Tin (II) selenide (SnSe) is an emerging 2D material with many intriguing properties, such as record-high thermoelectric figure of merit (ZT), purely in-plane ferroelectricity, and excellent nonlinear optical properties. To explore these functional properties and related applications, a crucial step is to develop controllable routes to synthesize large-area, ultrathin, and high-quality SnSe crystals. Physical vapor deposition (PVD) constitutes a reliable method to synthesize 2D SnSe, however, effects of various growth parameters have not yet been systematically investigated, and current PVD-synthesized flakes are often thick (>10 nm) with small lateral sizes (<10 µm). In this work, high-quality 2D SnSe crystals are synthesized via low-pressure PVD, which display in-plane ferroelectric domains observed by piezoresponse force microscopy and polarization-dependent reflection spectroscopy. Detailed studies regarding the roles of various parameters are further carried out, including substrate pre-annealing, growth duration, temperature, and pressure, which enable to rationally optimize the growth and obtain 2D SnSe crystals with lateral sizes up to ~23.0 µm and thicknesses down to ~2.0 nm (3–4 layers). This work paves the way for the controlled growth of large-area 2D SnSe, facilitating the future exploration of many interesting multiferroic properties and applications with atomic thickness.

1. Introduction

Tin (II) selenide (SnSe) is a member of group IV monochalcogenides (MX: M = germanium, tin; X = sulfur, selenium, tellurium), which is an emerging category of 2D materials with a puckered structure and distinct zigzag and armchair directions. In recent years, many fascinating properties of SnSe have been theoretically predicted and/or experimentally demonstrated. For example, SnSe is predicted as a high mobility 2D material and possesses a layer-dependent bandgap ranging from ~1.5 eV (monolayer) to ~0.9 eV (bulk) with strong optical absorbance, which endows it with excellent electronic and optoelectronic performances. The unique anisotropic structure of SnSe also gives rise to many attractive properties, such as an unprecedented thermoelectric figure of merit (ZT) of ~2.62 at 923 K along the b-axis (zigzag direction), large piezoelectric coefficients, and giant non-linear optical responses, which are expected to open up a variety of functional and multifunctional device applications including thermoelectric energy conversion, energy harvesting, and non-linear optics. Moreover, robust purely in-plane ferroelectricity has been observed in 2D SnSe as well as its SnS and SnTe counterparts even at monolayer thickness. The combination of semiconducting and ferroelectric features makes 2D SnSe a promising candidate for nanoscale ferroelectric devices such as non-volatile memory and nanoelectronics.
While there are rich opportunities of exploring intriguing properties of 2D SnSe and implementing it for various applications, a pivotal prerequisite is to obtain high-quality and ultrathin 2D SnSe crystals with large grain sizes that are suitable for device fabrication. To date, large-sized 2D SnSe has not yet been achieved by top-down exfoliation approaches, owing to a strong interlayer coupling resulted from the lone-pair electrons of Sn that prevents the effective mechanical exfoliation.\(^7\) and although ultrasonic and lithium-intercalation exfoliations in the liquid phase were able to overcome the interlayer binding energy and isolate ultrathin SnSe flakes, the resulted lateral sizes are usually very small (sub-micrometer).\(^{12,13}\) In this context, the bottom-up synthesis of 2D SnSe become more preferable, among which physical vapor deposition (PVD) stands out as a suitable method for obtaining high-quality, micrometer-scale, and stoichiometry-controlled SnSe flakes.\(^{14,15}\)

However, despite that several studies have successfully demonstrated the growth of SnSe crystals by PVD on various substrates, the obtained flakes are often thick (>10 nm) and/or with small lateral sizes (<10 \(\mu\)m).\(^{9,16}\) and the effects of various PVD parameters on the growth outcome are yet to be systematically studied and judiciously controlled.

In this work, we report the low-pressure PVD synthesis of high-quality 2D SnSe crystals with thinner thickness and larger lateral sizes. The as-synthesized SnSe displays high crystallinity and phase purity, as confirmed by Raman, X-ray photoemission spectroscopy (XPS), and scanning transmission electron microscopy (microscopy) (STEM). Intriguingly, in-plane ferroelectricity is observed in our 2D SnSe crystals, characterized by piezoresponse force microscopy (PFM) and polarization-dependent reflection spectroscopy. Moreover, we present a rational optimization of the PVD process by engineering the growth substrate and the mass transport of SnSe precursor through several key growth parameters, including mica substrate pre-annealing, growth duration, temperature, and pressure. Growth temperature and pressure are identified as crucial factors that affect the precursor evaporation, diffusion, and deposition processes and thus tune the ultimate size and thickness of SnSe crystals. Besides, it is found that the air-annealing of mica prior to the growth can lead to SnSe crystals with increased lateral sizes. Based on optimized growth parameters, we demonstrate that the growth at a relatively higher SnSe source temperature of 440 °C with a sufficiently long time can lead to large-sized flakes (>20 \(\mu\)m) with >5–8 \(\mu\)m thicknesses, while the growth at a reduced source temperature (370 °C) and higher reactor pressures enables ultrathin SnSe crystals with thicknesses down to 2.0 nm.

2. Results and Discussion

The PVD setup for synthesizing 2D SnSe crystals is schematically shown in Figure 1a. SnSe powders (5 g) were freshly ground using a mortar and pestle and placed in a crucible at the center of a single-zone tube furnace, and a piece of mica substrate was placed downstream (~10 cm away from SnSe powders). In order to promote the desorption of SnSe precursor and an effective mass transport to growth substrate, the PVD synthesis was carried out at low pressure with the base pressure as ~10 mTorr and the growth pressure <1 Torr. During the growth process, SnSe was evaporated in the hot zone of the furnace and deposited downstream onto mica under Ar/H\(_2\) flow. As a result of the temperature gradient along the

![Figure 1](https://www.advancedsciencenews.com/doi/abs/10.1002/aelm.202201031)

Figure 1. Low-pressure PVD synthesis and characterization of 2D SnSe. a) A schematic of the low-pressure PVD setup for synthesizing 2D SnSe crystals on mica. b) Typical low-magnification and c) high-magnification optical microscopy images of as-synthesized 2D SnSe with square-shaped morphology. d) AFM topography image and height profile of a typical SnSe crystal. e) Raman spectroscopy characterization of SnSe with different thicknesses. f,g) XPS characterization of 2D SnSe. Spectra of Sn 3d (f) and Se 3d (g) orbits are deconvoluted using three sets of doublet peaks and one set of doublet peaks, respectively.
flow direction, the morphology of as-synthesized SnSe varies at different locations along the mica substrate, and micrometer-sized 2D SnSe flakes are particularly observed at the region where the SnSe adsorption and desorption rates are balanced (Figure S1, Supporting Information). The yield, flake size, and thickness of deposited 2D SnSe could be further modulated by several parameters, including substrate pre-treatment, growth duration (t), furnace/SnSe source temperature (T), and growth pressure (P) that is adjusted by Ar flow rate, which will be discussed in later sections in detail. Figures 1b and c show typical low- and high-magnification optical images of as-synthesized SnSe flakes on mica (T = 440 °C, t = 45 min, Ar/H2 = 65/5 sccm), exhibiting square-shaped crystals with lateral sizes of ≈10–15 µm. The atomic force microscopy (AFM) measurement on a representative SnSe flake reveals a uniform thickness and flat surface with a thickness of 12.8 nm (Figure 1d).

Raman spectroscopy was performed to verify the formation of SnSe and examine its crystal quality (Figure 1e). Four clearly resolved peaks are observed in the spectra, which match well with frequencies of A₁g, B₁g, A₂g, and A₃g vibrational modes of orthorhombic SnSe.[9,10] PVD-synthesized SnSe flakes have different thicknesses, and thus we selected three flakes based on their optical contrasts on mica, namely thin (<5 nm), medium (~20 nm), and thick (>100 nm) flakes, to examine whether their characteristic vibrational modes vary as a function of thickness. In the Raman spectra shown in Figure 1e, it is observed that B₁g and A₂g modes blue-shift with the increase of thickness, while the A₃g mode redshifts. This result suggests that Raman spectroscopy may be utilized to rapidly characterize the thickness of 2D SnSe, and further work will be conducted to systematically study the layer thickness-dependent Raman response. We also performed Raman spectroscopy characterization on the continuous film regions located at downstream to investigate their phase evolution as a function of growth substrate location, and the results are shown in Figures S2 and S3 (Supporting Information). As shown in Figure S2 (Supporting Information), the as-grown SnSe film regions display a high phase-purity across >1.5 cm length along the flow direction. However, when the mica substrate was further placed toward downstream with lower temperature (~3 cm from the location of 2D SnSe flake growth), interestingly, we observed a large percentage of crystalline SnSeC (Figure S3, Supporting Information), which is also consistent with the previous work that utilizes a low substrate temperature for the PVD synthesis of SnSe. This suggests that controlling the substrate temperature may be the key to ensure the phase purity of the synthesized SnSe.

XPS was further carried out to investigate the chemical state and stoichiometry of Sn and Se in as-synthesized materials. Sn3d and Se3d core-level spectra were fitted by sets of doublet peaks and plotted in Figure 1f and g, respectively. Three sets of doublet peaks (representing Sn 3d₅/₂ and 3d₃/₂) are required to fit the Sn3d spectrum (Figure 1f). The peaks from higher to lower binding energies can be attributed to Sn⁴⁺, Sn⁴⁺, and Sn⁵⁺, respectively, and the set of peaks with the largest spectral weight is Sn⁵⁺, corresponding to SnSe. The observed Sn⁷⁺ and Sn⁵⁺ were likely resulted from the impurity in the precursor and/or by-products during the PVD synthesis that we discussed above, and thus these impurities were co-deposited on the mica surface with SnSe. The signal from these impurities, possibly Sn, SnO₂, or SnSe₂, was captured along with that of SnSe due to the relatively low spatial resolution (~200 µm) of XPS. In order to further evaluate the phase purity of our PVD grown SnSe crystals, we acquired the Raman spectra on 10 randomly selected flakes with varied thicknesses, and plotted them in Figure S4 (Supporting Information). No signatures of SnO₂ (B₁g mode at ~476 cm⁻¹)[11] or Sn (Raman peak at ~220 cm⁻¹)[12] was observed. This confirms that the suspected SnO₂ and Sn impurities observed in XPS are not originated from 2D SnSe flakes. However, a weak signal at ~185 cm⁻¹ was observed in some of the very thin SnSe flakes (<30 nm), which coincides with the B₁g mode of SnSe[13] and may suggest the presence of a small amount of SnSe₂ impurity.[14] In terms of the Se3d spectrum (Figure 1g), it can be well-fitted with a set of doublet peak representing Se 3d₅/₂ and 3d₃/₂. Quantitative analysis of the spectra reveals that the Sn/Se ratio is 0.99, which unambiguously indicates that the low-pressure PVD synthesis yields SnSe with a near-stoichiometric composition.

STEM characterization was carried out to reveal the structural information of 2D SnSe with nanometer-scale resolution. Figure 2a displays a low-magnification view annular dark-field (ADF)-STEM image of a 2D SnSe crystal transferred on a TEM grid. High-resolution ADF-STEM image was then acquired on the SnSe crystal, clearly showing the square-shaped lattice of SnSe (Figure 2b), and its corresponding fast Fourier transform (FFT) shown in the inset of Figure 2b exhibits a set of patterns with orthogonal symmetry, which further confirms the high crystallinity of our PVD-grown 2D orthorhombic SnSe crystals. Based on the measurement of FFT spots, lattice constants of SnSe were calculated as a = 4.454 ± 0.027 Å (armchair direction) and b = 4.282 ± 0.018 Å (zigzag direction). These results are comparable with the literature reports on orthorhombic SnSe.[15] PFM is widely used as a non-destructive technique for characterizing ferroelectric properties, and imaging ferroelectric domains of thin films by mapping the piezoelectric strain in the sample generated under AC bias.[16] To examine whether in-plane ferroelectric domains are present in our PVD-grown 2D SnSe flake, lateral PFM measurements were performed at room temperature on a representative flake (with a thickness of 12.0 nm; see Figure S5 (Supporting Information) for the optical image and AFM topography image of the corresponding flake). Figure 2c and d shows PFM amplitude and phase maps of the SnSe flake, and alternating bright and dark domains can be observed from both images, indicating that the local neighboring domains show different directions of spontaneous polarizations and respond different to the AC field in amplitude and phase. It is noted that the parallelly neighboring domains exhibit a 90° phase difference in the PFM phase map. Furthermore, in PFM amplitude and phase maps acquired in the SnSe flake rotated by 0° and 90°, respectively, it can be observed that the bright and dark domains still exist, with their relative intensities flipped (Figure S6, Supporting Information), which further indicate that the contrast in PFM images is due to the presence of 90° neighboring ferroelectric domains with in-plane direction. Polarization-dependent reflection spectroscopy was also employed to investigate the optical response of different domains in 2D SnSe. As shown in Figure 2e, a variation in reflection intensity is observed in 2D SnSe crystals when the incident polarization is along a diagonal line of SnSe, forming.

stripes of domains with different reflection contrast. Note that the region with low reflection intensity (displaying blue-colored intensity contrast in reflection images) is due to unintentional laser burning of the SnSe flake during sample measurements. When the incident polarization is rotated \( \pm 90^\circ \), the relative reflection intensities flipped in those domains (Figure 2f). This offers another clear evidence that our PVD-grown SnSe contains multiple in-plane ferroelectric domains with anisotropic reflection. We also performed polarization-dependent reflection spectroscopy characterization on several more SnSe flakes with domain sizes larger than the diffraction-limited resolution (\( >1 \mu m \) or more), and demonstrated that the in-plane ferroelectric domains did not accidentally occur (Figure S7, Supporting Information). It is noted that in our experiments, we found that many SnSe flakes with thicknesses of \( >10 \) nm exhibit ferroelectric domains. We think it is highly likely that since the 2D SnSe crystals were grown under non-equilibrium conditions, the metastable ferroelectric (AC) stacking could occur, considering its small energy difference with the stable antiferroelectric (AB) stacking.\(^{26,18}\) However, in much thicker SnSe flakes, ferroelectric domains were rarely observed. This thickness dependence of in-plane ferroelectricity is very similar to the case of the previously reported ferroelectric SnS grown by PVD.\(^ {29}\) We are currently using various other methods such as second harmonic generation spectroscopy, 4D-STEM, etc. to characterize and investigate the ferroelectric properties of our SnSe crystals, which reveal their fascinating characteristics, and these results will be reported in the future.

Aiming at optimizing the PVD growth and obtaining 2D SnSe with increased lateral sizes and reduced thicknesses, we further carried out a systematic study on how the growth result can be influenced by various growth parameters. Firstly, we investigated the pre-treatment of mica substrate toward improved growth. Muscovite mica (\( \text{KAl}_2\text{Si}_3\text{Al}_2\text{O}_{10}(\text{OH})_4 \)) has long been demonstrated as a suitable substrate for crystal growth due to the inert and dangling bond-free surface, and the matched symmetry with many types of materials, such as 2D MoS\(_2\), which enables epitaxy.\(^ {20}\) Freshly cleaved mica is used in most of the cases for the synthesis, however, since the residual K\(^+\) ions on the surface of as-cleaved mica has been shown to largely affect the crystal nucleation and growth,\(^ {23}\) we hypothesized that surface treatment of as-cleaved mica, such as thermal annealing, may alter the distribution of K\(^+\) ions on the surface and thus lead to SnSe synthesis modification. In this work, we annealed as-cleaved mica in air at 400 °C for 30 min prior to SnSe growth, and compared the morphology of obtained SnSe flakes with those grown on freshly cleaved mica under identical parameters (\( T = 440 \) °C, \( t = 30 \) min, \( Ar/H_2 = 65/5 \) sccm). Figure 3a and b display low- and high-magnification optical images of SnSe grown on annealed mica, showing a high density of square-shaped crystals with \( \approx 30 \) \( \mu m \) lateral sizes. The AFM image of a randomly selected flake confirms a flat surface and uniform thickness (\( \approx 6.6 \) nm) of SnSe on air-annealed mica (Figure 3c). As a comparison, low- and high-magnification optical images of SnSe grown on freshly cleaved mica surfaces are shown in Figure 3d and e. From the optical images, it can be found that the overall crystal sizes of SnSe on annealed mica are significantly larger than that on freshly cleaved mica. A statistical analysis of flake sizes is presented in the histogram in Figure 3f, further demonstrating that the average flake size of SnSe on annealed mica is \( \approx 40\% \) larger than SnSe on as-cleaved mica. Besides, based on the optical contrast analysis of flakes on annealed and freshly cleaved mica, no obvious thickness difference is observed between the two cases (Figure S8, Supporting Information; details of the SnSe thickness analysis method are shown in Experimental Section and the discussion of Figure 4f). To reveal the effect of air-annealing on the mica substrate, we first performed AFM topography measurements on freshly cleaved and annealed mica surfaces to examine whether the surface morphology is modified during annealing, such as changes in the step edge density or surface cleanliness. As shown in Figures S9a,b (Supporting Information),

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Figure 2. The structural, optical, and ferroelectric properties of 2D SnSe. a) Low-magnification ADF-STEM image of the 2D SnSe crystal. b) High-magnification ADF-STEM image of the 2D SnSe lattice. Inset: FFT of the STEM image with the spots labeled. c) Lateral PFM amplitude map of the 2D SnSe flake. d) Lateral PFM phase map of the 2D SnSe flake. e,f) Polarization-dependent reflection spectroscopy characterization of 2D SnSe (\( \pm 90^\circ \) polarization difference between (e) and (f)).
AFM topography images were acquired in 50 µm × 50 µm regions of both as-cleaved and annealed mica, and both surfaces exhibit flat morphology without significant step edges (an AFM topography image of a clearly resolved step edge is presented in Figure S10 (Supporting Information) as a reference), indicating a low step density on both substrates. Furthermore, AFM topography images of representative thin SnSe flakes also do not reveal the presence of step edges on the mica substrate under/near the SnSe flake region (Figures S9c,d, Supporting Information). Thus, these experimental results suggest that step edges are not responsible for the increased SnSe flake sizes on annealed mica. Besides, the calculation of root mean square roughness (R_q) of freshly cleaved and annealed mica based on Figures S9a,b (Supporting Information) yields comparable values of 0.124 nm and 0.139 nm, respectively, which is consistent with the previous result that mica is an ultraflat substrate with low surface roughness.[22] This result indicates that the surface roughness and cleanliness do not significantly change upon annealing.

XPS was also carried out to study and compare the surface chemistry of as-cleaved and annealed mica. XPS spectra of K 2p, O 1s, Al 2p, and Si 2p orbits (Figure S11, Supporting Information) show an n-type doping of mica surface, and quantitative XPS analysis indicates a reduction in the percentage of K atoms upon annealing (Table S1, Supporting Information), suggesting that residual K⁺ ions on the surface of as-cleaved mica surface may have been fully/partially removed during the air-annealing process. In a previous report by Stephens et al., it was found that K⁺ on the surface of air-cleaved mica can react with atmospheric CO₂ and H₂O to form K₂CO₃ nanocrystals, which serve as nucleation sites for the epitaxy of calcite crystals.[23] As a result, the increased SnSe crystal size on our air-annealed mica is likely to be related to the oxygen-assisted removal of surface K⁺ ions, which results in a reduction of heterogeneous nucleation sites and thus favors the lateral growth of SnSe (see the schematic illustration in Figure S12, Supporting Information). Our explanation is supported by previous results on the synthesis of many other 2D materials (e.g., graphene and transition metal dichalcogenides) with large grain sizes and improved uniformity, where similar ideas of using smooth substrates to suppress nucleation events have also been achieved.[24] In future work, more comprehensive characterizations of annealed mica are desired to further validate the proposed mechanism.

Next, we systematically studied effects of three growth parameters (i.e., growth duration, temperature, and growth pressure), which were quantitatively controlled during our synthesis process, on the resulting sizes and thicknesses of SnSe. In each case, a set of experiments was designed in a way that only the investigated parameter was tuned as variable with other growth parameters remained unchanged. To examine the effect of growth duration, the PVD was carried out for different growth time, with the furnace temperature at 440 °C and Ar/H₂ flow rates of 65/5 sccm. A full comparison of optical and AFM topography images of SnSe synthesized for 5–240 min is presented in Figure S13 (Supporting Information), and typical optical images of samples synthesized for 10 and 60 min are shown in Figure 4a,b for conciseness and clarity. It should be noted that high magnification optical images and AFM images shown in Figure S13 (Supporting Information) were captured on the SnSe flakes with maximum lateral sizes that were observed on the growth substrate. Optical images display a clear trend that the overall flake sizes increase as a function of growth time, and high-magnification optical images in

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**Figure 3.** Increasing the flake size of as-grown SnSe by pre-annealing the mica substrate. a,b) Representative low- and high-magnification optical images of 2D SnSe synthesized on the mica substrate that had been annealed in air at 400 °C for 30 min prior to the growth. c) AFM topography image and height profile of a typical SnSe crystal synthesized on annealed mica, displaying well-defined edges and a uniform thickness. d,e) Representative low- and high-magnification optical images of 2D SnSe synthesized on freshly cleaved mica using identical growth parameters. f) A histogram of the size distribution of SnSe flakes synthesized on freshly cleaved mica and annealed mica.
and a corresponding AFM topography image.

k) Optimized growth conditions for synthesizing large-sized SnSe crystals and a corresponding AFM topography image. A series of optical images of SnSe synthesized using 65/5 sccm (P = 340 mTorr) and 200/5 sccm (P = 755 mTorr) of Ar/H₂ carrier gas, respectively. i) Qualitative analysis of the thickness distribution of SnSe flakes synthesized at 370 and 440 °C, based on the relative R channel intensity in optical images of SnSe. g,h) Representative low- and high-magnification optical images of obtained SnSe as a function of growth duration. a,b) Representative low- and high-magnification optical images of 2D SnSe synthesized for 10 and 60 min, respectively. c) The maximum lateral sizes and lowest thicknesses of obtained SnSe as a function of growth duration. d,e) Representative low- and high-magnification optical images of 2D SnSe synthesized at 370 and 440 °C, respectively.

Figure S13 (Supporting Information) indicate that the obtained maximum flake size monotonously enlarges from 6.9 to 28.1 µm as the growth duration increases from 5 to 240 min. With increased growth time (e.g., 120 min and longer), SnSe flakes in the region with high nucleation density start to coalesce with each other, and as a result, large sized and isolated SnSe crystals are often found to be at the upstream of the high nucleation density region (Figure S14, Supporting Information). AFM was performed to investigate the growth duration-dependence of flake thicknesses (Figure S13, Supporting Information). Among measured SnSe flakes synthesized with different durations, the thinnest ones keep as ~5 nm within 120 min growth, while flake thickening occurs when the growth time further elongates (the thinnest flake grown for 240 min is ~8 nm). The obtained maximum lateral sizes and lowest thicknesses of SnSe are plotted as a function of growth time in Figure 4c. It should be also noted that the larger lateral size and lower thickness do not conflict, since we have observed that SnSe flakes with a larger lateral size are usually thin, and impressively, large and thin 2D SnSe (23.0 µm lateral size and 5.0 nm thickness) can be achieved in a 120 min growth (Figure 4j). The observed growth behavior may be resulted from the steady and adequate supply of SnSe precursors during the PVD process, as well as a strong interaction between vaporized SnSe and the atomically flat mica substrate that enables the continuous lateral growth of SnSe. With elongated growth time, it appears that SnSe flakes expand both vertically and laterally, and thus result in flake thickening at a later growth stage.

In above experiments with fixed growth temperature and pressure, it is found that the flakes remain ≥5 nm even in a very short growth period of 5 min, indicating that the thickness of flakes might have been determined during the nucleation stage. Then a follow-up question is whether the thickness of as-grown SnSe can be further reduced by tuning other parameters, including furnace temperature and growth pressure, which are likely to be important for the desorption/adsorption equilibrium of SnSe. To examine this, we first synthesized SnSe at a set of furnace temperatures (i.e., SnSe source temperature Tₛ), with other parameters remaining identical (t = 45 min, Ar/H₂ = 65/5 sccm). A series of optical images of SnSe synthesized at T = 370 °C – 470 °C are shown in Figure S15, and typical optical images of T = 370 °C (corresponding deposition temperature Tₛ = 270 °C) and T = 440 °C (corresponding Tₛ = 330 °C) samples are shown in Figure 4d,e for a clear

Figure 4. Effects of growth duration, temperature, and pressure on lateral size and thickness of obtained SnSe flakes. a,b) Representative low- and high-magnification optical images of 2D SnSe synthesized for 10 and 60 min, respectively. c) The maximum lateral sizes and lowest thicknesses of obtained SnSe as a function of growth duration. d,e) Representative low- and high-magnification optical images of 2D SnSe synthesized at 370 and 440 °C, respectively. f) Qualitative analysis of the thickness distribution of SnSe flakes synthesized at 370 and 440 °C, based on the relative R channel intensity in optical images of SnSe. g,h) Representative low- and high-magnification optical images of obtained SnSe as a function of growth duration. a,b) Representative low- and high-magnification optical images of 2D SnSe synthesized for 10 and 60 min, respectively.
comparison. From the optical images, it can already be clearly seen that the flake size displays a positive correlation with temperature, consistent with previous work.\textsuperscript{[9]} Regarding the thicknesses of SnSe flakes, it is observed in Figure 4d that many flakes grown at $T = 370 \degree C$ have low optical contrasts and become semi-transparent in the optical image, indicating a reduced thickness compared to flakes grown at $440 \degree C$, and further increasing the furnace temperature to $T = 470 \degree C$ leads to the growth of a high density of bulk SnSe with varied morphologies (e.g., crumpled, rolled-up, and folded SnSe crystals), as shown in Figures S16 and S17 (Supporting Information). Notably, most of the thin flakes grown at $T = 370 \degree C$ are with rounded edges or in rounded shape, and similar thickness-dependent shape variations have been observed in 2D SnS, where edges in ultrathin SnSe tend to reconstruct into microfacets, resulting in their rounded shapes.\textsuperscript{[24]} This constitutes another evidence that synthesis at lower temperatures can lead to reduced SnSe thickness. Furthermore, by analyzing the brightness of SnSe flakes relative to the bare mica background in optical images (see details in Experimental Section), we obtained the relative red (R), green (G), and blue (B) channel intensity values of various SnSe flakes synthesized at $T = 370$ and 440 $\degree C$, respectively. We then qualitatively studied the flake thicknesses by plotting their R channel intensity values in the histogram shown in Figure 4f. It should be noted that we expect that an identical trend would be observed if G or B channel intensity is plotted, because for SnSe flakes with different thicknesses, the relative intensities of their R, G, and B vary almost linearly, so the R channel intensity is a valid indicator for the flake thickness (more information can be found in Figure S18 (Supporting Information)). Since thinner flakes display lower RRGB intensities relative to the background, the corresponding data will appear on the left side of the histogram, and on the contrary, intensities of thicker flakes will be toward the right region. As a result, it can be well interpreted that the SnSe source temperature at 440 $\degree C$ yields to overall thicker flakes, while reducing the temperature to 370 $\degree C$ leads to the emergence of thinner SnSe. Similarly, the effect of growth pressure was evaluated by synthesizing SnSe at different system pressures that were adjusted by Ar flow, with other parameters remaining identical ($T = 370 \degree C$, $t = 4$ h; the growth time was elongated to increase the lateral size). Based on the SnSe flake contrast in optical images (Figures 4g-h; Figure S19, Supporting Information), it can be distinguished that a higher flow of Ar resulted higher pressure leads to smaller flakes, which is especially prominent when comparing SnSe synthesized under Ar/H$_2$ = 65/5 sccm (corresponding $P = 340$ mTorr) (Figure 4g) and 200/5 sccm (corresponding $P = 755$ mTorr) (Figure 4h). However, further increasing the flow rate of Ar above 300 sccm leads to drastically reduced yield and sizes of SnSe flakes (Figure S19, Supporting Information), indicating a significant reduction of deposition rate. This effect can be understood by the reduction of the mean free path (MFP) of evaporated SnSe precursor at a higher reactor pressure, which reduces the amount of precursor transported to the growth substrate and thus decreases the growth rate. A similar pressure-dependence of deposition rate has also been observed in the PVD of other non-2D materials.\textsuperscript{[25]} Using the image contrast analysis method that we have explained and applied earlier, the relative R channel intensity values of SnSe crystals grown at $P = 340$ and 755 mTorr, respectively, are compared in the histogram in Figure 4i. The results validate that a higher Ar flow and a higher growth pressure leads to a higher percentage of thin flakes. Based on the optimized temperature ($T = 370 \degree C$) and growth pressure ($P = 755$ m Torr, Ar/H$_2$ = 200/5 sccm) that are favorable for ultrathin SnSe growth, we further elongated the growth time to 8 h, attempting to further increase the lateral size of SnSe flakes. Under these optimized parameters, SnSe flakes with lateral sizes of 3–4 $\mu m$ and thicknesses down to 2.0 nm were obtained (Figure 4k). Currently, further characterization of these ultrathin SnSe flakes is hindered by the challenges of transferring them from mica substrates without damage (thicker flakes are much easier to be transferred), as well as preventing laser damage during optical measurements.

In order to perform more structural and ferroelectric property studies of these flakes, better transfer techniques for ultrathin SnSe and effective sample protection for optical studies need to be developed in the future.

Our optimized synthesis parameters and representative results, including larger flakes synthesized at a relatively higher temperature and lower pressure, and thinner flakes synthesized at a lower temperature and higher pressure, are demonstrated in the AFM images in Figures 4j,k. As a summary of our growth optimization, we compared the synthesis parameters and outcomes discussed in this manuscript with previously reported PVD-grown 2D SnSe,\textsuperscript{[9,26]} typical and parameters results of molecular beam epitaxy (MBE)-grown SnSe were also plotted as a reference (Figure S20, Supporting Information).\textsuperscript{[8b]} It can be found that our SnSe crystals are the thinnest among the reported ones grown by PVD, while the lateral sizes are 1–2 orders of magnitude larger than MBE-grown ones. We believe that two main reasons contribute to the growth of large-sized thin crystals in this work. Firstly, our developed air-annealing approach is likely to result in a decreased nucleation density of SnSe on the substrate surface, and thus the constant supply of precursor during PVD can continuously sustain the lateral expansion of SnSe and lead to enhanced crystal sizes. Secondly, as shown in Figures S20b–d (Supporting Information), when compared to previous reports, our parameters are located in a very different regime, where a lower SnSe source temperature, a lower growth pressure, and a significantly longer growth time are used during the PVD process. The temperature is rationally optimized and gives rise to a slower yet steady evaporation and deposition of the SnSe precursor over a longer period of growth time, while the reduced growth pressure ensures an adequate MFP of evaporated SnSe, further facilitating its diffusion and deposition. These factors may be helpful for maintaining the few-layered thickness of SnSe throughout the growth. Future work will be conducted along these directions to obtain ultrathin SnSe down to the monolayer limit.

3. Conclusion

We demonstrate in this work that low-pressure PVD is a powerful approach for synthesizing high crystallinity 2D SnSe that exhibit in-plane ferroelectricity. The influences of various factors during the PVD growth, including substrate pre-treatment, growth duration, temperature, and growth pressure, are...
systematically investigated, which improves our understanding of the relationship between these parameters and resulted flake sizes and thicknesses. The substrate annealing process and rationally engineered SnSe precursor supply result in the synthesis of 2D SnSe crystals with large lateral sizes and thinner thicknesses, more suitable for the study of 2D SnSe in the quantum limit. These large-sized and ultrathin SnSe may serve as an excellent platform for exploring their outstanding properties and applications that have been theoretically predicted, such as electronics, optoelectronics, non-linear optics, and energy harvesting.

4. Experimental Section

AFM: AFM measurement was performed on as-grown SnSe on mica by a Dimension 3100 scanning probe microscope from Veeco Instruments Inc.

Raman Spectroscopy: Raman spectroscopy characterization of 2D SnSe was carried out by a Horiba LabRAM HR800 confocal Raman system. The spectra were collected in ambient with a 532.5 nm laser excitation, using a backscattering configuration with an 1800 lines/mm grating.

XPS Measurement: XPS characterization was carried out on as-grown SnSe on mica using a PHI VersaProbe II XPS system with monochromated Al kω source (1486.6 eV). A beam size of 200 μm was used for spectra acquisition.

TEM Characterization: ADF-STEM images of 2D SnSe were collected using an FEI Titan aberration-corrected TEM operating at 300 kV at the electron microscope center in Rice University. A 25 mrad convergence angle and a ~40 mrad inner collection angle were applied.

Lateral PFM Measurement: The lateral PFM measurement was carried out on a commercial AFM system (Cypher VRS, Asylum Research). 2 V AC voltage was applied on the sample through a conductive tip (coated with Pt/Ir). The scanning angle of the tip was selected to be 90° to avoid any measurement artifacts.

Polarization-Dependent Reflection Spectroscopy: Reflection measurement was performed at room temperature with a Horiba XploRa system. A perpendicular incidence excitation with a linearly polarized tungsten-halogen white light source was used. The reflected light from the sample was collected by a 100x microscope objective, and then sent through a spectrometer with CCD camera to generate hyperspectral image of the sample.

SnSe Thickness Analysis via Optical Contrast: To qualitatively analyze the thickness of SnSe crystals resulted from growths at different furnace temperatures and pressures, the RGB intensities of each SnSe crystal and adjacent bare mica substrate in the optical images were obtained. Then the RGB intensities of mica substrates were subtracted from that of SnSe crystals, resulting in relative R, G, and B intensities that were used for plotting and visualizing SnSe thicknesses. For each set of growth parameters, 1-3 representative optical images were used for the optical contrast analysis, so that at least 30 SnSe crystals were analyzed in each case.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D materials, controlled growth, group-IV monochalcogenides, in-plane ferroelectricity, physical vapor deposition, substrate engineering

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