Morphology Control of Two-Dimensional Tin Disulfide on Transition Metal Dichalcogenides Using Chemical Vapor Deposition for Nanoelectronic Applications

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Abstract

Two-dimensional (2D) tin disulfide (SnS₂) crystals have been arousing immense attentions for flexible electronics and integrated circuits in next generation owing to their earth-abundant and non-toxic elemental components. Producing high quality crystal with controlled morphology, however, remains challenging due to the lack of understanding for its growth mechanism. Here, we demonstrate the direct chemical vapor deposition (CVD) growth and morphology control of 2D SnS₂ on CVD-grown WS₂ layers. In addition to the formation of type II van der Waals (vdW) vertical heterostructures with enhanced charge separation, the morphology of SnS₂ is found to be highly dependent on the underlying substrate surface, where

lateral growth could be stabilized with epitaxially aligned crystals on the defect-free surface whereas cluster growth appears on the defect-rich surface. This is attributed to the lower energy barrier of migration for adsorbed active species on the defect-free surface, resulting in facilitated surface diffusion compared to the defect-rich surface. The similar results also occur when switching the growth substrates to other 2D transition metal dichalcogenides such as MoS₂ layers, showing the importance of defect-free 2D substrates on the SnS₂ growth which is crucial for the applications in next-generation nanoelectronics such as photodetector or light emitting diode.

Introduction

The emergence of two-dimensional (2D) layered semiconductors has stimulated considerable interest for the future applications in flexible electronics and integrated circuits due to their extraordinary physical and electrical properties.¹⁻³ Assembly of these different 2D atomic crystals results in the formation of van der Waals (vdW) vertical heterostructures.⁴ This brings a series of fascinating physical properties including Klein tunneling,⁵ light-matter coupling,⁶ spin valley polarization,⁷ anti-ambipolar behavior,⁸ superior rectification ratio,⁹ tunable interlayer interaction,¹⁰ ultrafast charge transfer and efficient photocurrent generation.¹¹⁻¹² Some of which are even unable to obtain from the single component of 2D layered semiconductors. Additionally, the charge carrier mobility and energy band alignment of such heterostructures can be adjusted by altering different 2D materials components to meet various application requirements. The modulated electrical and optical properties by interlayer coupling are resulted from the effective charge transfer, which has a great potential in a variety of applications such as tunneling diodes,¹³⁻¹⁵ photodetectors,¹⁶ light emitting diodes,¹⁷ photovoltaic cells,¹⁸⁻¹⁹ and spin valleytronic devices.²⁰ For example, photodetectors based on

the SnSe₂/MoS₂ vdW heterostructure has been demonstrated with an enhanced photoresponsivity of up to 9100 A/W, which is higher by two orders of magnitude than those devices with single MoS₂ channels.²¹ Photovoltaic devices based on GaSe/MoSe₂, on the other hand, exhibit effective transport and separation of photogenerated charge carriers between individual layers.²² This strong interlayer coupling results in a gate tunable photovoltaic response with conversion efficiency of 0.3% and fill factor of 0.43, showing the promising features for the next generation 2D solar cell.

To construct the 2D vdW heterostructures, several approaches have been developed over the past few years. Multiple step layer-by-layer stacking using mechanical transfer techniques is the most common way to date due to its simple fabrication process.²³⁻²⁴ In spite of this, the lack of scalability and stacking orientation control restrict their applications and the unavoidable introduction of interfacial contamination is detrimental to the performance of the resulted devices. Direct chemical vapor deposition (CVD) growth strategy, in comparison, offers great advantages of size control and clean interface. It is therefore considered as a practical solution for the future large-scale industrial applications.²⁵⁻²⁷ Furthermore, compared to the vapor phase growth of conventional semiconductor-based heterojunctions, it is possible to build 2D vdW heterostructures without the restrictions of lattice-matching due to the lack of dangling bonds at the interfaces.²⁸

To dates, there are several reports demonstrating the successful CVD growth of vdW vertical heterostructures combining 2D layered semiconductors including WS₂/MoS₂,²⁹ MoS₂/WS₂,³⁰ MoS₂/WSe₂,³¹ WSe₂/MoSe₂,³² and ReS₂/WS₂.³³ Most of these 2D semiconductor components are Mo and W based chalcogenides, where their physical properties have been widely investigated in the past. In recent years, another metal chalcogenide with similar crystal structure to MoS₂ and WS₂, tin disulfide (SnS₂), has been widely exploited due to its earth-abundant and environmentally friendly and nontoxic constituents with prominent chemical

stability. In addition, the bandgap of SnS₂ is located in the green spectral region (2.2 eV), which is complementary to MoS₂ and WS₂ (1.8–2.0 eV) for the red light channel,³⁴ and could provide greater selectivity in wavelength for the future optoelectronic devices. The photoresponse performance of SnS₂-based devices has shown to be comparable to other 2D layered semiconductors such as MoS₂ and WS₂.^{35–37} However, in previous reports the CVD SnS₂ grown on commercial SiO₂ substrate exhibits high percentage of crystals with random growth directions or even stacked vertically without any order,^{38–39} which is detrimental for the device applications. The growth of single crystalline SnS₂ with well-defined shape still remains challenging.

In this study, we report the improved synthesis by switching the SnS₂ growth from SiO₂ to other 2D transition metal dichalcogenides such as WS₂ and MoS₂ via two-step CVD process. The atomically flat surface of WS₂ and MoS₂ enables the control of SnS₂ morphology from irregular shapes to truncated triangles or hexagons with well alignment. Another benefit for this is the realization of SnS₂-based heterostructures using direct growth method, which has great potential for the future device applications. The growth mechanism and the explanation of morphological difference were proposed. The morphology, crystal structure and chemical composition were also examined using scanning electron microscopy (SEM), Raman and PL spectroscopy analysis.

Results and discussion

Figure 1. Direct growth of SnS₂/WS₂ vertical vdW heterostructures via two-step CVD synthesis.

(a) Schematics of atomic configuration showing the two-step synthesis of SnS₂/WS₂ heterostructures. (b) Schematic illustration of the CVD experimental set-up for growing SnS₂ on WS₂ layers. (c) Optical image of CVD-grown monolayer WS₂ before the growth of SnS₂. (d) SEM image of showing the monolayer WS₂ triangle before the growth of SnS₂. (e) Optical image of the WS₂ after the growth of SnS₂ showing the growth preference of the SnS₂ growth on WS₂ surface rather than SiO₂. (f) SEM image of the monolayer WS₂ triangle after the growth of SnS₂ forming a vertical vdW heterostructure. (g) AFM image of the same heterostructure in (f) showing the thickness of the WS₂ triangle. (h) AFM image of the same heterostructure in (f) showing the thickness of the WS₂ triangle. (i) AFM height profile of the heterostructure in (f) showing the thickness of the WS₂ triangle. (j) AFM height profile of the heterostructure in (f) showing the thickness of the WS₂ triangle.

Zoomed-in AFM image of the blue dashed square in (g), showing the thickness of the as-grown SnS₂.
(i-j) Height profile of the WS₂ triangle and SnS₂ layers indicated by the dashed lines in (g) and (h).

Figure 1(a) schematically illustrates the growth of SnS₂/WS₂ vdW vertical heterostructure via a two-step strategy. The monolayer WS₂ was grown by CVD in the first step, the growth details and the analysis of the resulted WS₂ crystals are demonstrated in Figure S1. The schematic illustration in Figure 1(b) demonstrates the experimental setup for the second step CVD growth of SnS₂ with the pre-grown WS₂ placing on the ceramic crucible where the growth temperature is set to be around 450°C. The two furnaces are provided for the better control of temperature to generate the vapor of precursors. Sulfur and SnS precursors are placed in the center of furnace 1 and 2, respectively, while the pre-grown WS₂ is put at the downstream of furnace 2, around 6 cm away from the SnS powders. With a view to avoiding unnecessary reactions between two different precursors during the transport of vaporized atoms to the substrate, two concentric quartz tubes were used to separate the gaseous precursors before they reached to substrate surface.

To further elucidate the two-step CVD growth process, the characterization and comparison of WS₂ domains before and after the second step of SnS₂ growth is adopted. As demonstrated by optical and SEM image in Figure 1(c) and (d), the WS₂ grown in the first step is fairly uniform, over 90% of which are monolayer with a triangular shape and a typical lateral size of ~15 μm. After the second step of SnS₂ growth, shown in Figure 1(e) and (f), the WS₂ remains intact and the triangular domain is partially covered by SnS₂ with the domain size of ~10 μm. In addition, it can be seen that SnS₂ crystals are preferentially grown on the WS₂ surface rather than SiO₂/Si substrate, suggesting a strong selectivity for the growth. It is therefore manifested that the WS₂ layers could be superior templates for the growth of high quality SnS₂ layers when compared with the SiO₂/Si substrates, where in previous work pure SnS₂ layers synthesized by CVD tend to form thick multilayer and some of them are not flat.

The control of layer number uniformity for SnS₂ growth, however, still remains challenging. As shown in Figure 1(e), some of the SnS₂ layers display a monolayer to few-layer thickness with light blue color, while those yellowish SnS₂ crystals indicate thicker layers. The element analysis of thicker SnS₂ layers is shown in Figure S2. The corresponding AFM image of Figure 1(f) is demonstrated in Figure 1(g) with an enlarged AFM image (Figure 1(h)) showing the area marked by blue dashed square. The line profiles across different edges indicated by the dashed lines in Figure 1(g) and (h) are consequently measured, showing the details on layer number of both WS₂ and SnS₂. As shown in Figure 1(i), the step heights across the WS₂ and first triangular layer of SnS₂ edges are estimated to be 0.8 and 0.7 nm, respectively, suggesting a monolayer thickness. The hexagonal multilayer SnS₂ region (Figure 1(j)) is measured to be 7 nm, which is around 8 layers of SnS₂.

Figure 2. Optical characterization of the SnS₂/WS₂ vdW vertical heterostructure: (a) Optical image of the same heterostructure in Figure 1(g) showing the contrast between WS₂ and SnS₂ layers. (b) Raman spectrum of the SnS₂/WS₂ heterostructures, monolayer WS₂ and SnS₂ marked in (a). (c) PL spectrum of monolayer WS₂ and the SnS₂/WS₂ heterostructures marked in (a). (d) Raman spectrum of monolayer WS₂ with the Lorentzian fitting to extract E_{2g} and A_{1g} peaks. (e) Raman spectrum of monolayer SnS₂/WS₂ heterostructure (m-SWH) with the Lorentzian fitting to extract E_{2g} and A_{1g} peaks. (f) Raman spectrum of few-layer SnS₂/WS₂ heterostructure (f-SWH) with the Lorentzian fitting to extract E_{2g} and A_{1g} peaks. (g) PL mapping of the SnS₂/WS₂ heterostructure in (a). (h) PL spectrum of monolayer WS₂ with the Lorentzian fitting to extract exciton and trion. (i) PL spectrum of m-SWH with the Lorentzian fitting to extract exciton and trion. The scale bars in (a) and (g) are 5 μ m.

To further characterize the optical properties, the SnS₂/WS₂ heterostructures are employed by the Raman and PL analysis. Figure 2(a) shows the corresponding optical image of SnS₂/WS₂ heterostructure in Figure 1(f). Figure 2(b) demonstrated the Raman spectrum of the WS₂ monolayer and SnS₂/WS₂ heterostructures with different SnS₂ thickness, corresponding to the red, blue and green spots respectively in Figure 2(a). To compare with the SnS₂/WS₂ heterostructure, a 10 nm-thick SnS₂ crystal on SiO₂ was also measured as a reference, where the morphology and AFM measurement are evidenced in Figure S3. Using a Lorentz fitting, Raman signals for monolayer WS₂ (i) ranging from 280 to 380 cm⁻¹ can be deconvolved into five separated peaks shown in the Figure 2(d), two of which can be attributed to second longitudinal acoustic (2LA) vibration mode and in-plane (E_{2g}^1) vibrational mode located at ~351 and ~355 cm⁻¹, respectively. Another characteristic peak of monolayer WS₂ is the out-of-plane (A_{1g}) vibrational mode situated at ~418 cm⁻¹.⁴⁰ The Raman spectrum of SnS₂, in contrast, only shows one characteristic peak at ~314 cm⁻¹, corresponding to the out-of-plane (A_{1g}) vibrational mode.⁴¹ It can be seen that in Figure 2(b) the Raman signals of both monolayer SnS₂/WS₂ heterostructure (m-SWH, ii) and few-layer SnS₂/WS₂ heterostructure (f-SWH, iii) are roughly the superimposition of that in monolayer WS₂ and SnS₂ individually. The increase of A_{1g} peak intensity in the SnS₂/WS₂ heterostructures is likely due to a peak convolution between out-of-plane vibration modes of WS₂ and SnS₂. Similarly, Raman signals for both m-SWH and f-SWH ranging from 280 to 380 cm⁻¹, shown in Figure 2(e) and (f), can be deconvolved into six separated peaks including those WS₂ peaks and an additional characteristic A_{1g} peak from pristine SnS₂ by employing a Lorentz fitting. It is noted that the intensity of A_{1g} peak from SnS₂ decreases with the reducing layer thickness, the SnS₂ Raman signal in m-SWH therefore became difficult to detect.

The interaction of SnS₂ with WS₂ also affects the PL emission in their vdW heterostructure. As shown in Figure 2(c), the characteristic PL intensity is greatly quenched in

both m-SWH and f-SWH compared to that in monolayer WS₂. The PL mapping of the heterostructure in Figure 2(a) is demonstrated in Figure 2(g), showing the quenching area is on the entire SnS₂/WS₂ region. This is in great contrast with the pristine WS₂ before the SnS₂ growth where the PL mapping exhibits the emission homogeneity as demonstrated in Figure S1(f). This significant quenching may be attributed to the indirect bandgap of SnS₂ or the strong charge transfer at the interface of the heterostructure. To further analyze the interlayer interaction at the interface of the heterostructure, both the PL signal in monolayer WS₂ and SnS₂/WS₂ heterostructure were then deconvoluted into separate peaks by fitting two Lorentzian curves in the Figure 2(h) and (i). These two Lorentzian curves are attributed exciton (A) emission and trion (A⁻) emission. The corresponding photon energies for A and A⁻ in monolayer WS₂ are 1.951 eV and 1.974 eV, while those in the SnS₂/WS₂ heterostructure are 1.939 eV and 1.958 eV, respectively. The redshift of both exciton and trion peak in the heterostructure could stem from the tensile strain introduced from SnS₂. Because the lattice constant of monolayer WS₂ is 0.31 nm while that of the SnS₂ is 0.36 nm, this would introduce a tensile strain for monolayer WS₂ after the SnS₂ growth.⁴²⁻⁴³ The observed A⁻/A peak ratio of the heterostructure (Figure 2(i)) is much higher than that of the WS₂ monolayer (Figure 2(h)), indicating an efficient charge separation at the interface of the heterostructure after the excitation of photon. This charge transfer is the main reason of the PL emission quenching, where part of the charges in WS₂ layers transfer to the adjacent SnS₂ layers and reduce the excitonic emission. This is consistent with the inferred type II band offset according to previous density functional theory (DFT) calculation results.⁴⁴⁻⁴⁵ Besides, it is noted that the intensity of PL characteristic peak for monolayer WS₂ without the cover of SnS₂ in the heterostructure is still comparable to the pristine monolayer WS₂ and much larger than that of monolayer WS₂ with 5 min Sn doping shown in Figure S4, suggesting little substitution of Sn in the monolayer WS₂ after the SnS₂ growth for the synthesis of SnS₂/WS₂ heterostructure.

Figure 3. Surface-mediated growth and edge-mediated growth of SnS_2 on WS_2 monolayers: (a) Schematic illustrations explaining the growth mechanism and each step during the second step SnS_2 growth on the pre-grown monolayer WS_2 . (b) Low magnification SEM image demonstrating the growth of SnS_2 crystals on WS_2 monolayers under the 470°C growth temperature. (c) SEM image demonstrating the difference of SnS_2 growth mediated by the edge and surface of monolayer WS_2 . (d) Enlarged SEM image showing the detail on horizontal growth of SnS_2 on WS_2 surface. (e) SEM image

demonstrating the morphology of SnS₂ grown on the mirror tilt WS₂ domains. (f) Enlarged SEM image from the yellow dashed rectangular area in (e) showing the detail on cluster growth of SnS₂ on the domain boundary of WS₂. (g) SEM image showing the SnS₂ growth mediated by the edges of pre-grown WS₂. (h) Schematic illustration explaining the surface diffusion rate of adsorbed species on different types of surface during the growth of SnS₂. (i) Atomic configuration demonstrating the growth difference of SnS₂ grown on defect-rich and defect-free area in monolayer WS₂.

Figure 3(a) further explains the details on the growth of SnS₂ on the WS₂ monolayers, which involves several sequential steps. After convective and diffusive transport to the reaction zone, the precursor gas molecules firstly diffuse into the boundary layer near SiO₂ substrate and are adsorbed onto the substrate surface. Secondly, the adsorbed species often migrate some distance on the substrate through surface diffusion. After the migration of adsorbed species to the growth sites, the adsorbed species are incorporated into the crystal lattice and form chemical bonds through edge attachment. The adsorbed species, in addition, could also desorb from the substrate into the gas phase during these growth stages due to the high reaction temperature. When the temperature increases from 450°C to 470°C, the growth of SnS₂ becomes more reactive and could be both mediated by the surface and edges of WS₂ monolayers. The SEM images in Figure 3(b) and (c) demonstrates the morphological difference between SnS₂ grown on the WS₂ surface and the edge of WS₂. In addition, the growth preference of SnS₂ on WS₂ instead of adjacent SiO₂ remains and even occurs with the prolonged growth time (Figure S5), indicating that the growth of SnS₂ is highly substrate-dependent. The surface-mediated growth of SnS₂ shows a stable lateral growth resulting in crystalline hexagons (Figure 3(d)). In contrast, the edge-mediated growth of SnS₂ exhibits irregular shapes with a random growth direction (Figure 3(g)). The growth of SnS₂ on multiple monolayer WS₂ domains with domain boundaries between each other, shown in Figure 3(e), was also examined and displayed the similar morphological difference. The SEM image in Figure 3(f) shows the domain boundary

area marked by yellow dashed square in Figure 3(e). It can be seen that on domain boundaries on WS₂ the SnS₂ layers grow vertically in a random manner, which is similar to the edge-mediated growth. The vertical SnS₂ crystals on the WS₂ edges and domain boundaries were further characterized by Raman spectroscopy and both exhibited strong signals of the SnS₂ characteristic peaks (Figure S6), indicating the growth of thicker crystal.

The observed morphological difference of SnS₂ could be further explained by the different migration coefficient of adatoms on the WS₂ surface and edges, which leads to horizontal growth on WS₂ surface and cluster growth at the edge of WS₂. Unlike graphene and hBN, the vapor deposition growth of 2D layered SnS₂ is non-catalytic. Without the dominance of catalysts, the growth is subject to the influences of the interaction between the adsorbed adatoms and the substrate surface. For example, the initial nucleation bonding may affect the eventual morphology. The surface that is of abundant dangling bonds has higher chance to grow 3D structures. The surface diffusion of the adsorbed species could also play a vital role in determining the final crystal morphology. The surface diffusion coefficient D_{diff} can be expressed as

$$D_{diff} = A * \exp(-E_M/k_B T) \quad (1)$$

where the E_M is the energy barrier of migration for adsorbed species on the substrate surface, k_B is the Boltzmann constant and T is the temperature. The energy barrier of migration, which increases linearly with the number of surface dangling bonds, drastically affects the surface diffusion of the adsorbed species.⁴⁶ As shown in Figure 3(h), The atomically flat surface of WS₂ that is free of dangling bonds and defects could facilitate the surface diffusion with longer diffusion length of adsorbed species due to the lower E_M and higher D_{diff} . The adsorbed species on WS₂ surface therefore have much higher tendency to incorporate into the ideal growth sites with the lowest surface free energy. In contrast, the adsorbed species on the defective or

dangling-bond-rich surface such as WS₂ edges have slower surface diffusion rate and shorter diffusion length due to the higher E_M and lower D_{diff} . The domain boundaries of WS₂ consists of several pentagon-heptagon pairs,⁴⁷ where the unsaturated bonding would also affect the growth behavior of SnS₂. This results in the random nucleation or edge attachment forming irregular microstructures on defect-rich WS₂ edges and domain boundaries during the SnS₂ growth, while those on the defect-free WS₂ surface could show a well-defined hexagonal shape (Figure 3(i)). The large E_M and lower diffusion rate in WS₂ edges/domain boundaries could also promote the nucleation and lead to the thicker SnS₂ crystals. The SiO₂ substrates, likewise, are three-dimensionally bonded and have a high density of dangling bonds on the surfaces, causing a high energy barrier of migration for adsorbed species. This impedes the free migration of adsorbed species and the morphology of SnS₂ grown on SiO₂ often exhibits clusters or non-hexagon crystal shape.³⁵ The similar growth dependence on the substrate has also been observed in the case of other 2D materials such as NbS₂ and ReS₂,⁴⁸⁻⁵¹ which demonstrate the importance of substrate selection on the growth of 2D crystals with high quality. It is noted that some of the SnS₂ crystals could also grow in the out-of-plane direction on the WS₂ surface, which is indicated by the red dashed circle in Figure 3(e). This is ascribed to the high growth temperature of SnS₂, which could possibly introduce the local defects on the WS₂ surfaces.

Figure 4. Orientation relationship between the SnS₂ crystals and WS₂ monolayers: (a) Low magnification SEM displaying the orientation distribution of SnS₂ crystals within each monolayer WS₂. (b) Enlarged SEM image demonstrating the orientation preference of SnS₂ crystals within the same WS₂ domain. (c) Schematic illustration for the definition of the relative edge angle between the SnS₂ and WS₂ monolayers. (d) Statistical distribution of the relative edge angles of SnS₂ domains within WS₂ monolayers.

In addition to the microstructural difference for the SnS₂ growth, most of the SnS₂ crystals grown within WS₂ surface are well aligned in one orientation, which is demonstrated in Figure 4(a) and (b). The stacking angle between the WS₂ and SnS₂, illustrated in Figure 4(c), can be measured as the angle between the {11 $\bar{2}$ 0} plane of SnS₂ crystals and the {11 $\bar{2}$ 0} plane of WS₂ monolayers. Counting of ~1000 different SnS₂ crystals under the SEM yielded the stacking angle distribution shown in Figure 4(d), which revealed a preferred stacking angle of near 0°. This indicates the epitaxial relationship between the SnS₂ layers and WS₂ monolayers. In fact, the lattice constant of WS₂ and SnS₂ are 0.31 nm and 0.36 nm, respectively, and the calculated lattice mismatch is around 16.1%. Though the lattice mismatch between SnS₂ and WS₂ is larger than those epitaxial III-IV semiconductor heterostructures, it can be relaxed for

the growth of vdW heterostructures due to the weak interaction at the interface. The growth of SnS₂ on WS₂ is therefore attributed to the weak vdW interaction instead of chemical bonding, which is advantageous for the epitaxial growth due to the similar crystallographic order.

Figure 5. Direct CVD growth of SnS₂ on monolayer MoS₂ and the optical analysis of the SnS₂/MoS₂ vertical vdW heterostructures. (a) SEM image of as-grown MoS₂ showing the overall coverage before the SnS₂ growth. (b) SEM image of the monolayer MoS₂ showing the triangular star crystal shape with dendritic edges. (c) Low magnification SEM image of monolayer MoS₂ after the growth of SnS₂ layers. (d) SEM image showing the detail on horizontal growth of SnS₂ on MoS₂ surface. (e) SEM image of SnS₂ grown on the surface of SiO₂ showing the preference of growing in the out-of-plane directions. (f) SEM image showing the detail on cluster growth of SnS₂ on the edges of MoS₂. (g) Raman spectrum of the SnS₂/MoS₂ heterostructure, monolayer MoS₂ and SnS₂. (h) PL spectrum of monolayer MoS₂ and the SnS₂/MoS₂ heterostructure. (i) PL spectrum of monolayer MoS₂ with the

Lorentzian fitting to extract exciton and trion. (j) PL spectrum of SnS₂/MoS₂ heterostructure with the Lorentzian fitting to extract exciton and trion.

To confirm the morphological difference of SnS₂ resulted from the density of the surface defects, other 2D materials such as MoS₂ and hBN have also been adopted as the substrates for the SnS₂ growth. Figure 5(a) and (b) shows the morphology of CVD-grown monolayer MoS₂ prior to the growth of SnS₂. The details on the CVD MoS₂ growth are demonstrated in Figure S7. The growth of SnS₂ on monolayer MoS₂ in Figure 5(c-f) exhibits a similar trend to that on monolayer WS₂. Lateral growth of SnS₂ could be stabilized on the defect-free MoS₂ surface due to the smaller energy barrier of migration and larger diffusion coefficient (Figure 5(d)), while the cluster growth of SnS₂ is observed on the dangling-bond-rich SiO₂ surface (Figure 5(e)) and MoS₂ edges (Figure 5(f)). The Raman spectrum in Figure 5(g) displays both the characteristic signals of individual SnS₂ A_{1g} peak, MoS₂ E_{2g}^1 and A_{1g} peaks crystals in the SnS₂/MoS₂ heterostructure. There is no obvious peak shift of SnS₂/MoS₂ heterostructure compared to that of MoS₂, indicating that the MoS₂ monolayer remains high quality with little damage after the growth of SnS₂. The similar quenching of PL signals shown in Figure 5(h) in the SnS₂/MoS₂ heterostructure is attributed to the interlayer interaction and effective charge separation at the interface between MoS₂ and SnS₂. This is also evidenced by the increased intensity ratio of trion to exciton peak after the Lorentz fitting, demonstrated in Figure 5(i) and (j).

Likewise, the growth of SnS₂ on hBN through a two-step CVD strategy has also been investigated. In the first step, continuous monolayer hBN films were grown on oxidized Cu substrate adopting oxide-assisted CVD (OCVD) growth and using the ammonia borane as the growth precursor,⁵² followed by transfer from Cu surface to SiO₂ substrate (Figure S8(a-c)). In the second step, employing the as-grown hBN as the growth substrate, SnS₂ crystals were subsequently synthesized on continuous hBN film. The difference between growth behaviors

of SnS₂ crystals is demonstrated in Figure S8(d). The SnS₂ crystals grown on the hBN film exhibit a higher nucleation density, compared to those grown on the SiO₂, which may result from the higher roughness of transferred hBN film on SiO₂ due to the PMMA residual. Besides, it can be seen that SnS₂ crystals grown on hBN tend to exhibit more like trigonal and hexagonal shape (Figure S8(e) and (f)), while on SiO₂ surfaces SnS₂ crystals exhibit trapezoidal shape (Figure S8(g) and (h)). On the basis of these SnS₂ growth results in both transition metal dichalcogenides and hBN, it is inferred that the presence of a clean and continuous film of 2D materials without additional transfer process is beneficial for the growth of 2D crystalline SnS₂ as they are completely passivated without any dangling bonds at the atomically clean and ultra-smooth surface and could change the interface energy of SnS₂ and the growth substrate, therefore stabilizing the lateral growth of SnS₂.

Conclusion

In summary, we have successfully synthesized ultrathin SnS₂ crystals by employing 2D WS₂ triangles as the vdW growth substrates. The surface structure of underlying WS₂ layers is found to be critical in determining the growth behavior of SnS₂. During the growth stage, the atomically flat and inert surface of the WS₂ layers could lower the energy barrier of migration for adsorbed active species and accelerate the surface diffusion compared to the area nearby edges and domain boundaries, which are often with a high density of unsaturated dangling bonds. This results in SnS₂ growth well aligned to the WS₂ lattice and forms crystalline hexagons on the flat WS₂ surface whereas at the edge and domain boundaries of WS₂ the SnS₂ grows vertically in a random manner. The similar phenomenon is also observed on other 2D materials such as MoS₂ and hBN, proving the growth behavior is universal and implying the significance of employing substrates that are free from dangling bonds or defects for the SnS₂ growth. This enables the controllable synthesis of flat 2D SnS₂ with high quality, improving the applicability in future nanoelectronic applications.

Methods

CVD growth of WS₂ and MoS₂ monolayers

The CVD monolayer WS₂ and MoS₂ was grown on SiO₂ substrates based on our previously reported CVD approach.⁵³⁻⁵⁶ Before growth, the substrate was cleaned in acetone and isopropanol (IPA) for 10 min each, followed by a 5 min oxygen plasma treatment.

The CVD experimental setup for the WS₂ growth using S and WO₃ as precursors was demonstrated in Figure S1(a). 200 milligrams of sulfur powder was loaded at the center of furnace 1 in the outer 1 in. quartz tube, while 100 mg of WO₃ powder was placed at the center of furnace 2, in an inner quartz tube with a smaller diameter of 1 cm. The SiO₂ substrate was

then placed downstream in furnace 2, about 8.5 cm away from WO_3 powder. The growth system was first flushed with 500 sccm Ar for 30 min to drive off the oxygen, followed by a preintroduction of S by heating the S powder up to 180 °C to create a sulfur-rich environment. After which furnace 2 was ramped to 1050 °C and the reaction was then conducted under the temperature of 1150 °C for 3 min with H_2 gas flow of 25 sccm and Ar gas flow of 225 sccm. After that, furnace 2 was set down to room temperature with an Ar flow of 10 sccm, while furnace 1 was heated up to 400°C. The flow rate was set back to 500 sccm when furnace 2 reached 950 °C to purge the abundant S away from the system. Finally, the growth synthesis ended up with fast cooling process when furnace 2 decreased under 850 °C.

The CVD experimental setup for the MoS_2 growth was demonstrated in Figure S7(a). The growth occurred with the precursors of molybdenum trioxide and sulfur in APCVD using Ar as the carrier gas. 500 mg of S powder was loaded in the outer 1 in. quartz tube at the central area of furnace 1, while 20 mg of MoO_3 was placed in the inner quartz tube at the upstream of furnace 2, being around 12 cm away from its left opening. The substrate was placed vertically in the center of furnace 2. After the system was flushed for 60 min with argon, S vapor was preintroduced into the growth region for 15 min by heating furnace 1 to 180°C. Then the temperature of the second furnace was increased to ~800°C and kept for 15 min under 150 sccm argon flow, and at the same time, the location where MoO_3 powder was placed reached a temperature of around 300°C. Next, the argon flow rate was reduced to 10 sccm and maintained for 25 min, followed by a fast cooling process.

Direct growth of vertical SnS_2 on the surfaces of WS_2 and MoS_2

Employing the as-grown WS_2 and MoS_2 as templates, the SnS_2 was subsequently grown on top of these transition metal dichalcogenides using tin sulfide and sulfur as precursors. During the growth of SnS_2 , 100 mg of sulfur powders was loaded at the center of furnace 1 in

the outer 1 inch quartz tube, while 20 mg of tin sulfide (SnS) was placed at the center of furnace 2, in an inner tube with smaller diameter of 1 cm. The SiO₂ substrate was then placed downstream in the furnace 2, about 6 cm away from the SnS precursor. The CVD growth of SnS₂ was conducted at the atmospheric condition. After loading the precursors and growth substrate, the whole system was flushed with 500 sccm Ar gas for 30 min to remove the residual air and then the furnace 1 and 2 were raised to 160°C and 220°C respectively under the 70 sccm Ar flow to create a sulfur sufficient atmosphere. After introducing sulfur vapor for 15 min, the temperature of furnace 2 was increased to 550°C and the temperature of furnace 1 was increased to 180°C to conduct the SnS₂ growth. After 15 min growth, the Ar flow rate was first decreased to 10 sccm, enabling the S molecules in the outer tube to diffuse into the inner tube and sulphurizing the SnS powder to reduce the supplied amount of SnS gaseous precursor, followed by fast cooling process with 500 sccm Ar gas flow to remove the residual gas precursors and stop the reaction.

Characterization of SnS₂/WS₂ and SnS₂/MoS₂ vertical heterostructures

Scanning electron microscopy (SEM) was performed using a Hitachi-4300 FEG with an accelerating voltage of 3.0 kV. Raman spectroscopy was carried out using a JY Horiba LabRAM Aramis imaging confocal Raman microscope under an excitation wavelength of 532 nm at 12.5 mW power focused to a 1 μm spot size. For the PL measurement, the laser power was decreased to 125 μW for monolayer WS₂ and 1.25 mW for the heterostructures. Atomic force microscopy (AFM) was performed using an Asylum Research MFP-3D in AC mode with a silicon AC-160TS cantilever (Olympus, spring constant ~42 N/m and resonant frequency ~300 kHz). Measurements were all done in room-temperature under ambient pressure.

Associated content

Supporting information

Atmospheric pressure chemical vapor deposition (CVD) synthesis of WS₂ domains on the SiO₂ substrate, EDX elemental analysis of the multilayer SnS₂ in the SnS₂/WS₂ vertical van der Waals (vdW) heterostructure, characterization of the SnS₂ on SiO₂ substrate, comparison of PL characterization peak intensity between the pristine monolayer WS₂, monolayer WS₂ in the SnS₂/WS₂ heterostructure and Sn doped WS₂ monolayer obtained from 5 min Sn doping of WS₂ layers, growth of SnS₂/WS₂ heterostructures under 470°C with prolonged growth time: 30 min, Raman characterization of the vertical SnS₂ crystals on the WS₂, atmospheric pressure chemical vapor deposition (CVD) synthesis of MoS₂ domains on the SiO₂ substrate, CVD growth of SnS₂ on the transferred hBN layers.

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