Supplementary Information (SI) for ChemComm.

Supporting information for:

Gradient Aerosol-Assisted Chemical Vapor Deposition for Vertically Graded Thin-Films of $Mo_xW_{1-x}S_2$ and $W_xMo_{1-x}S_2$

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Contents

Experimental

Chemicals

All solvents and reagents were used as purchased from Sigma-Aldrich or Fisher, without any additional purification. These includes acetone ($(CH_3)_2CO$, ≥99.5%), 2-propanol ($(CH_3)_2CHOH$, ≥99.7%) methanol (CH_3OH, 99.8%), tetrahydrofuran ($(CH_2)_4O$, ≥ 99.9%), sodium diethyldithiocarbamate trihydrate ($(C_2H_5)_2NCSSNa\cdot3H_2O$, ≥99.0%), molybdenum hexacarbonyl ($Mo(CO)_6$, ≥98.0%), tetraethylthiuram disulfide($(C_2H_5)_2NCSS_2CSN(C_2H_5)_2$, ≥97.0%) and ammonium tetrathiotungstate ($(NH_4)_2WS_4$, ≥99.9%).

Instrumentation

Thermogravimetric analysis was conducted using a Mettler-Toledo TGA/DSC1 analyzer under the following conditions: a temperature range of 30–600 °C, a heating ramp rate of 10 °C/min, and a nitrogen atmosphere. Elemental analyses of the precursors were performed by the microanalytical laboratory at the University of Manchester. FT-IR spectra were obtained using a Bruker Alpha II spectrometer. Mass spectrometry was performed with a Thermo Orbitrap Exactive Plus Extended Mass Range mass spectrometer, utilizing electrospray ionization (ESI) in positive mode. Grazing Incidence powder X-ray diffraction (GI-XRD) was carried out using a Philips X'Pert (now PANaytical) – MPD theta-theta diffractometer (400 mm diameter) with a PW1711 proportional point detector in Bragg-Brentano geometry. The setup employed a Copper Line Focus X-ray tube with a Ni kβ absorber (0.02 mm; $K\beta = 1.392250$ Å) and Kα radiation ($K\alpha1 = 1.540598$ Å, $K\alpha2 = 1.544426$ Å, Kα ratio 0.5, $K\alpha av = 1.541874$ Å) with an incidence angle in Omega of 3°

and a step size of 0.02°. Raman spectroscopy measurements were performed using a Horiba LabRAM Evolution HR Raman spectrometer at the University of Manchester Photon Science Institute. Excitation was achieved using lasers at 633 nm and 10x lens. Data obtained were analysed using The LabSpec 6 software was used to analyse the data obtained. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were performed using a Tescan SC SEM equipped with an Oxford EDX detector. Depth profiling was achieved using the GD-Profiler 2™: pulsed-RF glow discharge optical emission spectrometer.

Synthesis of Diethyldithiocarbamate Precursors

The molybdenum (IV) and tungsten (III) diethyldithiocarbamate used as precursors in this study were synthesised by adapting previously published procedures.[1, 2]

Tris(diethylthiocarbamato) molybdenum (IV), $Mo(S_2CN(C_2H_{10})_2)_4$

1 g of molybdenum hexacarbonyl (3.8 mmol) and 2.2 g of tetraethylthiuram disulfide (7.6 mmol) were dissolved in 30 mL of degassed acetone and heated under reflux at 80 °C for two hours. After cooling to room temperature, a black microcrystalline precipitate formed, which was collected by vacuum filtration, washed with pentane (3 × 30 mL), and dried overnight in a vacuum oven. The final black powder was analysed and used for deposition experiments as a Mo-S single source molecular precursor.

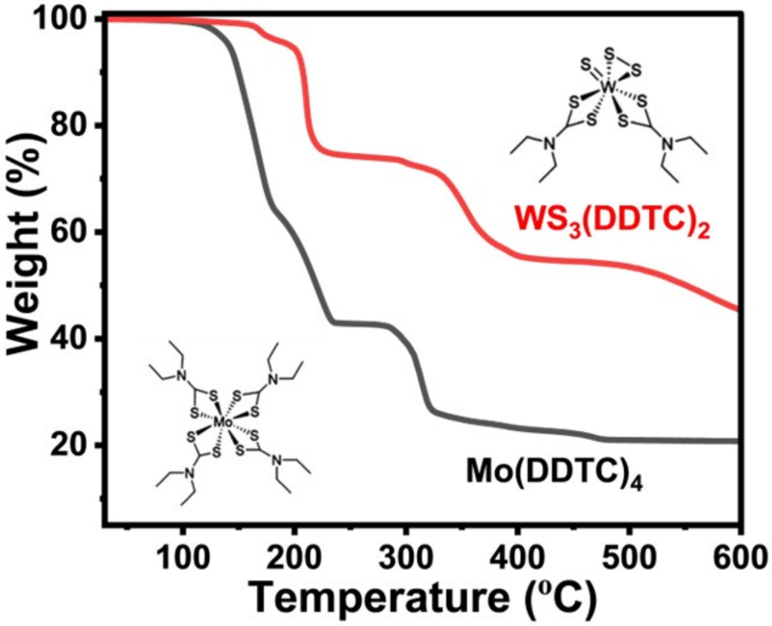
Yield: 68% (1.73 g, 3 mmol); CHNS elemental analysis: calculated for C20H40N4S8Mo: (%) C, 34.9; H, 5.9; N, 8.1; S, 37.2; Mo, 13.9; found: (%) C, 34.9; H, 5.8; N, 8.1; S, 36.9; Mo, 14.2.

Bis(diethylthiocarbamato) disulfide thioxo tungsten (IV), $WS(S_2)(S_2CN(C_2H_5)_2)_2$

7.6 g of sodium diethyldithiocarbamate trihydrate ($Na(S_2CN(C_2H_5)_2)\cdot 3H_2O$) (33.77 mmol) and 2.91 g of ammonium tetrathiotungstate ($[NH_4]_2[WS4]$) (8.36 mmol) were dissolved in 300 mL of water and vigorously stirred for homogeneous mixing. The pH was adjusted to 2 by gradually adding a 2 M hydrochloric acid (HCl) solution. Initially, a yellow precipitate formed, which eventually turned dark green as more HCl was added. The resulting precipitate-filled solution was stirred for 30 minutes, then filtered, washed thoroughly with water, and vacuum dried. The crude product was dissolved in 250 mL of acetone, filtered, and the precipitates were washed with acetone (3 × 40 mL), yielding an orange-brown powder and a dark green solution. The green solution was evaporated and vacuum dried, affording the title compound, $WS_3(S_2CN(C_2H_5)_2)_2$, a dark green powder. This was analysed and used as a Mo-S single source precursor.

Yield: 58% (2.78 g, 4.82 mmol); CHNS elemental analysis: calculated for C10H20N2S7W: (%) C, 20.8; H, 3.5; N, 4.9; S, 38.92; found: (%) C, 20.8; H, 3.5; N, 4.8; S, 38.29.

FTIR and TGA Study of Molecular Precursors



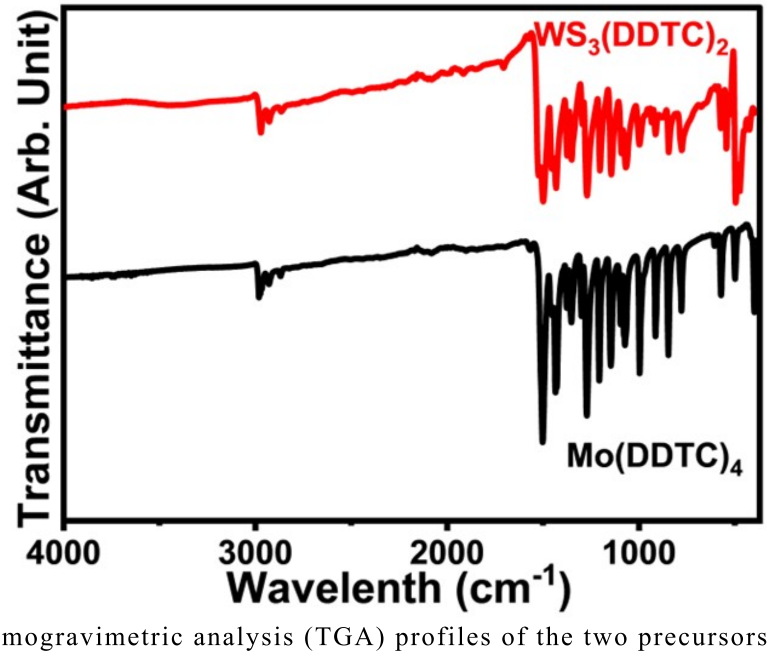


Figure S1: Thermogravimetric analysis (TGA) profiles of the two precursors respectively.

Figure S2: Infrared Spectroscopy the two precursors, Mo(DDTC)$_4$ and WS$_3$(DDTC)$_2$.

GACVD Set-up and Experiment Process Parameters

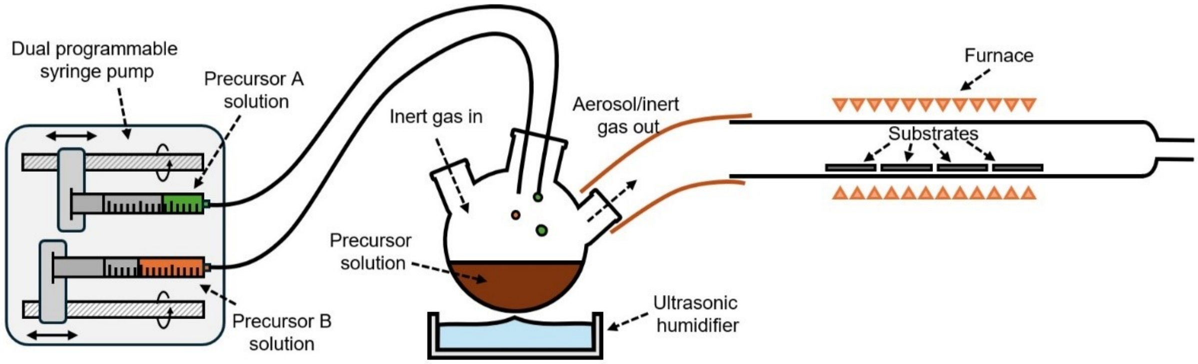


Figure S3: Shows a schematic diagram of the GACVD apparatus.

Table S1: The process parameters imputed to the programmable dual syringe pump to deliver MoDDTC and WDDTC precursors (with a concentration of 0.02 M).

Mo$_x$W$_{1-x}$S$_2$		**Duration**	**W$_x$Mo$_{1-x}$S$_2$**		**Duration**
Mo(DDTC)$_4$	**W(DDTC)$_2$**		**Mo(DDTC)$_4$**	**W(DDTC)$_2$**	
0 mL	4 mL	15 min	8 mL	0 mL	15 min
1 mL	3 mL	15 min	6 mL	2 mL	15 min
2 mL	2 mL	15 min	4 mL	4 mL	15 min
3 mL	1 mL	15 min	2 mL	6 mL	15 min
4 mL	0 mL	15 min	0 mL	8 mL	15 min

Grazing Incident X-ray Diffraction

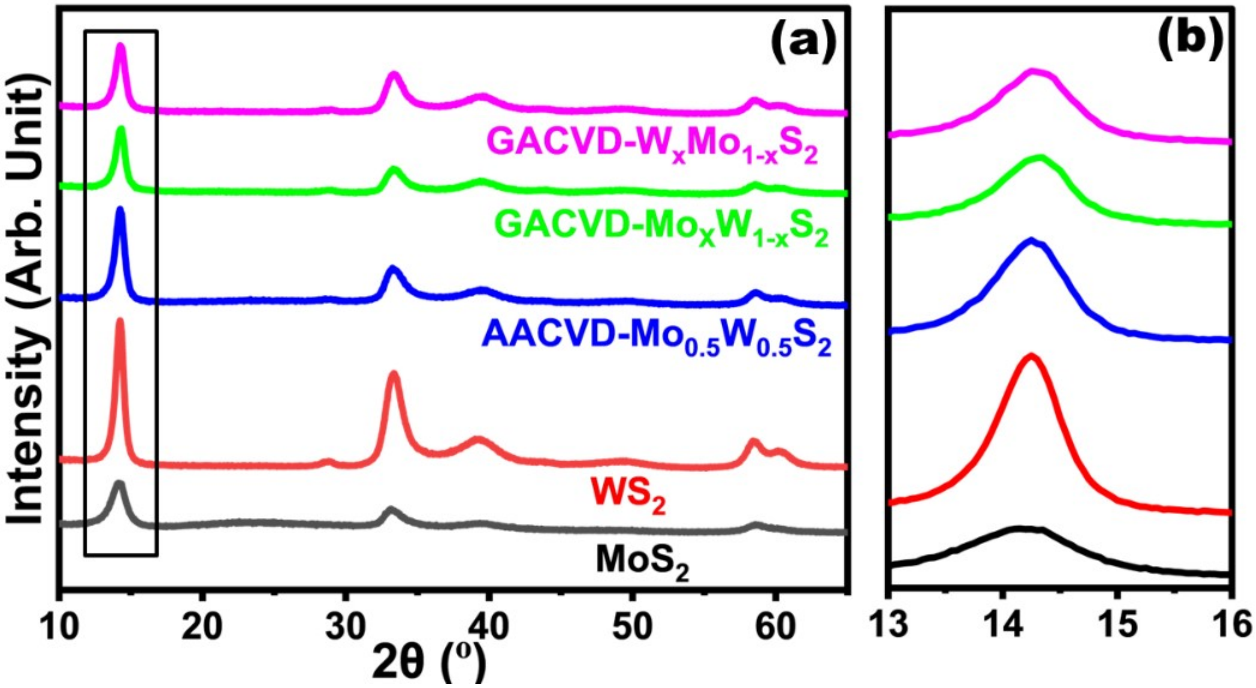
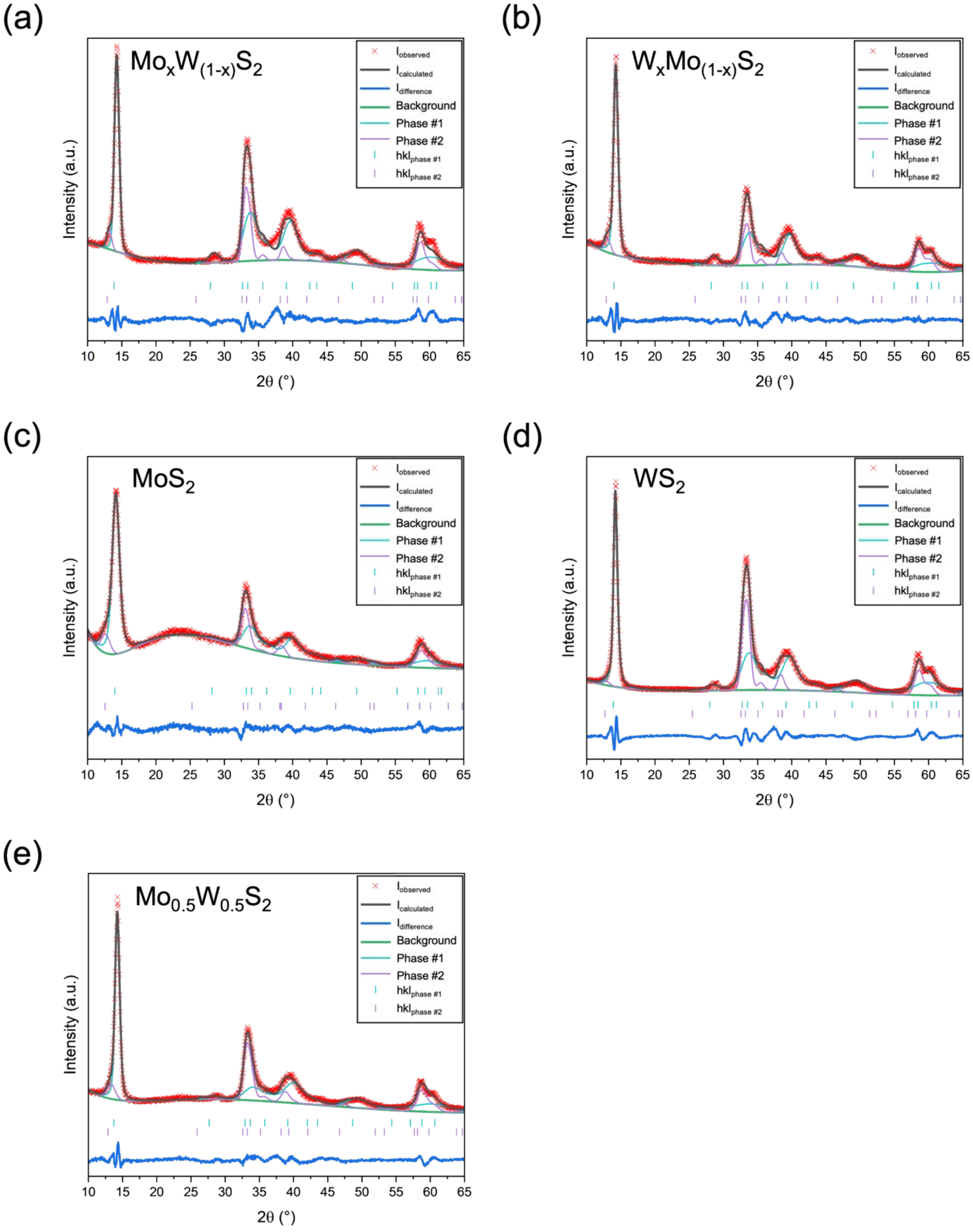


Figure S4(a, b): GIXRD patterns for the two films samples from GACVD: $Mo_xW_{1-x}S_2$, $W_xM_{1-x}S_2$ and three sample from the parent AACVD: MoS_2, WS_2 and $Mo_{0.5}W_{0.5}S_2$.



Rietveld Refinement Fit Data

Figure S5: Rietveld fits of the GIXRD patterns for two films produced via GA-CVD (a) $Mo_xW_{1-x}S_2$ (b) $W_xM_{1-x}S_2$ and three sample from standard AACVD (c) MoS2 (d) WS2 and (e) $Mo_{0.5}W_{0.5}S_2$. All films were fabricated at 450 °C. The experimental data is shown as red crosses, the total calculated fit is shown as a black line along with the difference to the experimental data in dark blue and the background in green. The light blue and pink lines show the contribution to the total fit from the two predicted phases, with the corresponding hkl ticks in the same colour.

Unit Cells Parameters from Rietveld Fit

Table S2: Extracted crystalline unit cell parameters from GIXRD patterns of the film materials fitted to using a Rietveld refinement. Last two columns are standardized reference from ICSD.[3, 4]

	$Mo_xW_{(1-x)}S_2$		$W_xMo_{(1-x)}S_2$		$Mo_{0.5}W_{0.5}S_2$		MoS_2		WS_2		MoS_2 (ICSD #644259)	WS_2 (ICSD #651384)
R_{wp}	9.2		7.7		6.8		5.5		9.3		ICSD #644259	ICSD #651384
	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2		
a = *b* / Å	3.165 ±0.008	3.169 ±0.009	3.157 ±0.003	3.171 ±0.001	3.138 ±0.010	3.170 ±0.012	3.113 ±0.004	3.151 ±0.001	3.155 ±0.007	3.172 ±0.008	3.166 ± 0.005	3.16 ± 0.002
c / Å	12.753 ±0.045	13.772 ±0.049	12.646 ±0.034	13.778 ±0.030	12.886 ±0.068	13.740 ±0.069	12.649 ±0.005	14.083 ±0.030	12.739 ±0.047	13.979 ±0.047	12.305 ± 0.003	12.358 ± 0.005
Vol / $Å^3$	110.62 ± 0.67	119.80 ± 0.77	109.14 ± 0.22	119.96 ± 0.28	109.88 ± 0.90	119.60 ± 1.06	110.13 ± 0.31	121.11 ± 0.27	109.82 ± 0.61	121.83 ± 0.73	106.82	106.94
wt. %	73	27	68	32	64	36	66	34	71	29		

Scanning Electron Microscopy Images

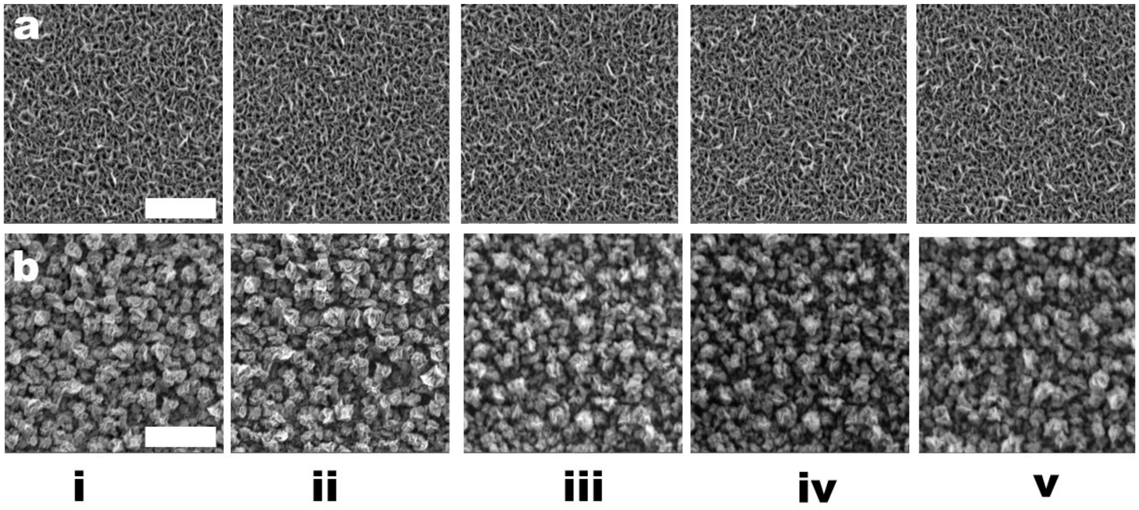


Figure S6(a-c): Shows a. Scanning electron microscopy micrograms of the GACVD films a) (i-iv). $Mo_xW_{1-x}S_2$ b) (i-iv). $W_xM_{1-x}S_2$ fabricated at 450 °C. Scale bars represent 5 µm.

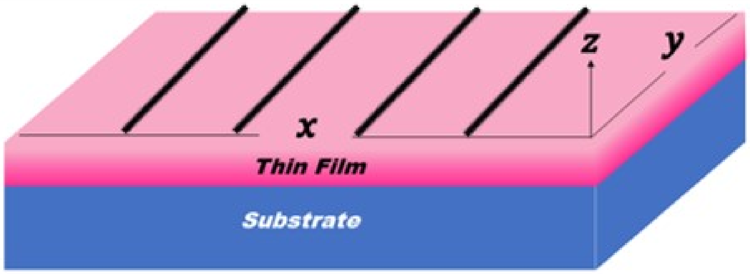


Figure S7: An illustrative layout of how the graded films deposited on a 20 mm by 15 mm substrates were divided into five for SEM-EDX surface morphology and elemental composition studies.

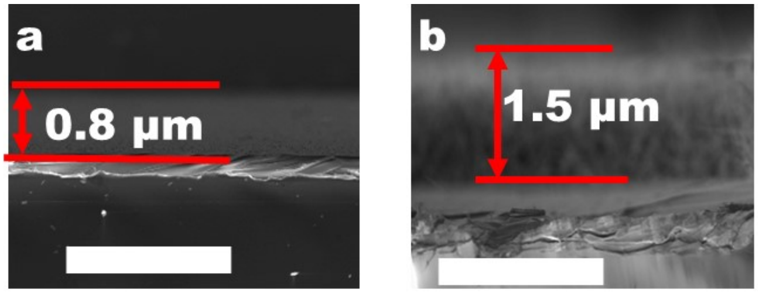


Figure S8(a, b): Are cross-sectional SEM for and $W_xM_{1-x}S_2$ and $Mo_xW_{1-x}S_2$, respectively, showing continuously grown crystalline film. Scale bars represent 2 µm.

Energy Dispersive X-Ray Spectroscopy and Glow Discharge Optical Emission Spectroscopy

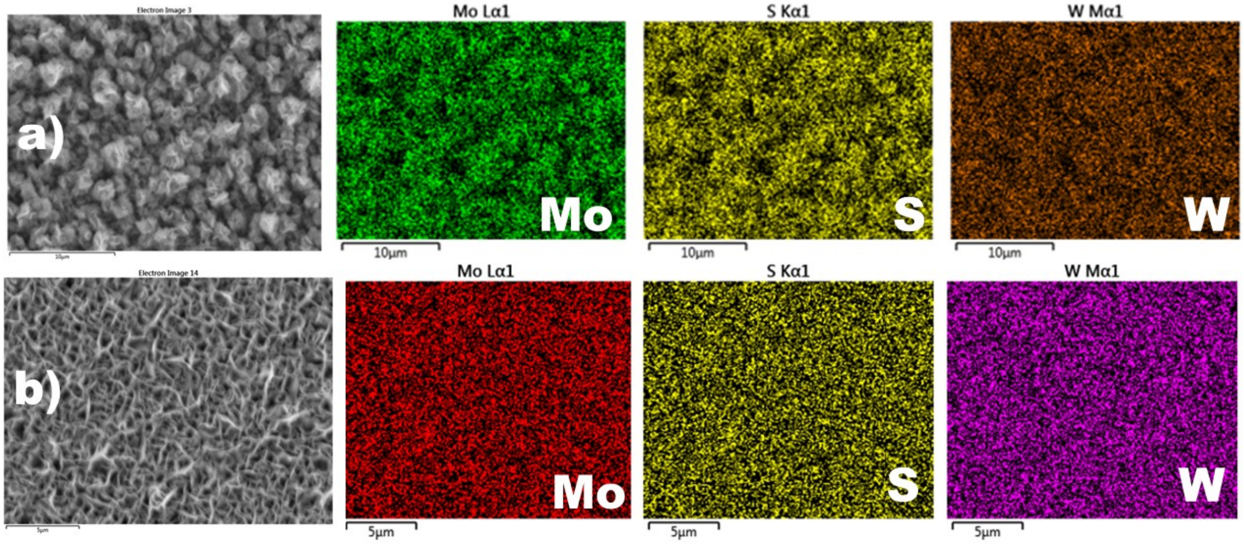


Figure S9(a, b): Representative energy dispersive X-ray spectroscopy maps of GACVD a. $Mo_xW_{1-x}S_2$, Scale bars represent 10 µm b). WxM1-xS2 fabricated at 450 °C, Scale bars represent 5 µm.

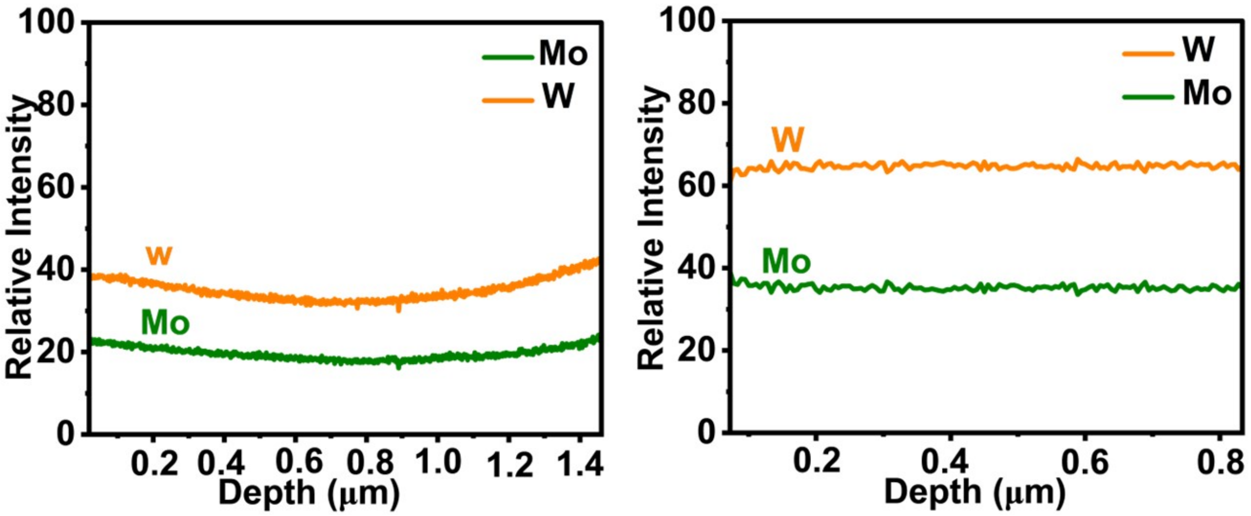


Figure S10: Glow discharge Optical Emission Spectroscopy Depth profiles of two different samples of equimolar $MoWS_2$ thin film prepared by Aerosol assisted chemical vapour deposition.

References

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