) (central wavelength: 800 nm, pulse duration: 100 fs, repetition: 80 MHz) in conjunction with a supercontinuum generator (SCG-800, Newport) provided two incident laser beams: pump light and probe light. The pump and probe laser beams were then focused collinearly onto the sample surfaces using a water-immersion objective lens. The multimodal nonlinear optical imaging signals were detected using multichannel photomultiplier tubes (PMTs) in the epi direction, while the nonlinear optical spectra were collected using a spectrometer in the forward direction. For polarization-dependent nonlinear optical spectral measurement, a polarizer was placed in front of a spectrometer and parallel to the polarization of the incident pump-probe beams. The angular dependence of the nonlinear optical signal was measured by rotating the samples with steps of 10 degrees.

AFM and KPFM measurements. The AFM and KPFM images were obtained using a Bruker Multimode 8 AFM system. An AFM tip (SCANASYST-AIR, Bruker Nano Inc., USA) was applied to probe the topography and thickness of the samples in the peak-force working mode, while the KPFM measurements were performed using a conductive tip (SCM-PIT, Bruker, USA) with a resonant frequency of 75 kHz, a lift height of 20 nm, and the AC bias of 0.5 V.

TEM measurements. The crystalline quality of as-grown MoS₂ crystals was evaluated using a transmission electron microscope (TEM, Tecnai Osiris S/TEM, FEI, USA) operated at acceleration voltage of 200 kV, equipped with a super-X windowless EDS detector.

Theoretical calculations. The first-principles calculations were performed using projected augmented wave (PAW)⁷⁸ method as implemented in Vienna ab initio Simulation Package

(VASP).⁷⁹ The cutoff energy for plane wave is selected to be 520 eV. A Γ -center $4\times 4\times 1$ Monkhorst-Pack⁸⁰ K-mesh is employed for Brillouin zone integration. Supercell method is used for the defects (S-vacancy). We first construct a monolayer MoS₂, periodic in-plane yet be separated by a vacuum layer along c direction. The S atoms are removed gradually and symmetrically above and below Mo layer. Since it has been shown that sulfur vacancies on MoS₂ tend to form line defect,⁸¹ we simply assume the vacancies form a row (Figure S12a). The ionic relaxation is performed in the presence of defects using quasi-Newton method, and the Hellmann-Feynman forces are converged to 0.005 eV/Å. In addition, for pure compound (monolayer Mo and monolayer MoS₂), the structure is fully optimized. The layer-averaged electrostatic potential, including both Hartree energy and Ewald energy, is illustrated in Figure S12b. Work function is computed by comparing the electrostatic potential of vacuum and the Fermi level, extracted from *ab-initio* (Figure S12c).

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ASSOCIATED CONTENT

Supporting Information available: The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>.

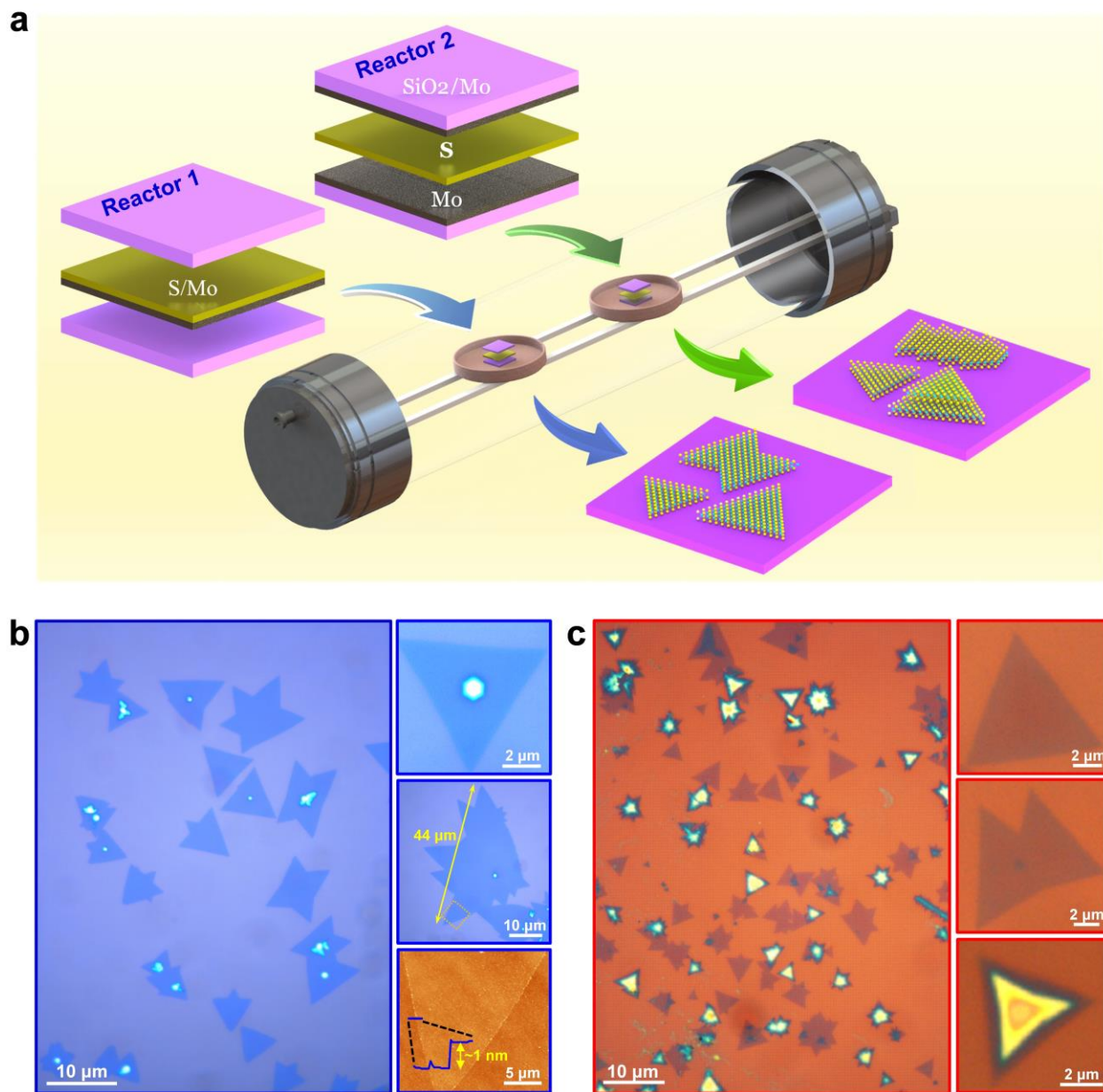


Figure 1. Growth of monolayer and few-layer MoS₂ single crystals through space-confined, solid-phase sulfurization strategy. (a) Schematic drawing of two sandwich-structured reactor configurations for space-confined solid-phase growth of highly crystalline MoS₂ atomic layers. Reactor Type 1: substrate/Mo-S/substrate. Reactor Type 2: substrate-Mo/S/Mo-substrate. (b) Typical examples of the as-grown monolayer MoS₂ grains via Reactor Type 1. Insets in (b): (top) zoomed-in optical image of a MoS₂ triangular flake with a symmetric six-lobe geometry nucleation site at the center, (middle) large-size MoS₂, and (bottom) corresponding AFM image with height profile demonstrating its monolayer characteristic. (c) Optical images of monolayer and few-layer

MoS₂ samples fabricated via Reactor Type 2. The insets in (c) are zoomed-in optical images of individual MoS₂ (top, middle) monolayers, and (bottom) few-layers.

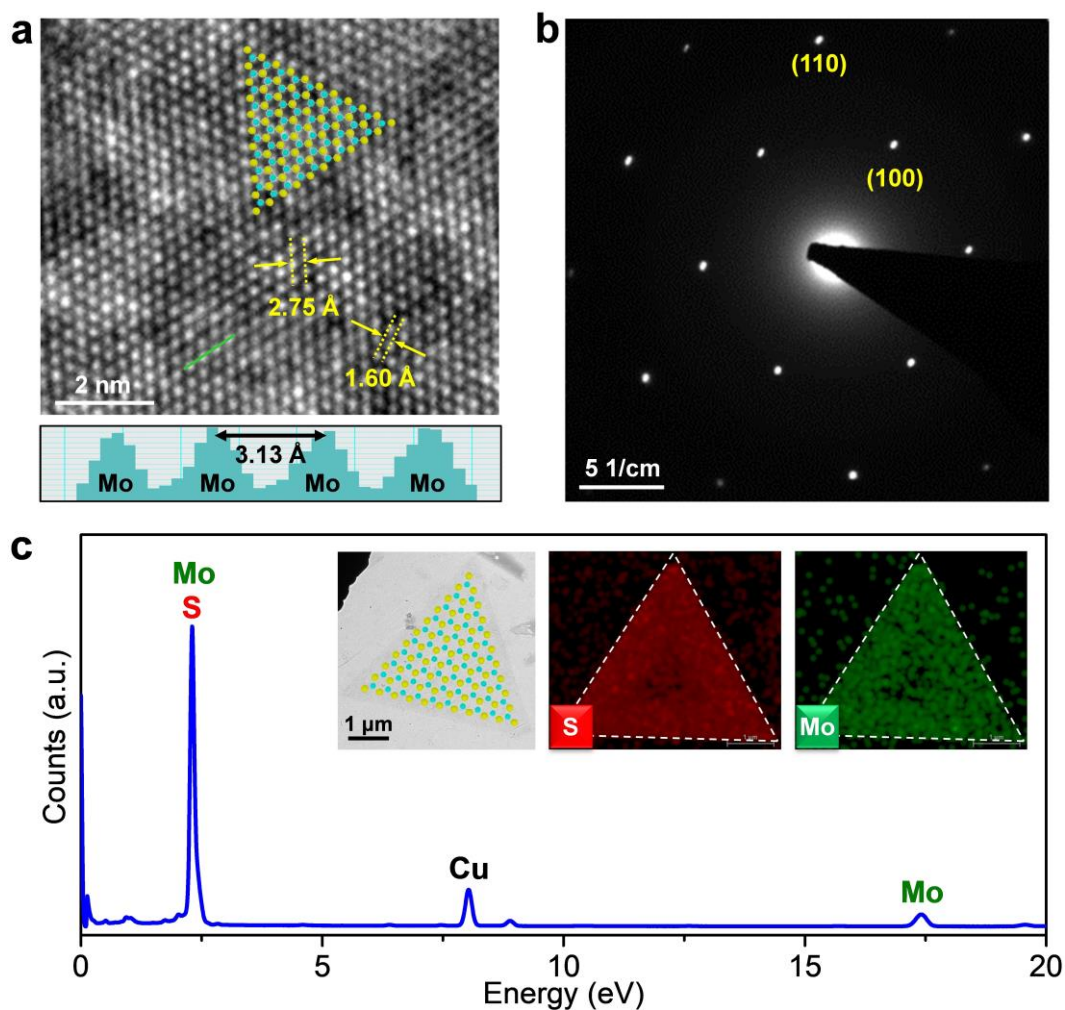


Figure 2. Structural and crystalline quality characterization of the as-grown single-crystal MoS₂ domains. (a) High-resolution TEM image of the as-grown MoS₂ single crystal with a schematic of the atomic positions, where the bright spots correspond to Mo atoms. Inset: cross-sectional intensity profile along the green line in (a). (b) SAED pattern of the as-grown MoS₂ single crystal, confirming the pure 2H phase structure. (c) EDS spectrum collected from the as-grown MoS₂ single crystal. Inset: low-resolution TEM image of the same sample and the corresponding elemental mapping of S (red) and Mo (green).

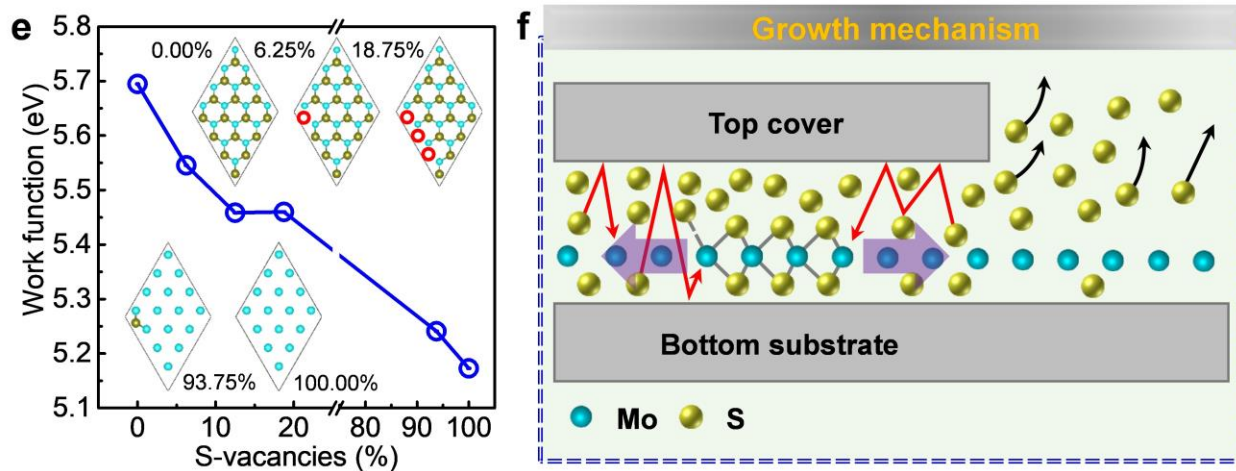
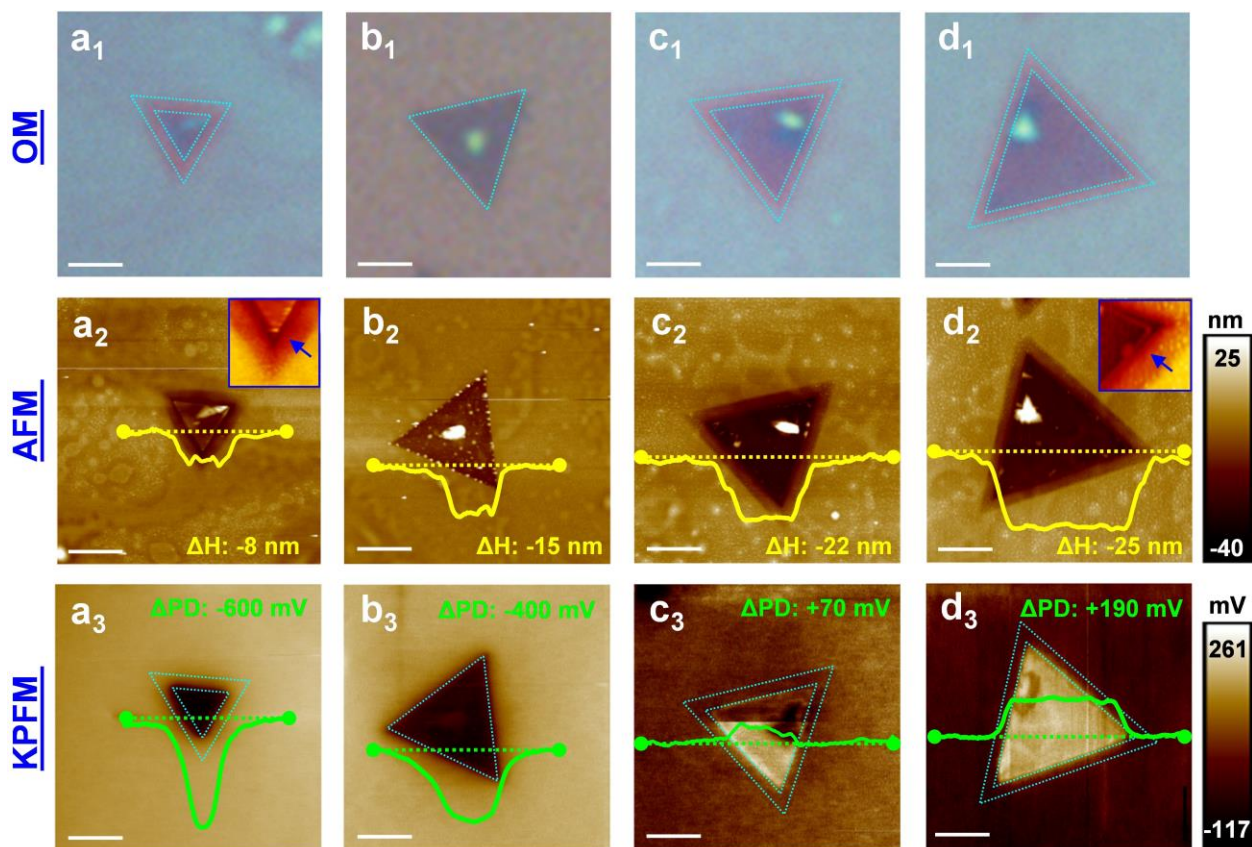


Figure 3. Solid-phase reaction growth mechanism of monolayer MoS₂ single crystal domains.

(a₁-d₁) Typical optical images showing the initial growth of triangular-shaped MoS₂ with different degrees of sulfurization. (a₂-d₂) AFM height topographies of corresponding samples in (a₁-d₁). Insets in (a₂-d₂) shows the height profiles along the yellow dashed lines. The top-right insets in (a₂,d₂) present the magnifying edge areas, where the as-grown MoS₂ grains are pointed by the blue arrows, and a broad transition area is clearly observed. (a₃-d₃) KPFM imaging of corresponding

samples in (a₁-d₁). Insets in (a₃-d₃) shows line-scan surface potential profiles along the green lines. Scale bars: 2 μm. (e) The work functions of monolayer MoS₂ with respect to the sulfur (S)-vacancy concentration. Inset: structural models for monolayer MoS₂ with different concentrations of S-vacancies. (f) Schematic illustration showing the proposed space-confined solid-phase sulfurization reaction mechanism. Red arrows represent sulfur atom rebound in the confined reaction space, black arrows indicate rapid sulfur evaporation without top cover, and broad purple arrows indicate lateral epitaxial growth in the confined region.

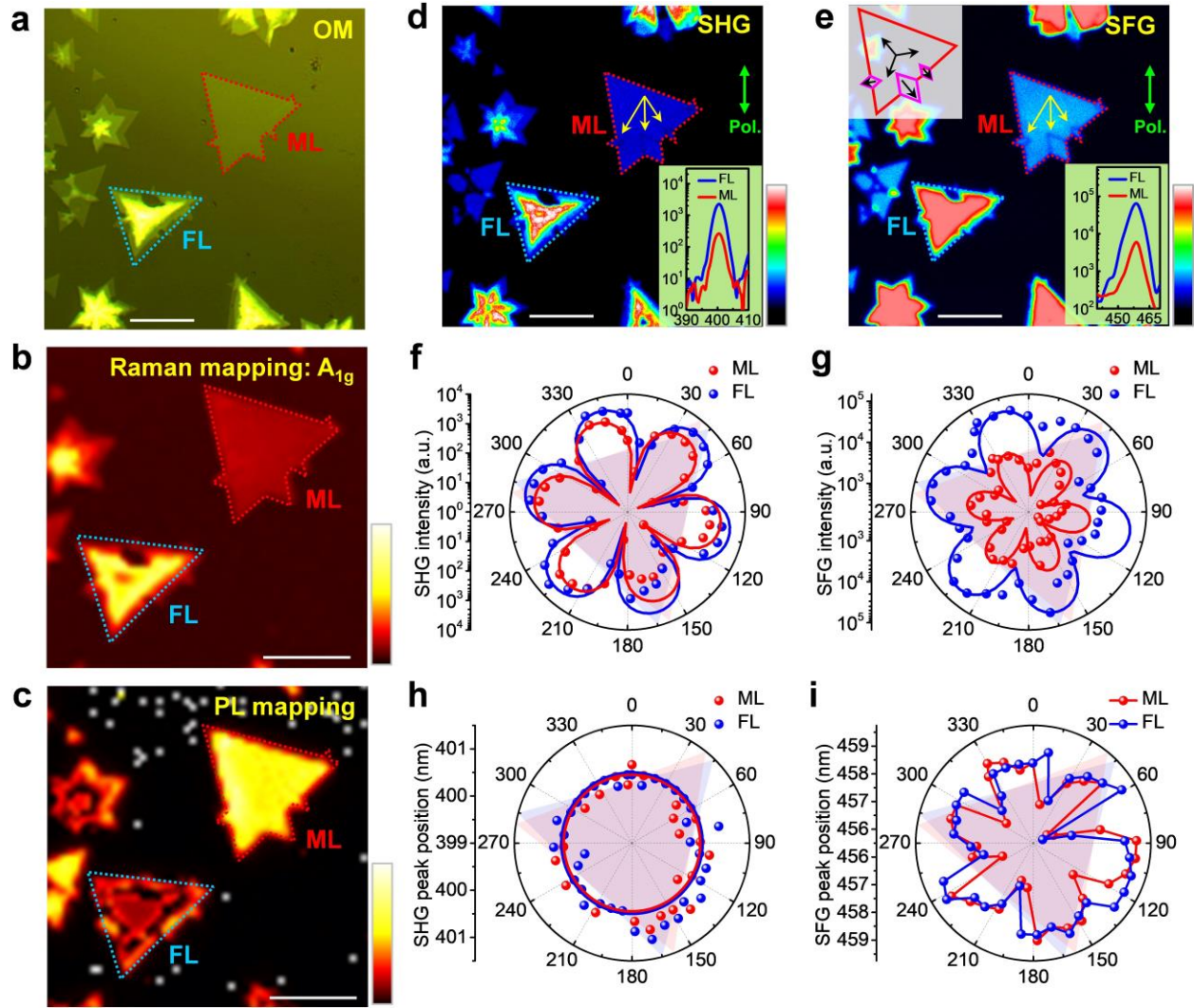


Figure 4. Optical quality evaluation of the as-grown SPS MoS₂ samples. (a) Optical image of the as-grown MoS₂ flakes with different layer thicknesses after transference onto fused silica. The dashed lines in red and blue depict the MoS₂ monolayer and few-layer, respectively. (b-e) (b) Raman intensity mapping of the A_{1g} band, (c) PL peak intensity mapping from the A⁰ exciton, (d) SHG imaging, and (e) SFG imaging of the as-grown monolayer and few-layer MoS₂ in the same area as shown in (a). The insets in (d,e) compare the nonlinear optical signals of (d) SHG and (e) SFG for the monolayer and few-layer MoS₂, where the red and blue curves refer to monolayer and few-layer MoS₂, respectively. (f,g) The polar plots of the parallel polarization (f) SHG and (g) SFG intensity as a function of monolayer and few-layer MoS₂ rotation angle. (h,i) The polar plots of the parallel polarization (h) SHG and (i) SFG peak position as a function of monolayer and few-layer MoS₂ rotation angle. Scale bars: 10 μm.

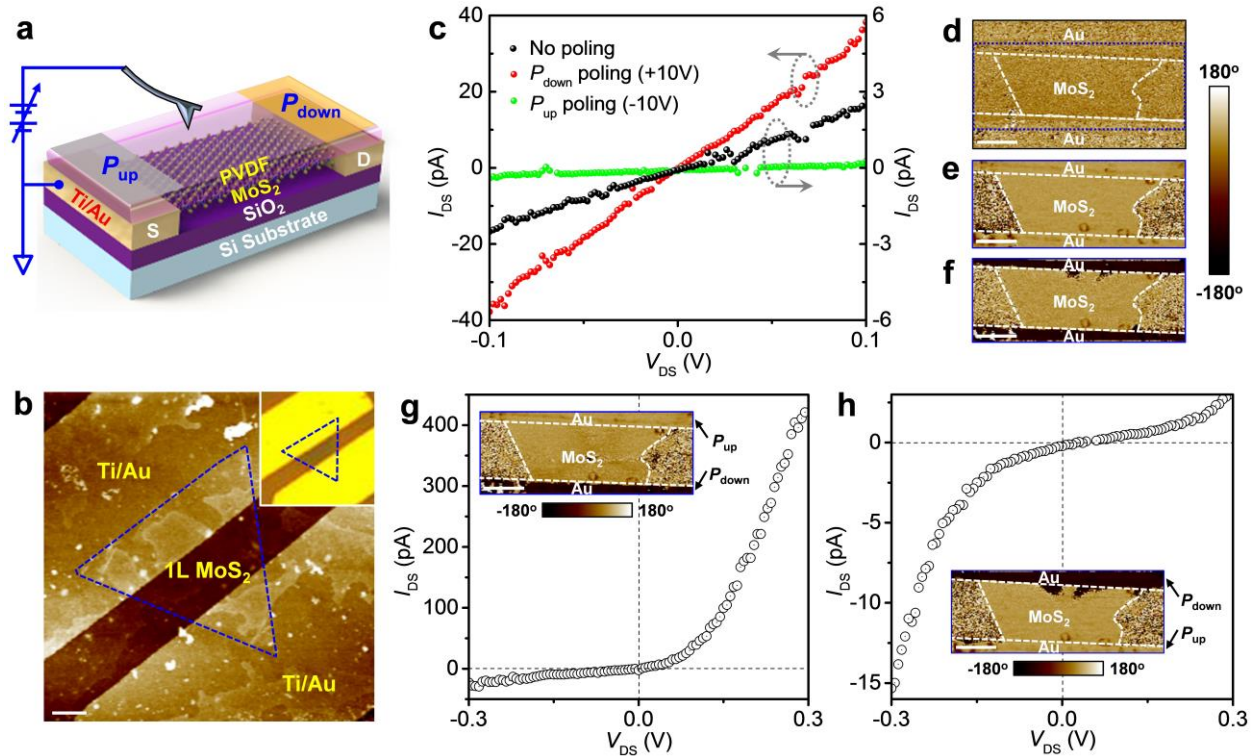


Figure 5. The fabrication and characterization of a programmable monolayer MoS₂-metal heterojunction via ferroelectric domain patterning. (a) Schematic of the MoS₂-metal heterojunction construction process. (b) AFM topography and optical image (inset) of a fabricated monolayer MoS₂ device with an ultrathin PVDF-TrFE top-layer. Scale bar: 1 μ m. (c) Typical room-temperature output characteristics for sample in (b) in the initial un-poled state (black), and after poling the ferroelectric top-layer via a conductive AFM tip with a bias voltage of +10 V (red) and -10 V (green). (d-f) The PFM phase images (d) in the initial state, and after poling with a tip bias of (e) +10 V and (f) -10 V. Scale bars: 1 μ m. (g,h) Room-temperature I_{DS} - V_{DS} characteristics of the same device at the (g) P_{down} (upper electrode)- P_{up} (lower electrode) state and (h) P_{up} (upper electrode)- P_{down} (lower electrode) state, respectively. Insets: PFM phase images. Scale bars: 1 μ m.

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