Supporting Information

2D to 3D Growth of Transition Metal Diselenides by Chemical Vapor Deposition: Interplay between Fractal, Dendritic and Compact Morphologies

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S1: PL Intensity Map

Figure S1 shows the PL intensity map across a monolayer MoSe$_2$ domain indicating the overall uniformity. A higher PL intensity at the edges could be due to different edge-termination and/or defects.\textsuperscript{1}

![Figure S1: (a) Optical image and (b) PL intensity mapping of an MoSe$_2$ domain.](image-url)
S2: Transition of Growth Mode – From Fractal to Compact Domain

The transition of the growth mode from fractal to the compact is further confirmed in Fig. S2. MoSe$_2$ growth at an intermediate temperature (800 °C) reveals a domain with a nearly hexagonal shape. Corresponding full width at the half maximum (FWHM), as calculated from Raman spectra and plotted in Fig. S2(d), confirm a gradual improvement in the material crystallinity as the growth temperature increases.$^2$

Figure S2: SEM micrographs (a-c) and FWHM as calculated from Raman spectra (d) showing the improvement of the crystallinity with increasing growth temperature.
S3: Preferred Growth Directions in a Branched Domain

 Preferential diffusion directions of adatoms, in addition to the edge attachment, results in accelerated growth in one preferred direction leading to dendritic structures.\textsuperscript{3,4} Figure S3 shows various needle-like growth of branched domains marked with the preferential directions that merge with the three crystallographic orientations of a hexagon. A slight variation in the shape of branched domains is also observed in Fig. S3. This variation depends largely on the local ratio of Mo and Se and may vary with the location of the substrate. Similar observation has also been made for MoS\textsubscript{2} growth.\textsuperscript{4,5}

Figure S3: SEM micrographs of different MoSe\textsubscript{2} branched domains following six-fold symmetry (a-d). Branching occurs only at an angle of 60° with respect to the central needle branch. Fractal dimensions as calculated from the branched domains are shown (e-g).
S4: Fractal Dimension Analysis of Fractal Domains

Figure S4 shows fractal dimension analysis of MoSe<sub>2</sub> domains grown at 750 °C. Corresponding SEM images are shown in insets (a-f). Figures (a)-(f) show corresponding SEM micrographs from six different locations on the MoSe<sub>2</sub> film moving downstream.

Figure S4: (a-f) Fractal dimensions as calculated from the MoSe<sub>2</sub> domains. Scale bars for all the images are 5 μm.
S5: Homogeneity of Different Growth Modes

(i) Compact Growth

Figure S5 (i) shows the homogeneity across a single batch for compact mode MoSe$_2$ grown at 900 °C. Domains are predominantly triangular and spread across a large region of the sample [Fig. S5 (i) (a)]. As we move downstream along the sample [Fig. S5 (i) (b-g)] the nucleation density decreases since the deposition area is further away from the metal-oxide precursor.

Figure S5 (i): (a) Optical microscopy image of compact-mode MoSe$_2$ monolayer domains grown on Si/SiO$_2$. Different locations are marked as (b) → (g). Corresponding SEM micrographs (b-g) show homogeneity in terms of shape and size. Scale bars for all the images are 50 μm.
(ii) Fractal Growth

Figure S5 (ii) shows the homogeneity across a single batch for fractal mode MoSe$_2$ grown at 750 °C. As shown in the SEM images [Fig. S5 (ii) (b-g)] the growth comprises of fractal domains only (zoomed in view of a domain from each zone is shown in inset). The nucleation density falls as we move downstream further away from the MoO$_3$ precursor as previously observed in case of the compact mode growth.

Figure S5 (ii): (a) Optical microscopy image of fractal-mode MoSe$_2$ monolayer domains grown on Si/SiO$_2$. Different locations are marked as (b) → (g). Corresponding SEM micrographs (b-g) show homogeneity of fractal mode growth. Scale bars for all the images are 50 µm.
(iii) Dendritic Growth

Figure S5 (iii) shows different areas from a sample grown in dendritic growth mode (at 900 °C and increased metal flux). Moving downstream along the sample, nature of the dendrites changes owing to the local variation in temperature and/or metal flux. From Fig. S5 (iii) (b-g), as the metal flux reduces, the growth rate slows down and the incoming adatoms have a higher tendency to rearrange themselves via edge diffusion. As a result, the domains approach a more compact structure (insets).

Figure S5 (iii): (a) Optical microscopy image of dendritic-mode MoSe$_2$ monolayer domains grown on Si/SiO$_2$. Different locations are marked as (b) → (g). Corresponding SEM micrographs are shown in (b-g). Scale bars for all the images are 50 μm.
S6: Reproducibility of Different Growth Modes

Figure S6 shows the reproducibility of the compact, fractal and dendritic modes of MoSe$_2$ growth. Three different batches are shown in each case. For the compact mode, growth-1 has a majority of hexagonal domains, while growth-2 and growth-3 are dominated by MoSe$_2$ triangles. The size distributions corresponding to each growth (insets) show majority of the domains fall within the 10 – 20 μm range, thereby reasserting the homogeneity of the growths. Three different batches of fractals and dendrites are shown in Fig. S6 (b) and (c), respectively. Although the growth mode remains the same for each case, depending on the local flux and/or temperature, a variation in the shapes/sizes/densities of compact/fractal/dendritic domains are observed (as also discussed in Sec. S5).

Figure S6: Reproducibility of different growth modes – (a) Compact, (b) Fractal, and (c) Dendritic. Insets in (a) show the size distributions of MoSe$_2$ compact domains.
S7: 3D Growth under Higher Temperature and Flux

Growth at 1000 °C with higher metal flux promotes growth of multilayer domain.

Figure S7: (a-b) AFM images and (c) corresponding height profiles from MoSe₂ samples grown at 1000 °C with higher metal flux.
**S8: Early-stage Growth – Variation with Temperature**

To understand the early stages of the growth we conducted 5 min growths at different temperatures. We observed that the domains assume a random shape in the 5 min growth [Fig. S8(a)] in contrast to the perfect hexagonal shape for a 10 min growth [Fig. 2(a)]. For the growth at 950 °C, the added thermal energy facilitates the reshaping of the adatoms and the domains become triangular in shape [Fig. S8(b)]. However, vertical growth is promoted at higher temperature, as evident from the corresponding SEM image in Fig. S8(b). For a 1000 °C growth, desorption of the adatoms becomes more prominent and domains decrease in size [Fig. S8(c)].

Figure S8: Optical (upper panel) and SEM (lower panel) micrographs from MoSe$_2$ growth for 5 min on Si/SiO$_2$ substrates at different temperatures – (a) 900 °C, (b) 950 °C, and (c) 1000 °C.
S9: Evolution of Morphology with Growth Duration

Figure S9 shows the MoSe$_2$ growth on Si/SiO$_2$ substrates at 900 °C for different growth durations. All other growth parameters including the Se flux were kept the same for all of them. As expected, the coverage increases with increasing growth time. With increasing growth time, an incomplete shape of MoSe$_2$ domain in Fig. S9(a) turns into a symmetry-driven hexagonal compact domain, in Fig. S9(b). As we keep growing [for example, 20 min in Fig. S9(c)] individual triangular and/or hexagonal MoSe$_2$ domains grow laterally and merge with the neighboring domains. This results in different types of grain boundary defects (e.g., mirror twins, tilt twins, etc.).$^7$ Presence of grain boundaries due to the merging of individual MoSe$_2$ domains are evident in Fig. S9(c).

Figure S9: Optical (upper panel) and SEM (lower panel) micrographs from MoSe$_2$ growth on Si/SiO$_2$ substrates at 900 °C for different growth time – (a) 5 min, (b) 10 min, and (c) 20 min.
Figure S10 shows how the domain sizes and nucleation density vary with growth at different combinations of temperature and flux. Under optimum temperature (900 °C) and metal flux, domains are compact ranging from 10-40 μm in size with the lowest nucleation density. For the growth at lower temperature (750 °C), domains are fractal. Although the domain sizes are comparable to the ones under optimal condition, the nucleation density increases due to decreased desorption at lower substrate temperature. With increase in the flux, the domains are bigger, but the growth mode transitions into the dendritic regime. Corresponding nucleation density also increases (from optimal condition) due to more availability of metal adatoms. For the growth at 1000 °C, as expected, the domain sizes reduce drastically due to higher desorption rate. Elevated temperature leads to more evaporation of metal (metal precursor being placed under the substrate, as shown in Fig. 1) that presumably increases the nucleation density. Under the higher flux condition at 1000 °C, metal-rich environment (higher metal flux) increases the nucleation density further (~20 times from the optimal growth).

Figure S10: (a) Domain size and (b) nucleation density under different growth conditions.
S11: Island Growth under Se-Deficient Condition

Figure S11 shows MoSe$_2$ growth at 750 °C on Si/SiO$_2$ substrates for lower Se flux. Se-deficient conditions were achieved by setting the Se temperature at 220 °C. As the Se temperature is well below than the optimal temperature (300 °C), we observe 3D growth promoted due to lower Se flux (Se-deficient condition). In addition, lower growth temperature results in fractal domains, as expected [similar to the growth shown in Fig. 2(c) and 2(d)].

Figure S11: 3D growth at 750 °C under lower Se flux.
S12: X-ray Photoelectron Spectroscopy Survey Scan

Figures S12 (a) and (b) show the XPS survey scans of the MoSe$_2$ and WSe$_2$ thin films, respectively. From XPS survey spectra all the major peaks are identified and labeled as Mo (W) and Se, and Si from the substrate. Presence of C and O in the survey spectra are likely due to adsorbed atmospheric molecular contamination from moving/storing the samples ex situ to the XPS system.$^9,10$ The underlying Si/SiO$_2$ substrates also contribute to the oxygen peak. The C-1s peak was used for the calibration of binding energy.

Figure S12: XPS survey spectra from (a) MoSe$_2$ and (b) WSe$_2$ grown on Si/SiO$_2$ substrates.
S13: Temperature Profile during Growth

Figures S13 shows the temperature program for the growth under Se-rich and Se-deficient conditions. Two heaters were used to separately control the temperatures of the substrate (as well as MoO$_3$ and WO$_3$ precursors) and Se source. For the Se-rich condition [as shown in Fig. S13 (a)], Se source was heated after the substrate reaches 550 °C, whereas, for the Se-deficient condition [as shown in Fig. S13 (b)], the Se source was heated after the substrate reaches 750 °C.

Figure S13: Temperature profile during MoSe$_2$ growth on Si/SiO$_2$ substrates for two different conditions – (a) Se-rich and (b) Se-deficient.
References


