Supporting Information

Two-Step Growth of Uniform Monolayer MoS\textsubscript{2} Nanosheets by Metal-Organic Chemical Vapor Deposition

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S1. MOCVD growth of continuous film of MoS$_2$ on Si/SiO$_2$ substrate

Figure S1 shows the atomic force microscopy image of as-grown MoS$_2$ grown via MOCVD. Growth at 850 °C for 1 min yields a continuous film grown on Si/SiO$_2$ substrate. The step was created intentionally by a tweezer scratch.

Figure S1: MOCVD growth of continuous film of MoS$_2$ on Si/SiO$_2$ substrate.
S2. Raman Spectra Comparison of MOCVD-grown MoS$_2$ and Bulk Exfoliated MoS$_2$

Figure S2 shows the Raman spectra comparison between MoS$_2$ grown via MOCVD to that of exfoliated monolayer flake from bulk samples. The peak intensities of the first order Raman modes for the as-grown film are much lower compared to bulk exfoliated, as seen in Fig. S2(a) which significantly improves after sulfurization [Fig. S2(b)]. The 2LA(M) peak that was absent in the as-grown film also appears post sulfurization. The full width at half maxima of the A$_{1g}$ Raman peak improves from 5.17 cm$^{-1}$ in case of as grown film to 4.23 cm$^{-1}$ after annealing in sulfur environment which is much closer to the value for exfoliated flake (3.51 cm$^{-1}$), as seen in Fig. S2(c).

Figure S2: Comparison of Raman spectra between monolayer exfoliated flake and MOCVD grown MoS$_2$ (a) as-grown film, and (b) following sulfurization at 850 °C for 30 min. (c) Improvement in A$_{1g}$ Raman peak full width at half maxima upon sulfurization.
S3. Raman Spectra Comparison of MOCVD-grown MoS\(_2\) Before and After Sulfurization

Raman spectra from the as-grown sample and the sample sulfurized at 850 °C for 30 min are compared in Fig. S3. Following sulfurization process, Raman peak intensities are greatly enhanced and linewidths of \(E_{12g}\) and \(A_{1g}\) Raman peaks are decreased indicating improved crystallinity.

![Raman Spectra Comparison](image)

Figure S3: Comparison of Raman spectra of MOCVD grown MoS\(_2\) film before and after sulfurization at 850 °C for 30 min.
**S4. Presence of Grain Boundaries in Sulfurized MOCVD Film**

Figure S4 shows grain boundaries in MoS$_2$ films after sulfurization at 850 °C for 30 min. Different types of grain boundaries (GBs), *e.g.*, mirror twins, tile twins, etc. are observed sporadically [as also observed in Fig. 2(h)]. Presence of GBs are also reported in APCVD grown MoS$_2$ $^{1-3}$. These grain boundaries may serve as sinks and sources for point defects and can adversely affect the mobility$^{2-4}$.

Figure S4: Different grain boundaries in sulfurized MoS$_2$ domains.
S5. Homogeneity of the Sulfurized MOCVD Film

Similar to the SEM studies the MOCVD film following sulfurization [as in Fig. 2(g)], Raman spectra at multiple points are shown in Fig. S5. Raman spectra corresponding to different points across the substrate match very well indicating homogeneous distribution of MoS$_2$ domains.

Figure S5: Raman spectra at different points across the substrate
S6. Variation of $E_{1g}^{1}$ Raman peak FWHM with Sulfurization Temperature

Figure S6 shows variation in the full width at half maximum (FWHM) of the $E_{1g}^{1}$ Raman peak with increased sulfurization temperature. As the sulfurization temperature increases, linewidth of the $E_{1g}^{1}$ peak decreases from 8.1 cm$^{-1}$ to 3.77 cm$^{-1}$. Inset shows corresponding Raman spectra showing the variation in normalized peak intensities and linewidth in the first order peaks.

![Graph showing variation of $E_{1g}^{1}$ Raman peak FWHM with sulfurization temperature](image)

Figure S6: Variation of $E_{1g}^{1}$ Raman peak for different sulfurization temperatures. Corresponding Raman spectra are shown in inset.
S7. Effect of Sulfurization Temperature on Morphology

Figure S7 shows the transformation of continuous MOCVD-grown MoS$_2$ film into monolayer domains upon sulfurization at various temperatures for a duration of 30 min. No significant improvement is observed optically as the film is sulfurized at 550 °C and 650 °C as seen in Fig. S7(a-b). However, for a sulfurization temperature of 750 °C, some indefinite patches of MoS$_2$ appear [Fig. S7(c)]. At 850 °C, sharp triangular domains of 1L MoS$_2$ are formed. [Fig. S7(d)].

Figure S7: Morphology evolution of MOCVD grown film with sulfurization temperature: Optical microscopy images following sulfurization at (a) 550 °C (b) 650 °C (c) 750 °C (d) 850 °C for a duration of 30 min.
**S8. Sulfurization of As-Grown MoS$_2$ Film at 950 °C for 30 min**

Figure S8 shows the Raman spectrum from MOCVD-grown MoS$_2$ film following sulfurization at 950 °C for 30 min. Sulfurization at higher temperature leads to patches of thicker MoS$_2$ distributed sparsely across the substrate (inset). A peak separation between the E$_{2g}^1$ and A$_{1g}$ is observed to be ~ 26.4 cm$^{-1}$ which corresponds to bulk MoS$_2$.

![Raman spectrum](image)

Figure S8: Sulfurization of As-Grown MoS$_2$ Film at 950 °C for 30 min.
S9. Effect of Sulfurization Duration on Morphology

Continuous as-grown film [Fig. S9(a)] gradually improves with sulfurization duration. No significant change is observed for the film sulfurized for 5 min [Fig. S9(b)]. However, the morphology evolves significantly with time and the film transforms into isolated monolayer triangular domains distributed uniformly across the entire substrate following sulfurization at 850 °C for 30 min [Fig. S9(c)].

Figure S9: Effect of sulfurization duration: (a) As-grown continuous MoS₂ film grown by MOCVD method. (b) No significant change is observed for the film sulfurized at 850 °C for 5 min. (c) Sulfurization for 30 min produces monolayer isolated MoS₂ triangular domains.
S10. Variation of PL FWHM with sulfurization duration

Figure S10 shows variation in the full width at half maximum (FWHM) of PL peaks for MoS$_2$ sulfurized at 850 °C for different durations. As observed, FWHM gradually improves with increasing sulfurization duration indicating improvement in crystallinity.

Figure S10: Variation of PL peak FWHM for different sulfurization durations.
S11. X-ray Photoelectron Spectroscopy Survey Scan

Figures S11 (a) and (b) show the XPS survey scans of the MOCVD-grown MoS$_2$ films before and after sulfurization process, respectively. From XPS survey spectra all the major peaks are identified and labeled as Mo and S, and Si from the substrate. Presence of C and O in the survey spectrum from the as-grown film is evident. In addition to the adsorbed atmospheric molecular contamination from moving/storing the samples ex situ to the XPS system$^{6,7}$ and underlying Si/SiO$_2$ substrates contributing to the oxygen peak, metal organic precursors contribute significantly to the carbon contamination of the grown film. After-growth sulfurization process at 850 $^\circ$C for 30 min proves to be an efficient way to suppress the contaminations to a great extent and hence, improving the overall film quality. Here, the C-C component at 284.8 eV belonging to the C-1s spectrum of adventitious carbon contamination is used as a charge referencing for all the XPS spectra. This method of using aliphatic carbon peak as charge correction reference may sometimes be unreliable since the nature and thickness of the film may vary. However, it can be a convenient method of referencing when relative peak shifts and not absolute peak positions are considered, as is the case here.
Figure S11: XPS survey spectra from MoS$_2$ film grown on Si/SiO$_2$ substrates by MOCVD process (a) before and (b) after sulfurization process.
S12. Improvement of MoS$_2$ Stoichiometry with Sulfurization Temperature

Figure S12 shows stoichiometries of as-grown MoS$_2$ film following sulfurization at different temperatures. The stoichiometry gradually improves with increasing sulfurization temperatures.

Figure S12: MoS$_2$ stoichiometries with sulfurization temperature
S13. Variation of Normalized MoO$_3$/MoS$_2$ Peak Ratios with Sulfurization Temperature

Figure S13 shows the comparison of MoO$_3$/MoS$_2$ peak intensity ratios for as-grown MoS$_2$ films before and after sulfurization at different temperatures. The ratio decreases with increasing sulfurization temperature.

![Normalized MoO$_3$/MoS$_2$ peak ratios for MoS$_2$ films sulfurized at different temperatures.](image)

Figure S13: Normalized MoO$_3$/MoS$_2$ peak ratios for MoS$_2$ films sulfurized at different temperatures.
S14. Electrical Properties of Back-gated FETs Fabricated on As-Grown MOCVD MoS$_2$

Figure S14 shows the electrical properties of MOCVD-grown film before sulfurization. Back-gated FETs fabricated on as-grown film shows no apparent gate modulation as evident from the near-constant drain and source current for a -60 V to +60 V back-gate voltage change, shown in Fig. S14(a). The gate leakage current ($I_{BG}$) is at least four orders of magnitude lower than the drain/source current and the drain current ($I_D$) is nearly equal to the source current ($I_S$). The output characteristics reach a drain current of 200 nA/μm at a drain voltage of 4 V, again with no gate effect as seen from the overlapping currents for varying gate voltages ($V_{BG}$) in the range of 20 V to 60 V with an increment of 10 V. The absence of gate modulation has also been observed in other MOCVD-grown TMDs$^8$ and may be attributed to the predominance of localized charge-carrier states arising from the defects and grain boundaries in the grown film$^4$.

![Figure S14](image-url)

Figure S14: (a) Transfer and (b) output characteristics for as-grown MOCVD MoS$_2$-based transistor with a channel length 500 nm.
References

(1) Roy, A.; Ghosh, R.; Rai, A.; Sanne, A.; Kim, K.; Movva, H. C. P.; Dey, R.; Pramanik, T.; Chowdhury, S.; Tutuc, E.; Banerjee, S. K. Intra-Domain Periodic Defects in Monolayer MoS$_2$. Appl. Phys. Lett. **2017**, *110* (20), 201905. https://doi.org/10.1063/1.4983789.

(2) Giannazzo, F.; Bosi, M.; Fabbri, F.; Schilirò, E.; Greco, G.; Roccaforte, F. Direct Probing of Grain Boundary Resistance in Chemical Vapor Deposition-Grown Monolayer MoS$_2$ by Conductive Atomic Force Microscopy. Phys. Status Solidi RRL – Rapid Res. Lett. **2020**, *14* (2), 1900393. https://doi.org/10.1002/pssr.201900393.

(3) Ly, T. H.; Perello, D. J.; Zhao, J.; Deng, Q.; Kim, H.; Han, G. H.; Chae, S. H.; Jeong, H. Y.; Lee, Y. H. Misorientation-Angle-Dependent Electrical Transport across Molybdenum Disulfide Grain Boundaries. Nat. Commun. **2016**, *7* (1), 10426. https://doi.org/10.1038/ncomms10426.

(4) Roy, A.; Movva, H. C. P.; Satpati, B.; Kim, K.; Dey, R.; Rai, A.; Pramanik, T.; Guchhait, S.; Tutuc, E.; Banerjee, S. K. Structural and Electrical Properties of MoTe$_2$ and MoSe$_2$ Grown by Molecular Beam Epitaxy. ACS Appl. Mater. Interfaces **2016**, *8* (11), 7396–7402. https://doi.org/10.1021/acsami.6b00961.

(5) Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS$_2$: Evolution of Raman Scattering. Adv. Funct. Mater. **2012**, *22* (7), 1385–1390. https://doi.org/10.1002/adfm.201102111.

(6) Barr, T. L.; Seal, S. Nature of the Use of Adventitious Carbon as a Binding Energy Standard. J. Vac. Sci. Technol. A **1995**, *13* (3), 1239–1246. https://doi.org/10.1116/1.579868.

(7) Swift, P. Adventitious Carbon—the Panacea for Energy Referencing? Surf. Interface Anal. **1982**, *4* (2), 47–51. https://doi.org/10.1002/sia.740040204.

(8) Okada, M.; Okada, N.; Chang, W.-H.; Endo, T.; Ando, A.; Shimizu, T.; Kubo, T.; Miyata, Y.; Irisawa, T. Gas-Source CVD Growth of Atomic Layered WS$_2$ from WF$_6$ and H$_2$S Precursors with High Grain Size Uniformity. Sci. Rep. **2019**, *9* (1), 17678. https://doi.org/10.1038/s41598-019-54049-6.