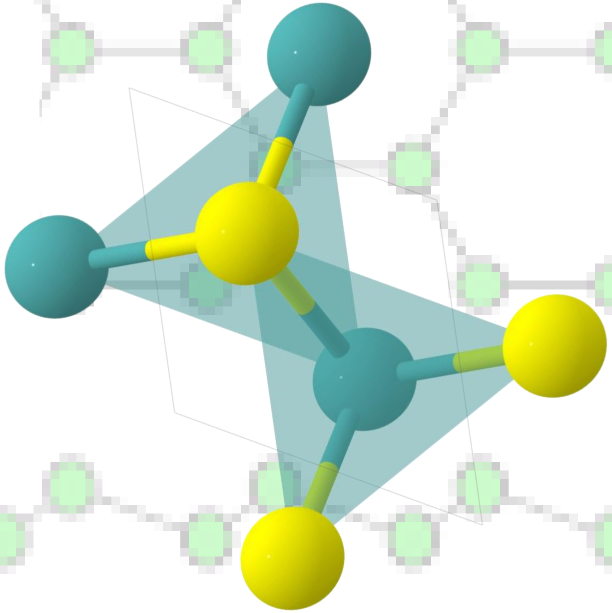
Optimized synthesis of dichalcogenide films via chemical vapor deposition

SPROJ Final Presentation



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- MoS_2
- Apparatus
- Stepwise synthesis
- Optimizing thickness
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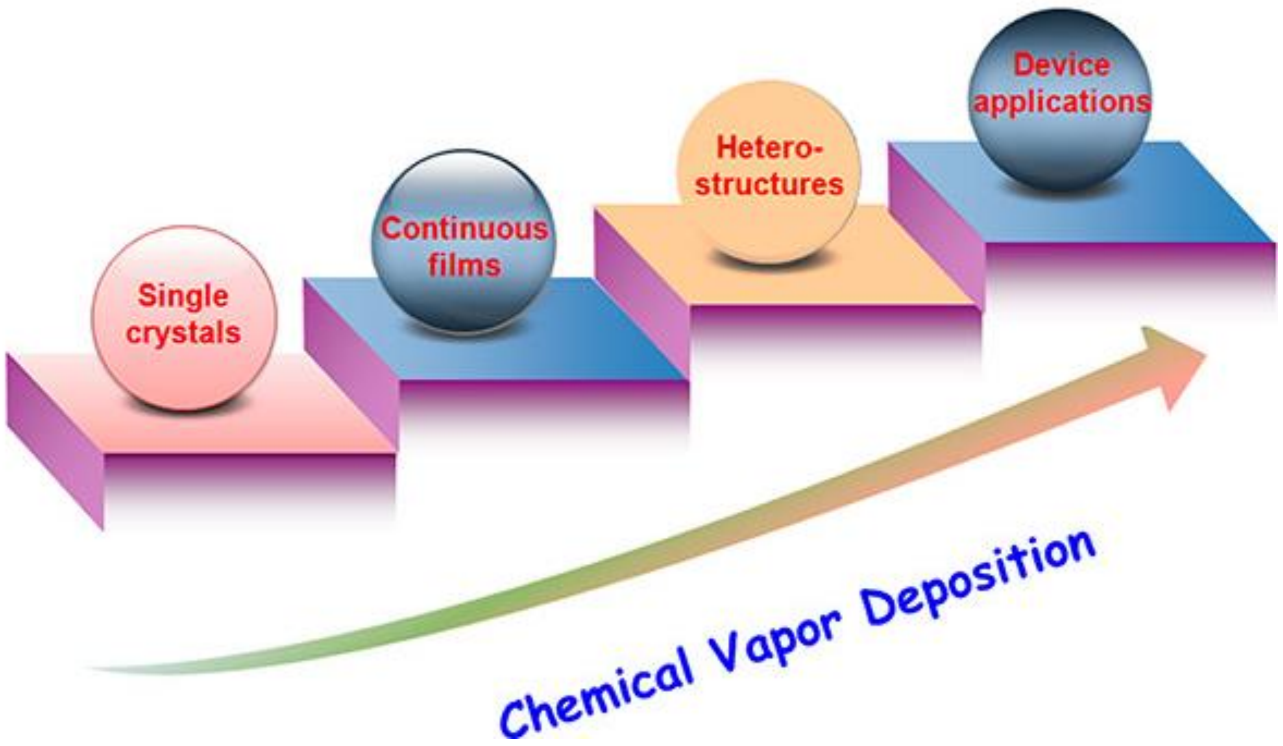


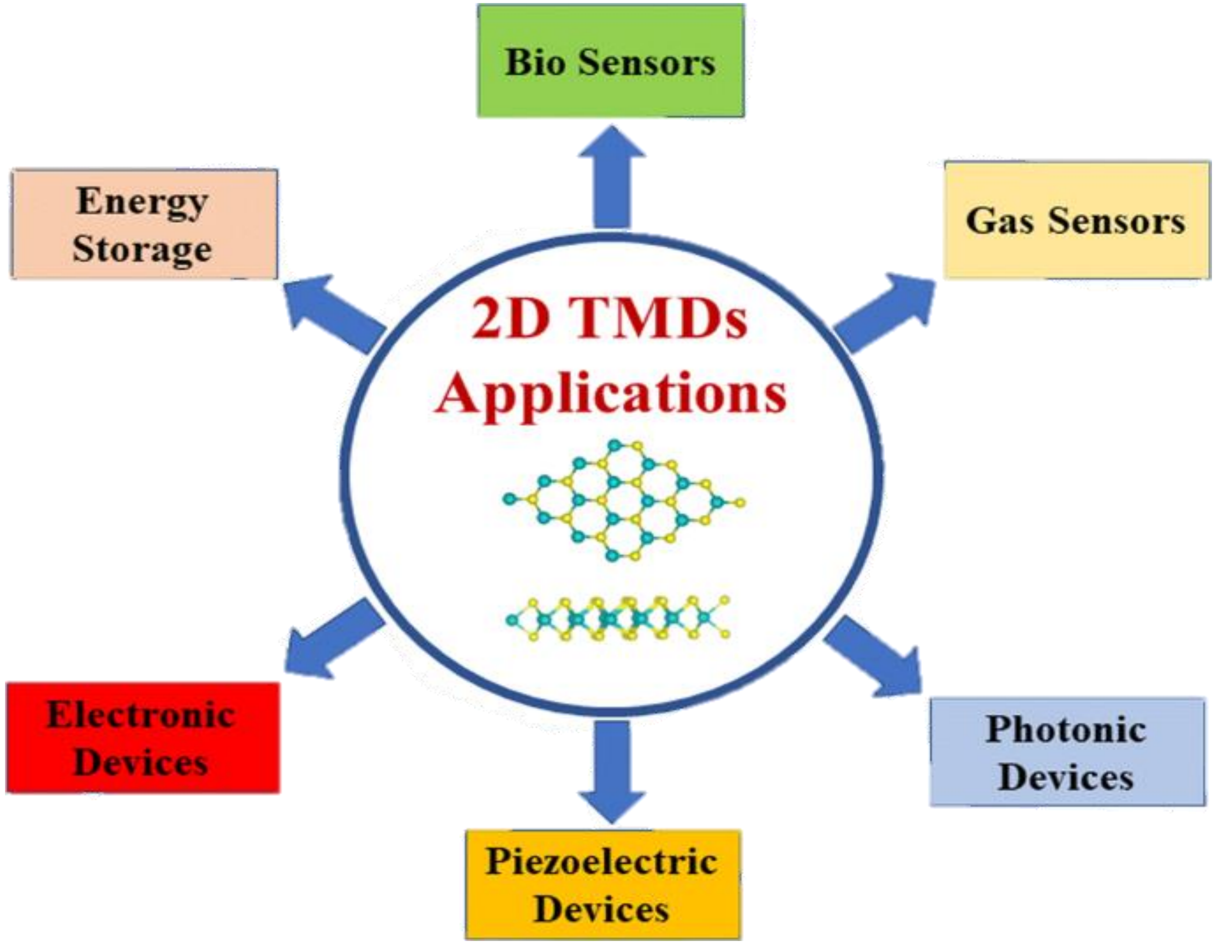
(Kai, Liu. *Et al* 2018)

Research Map

Optimize Apparatus	• Chemical Vapor deposition furnace
Choose	• MoS_2
Optimize thickness	• Literature review • Optimization of parameters
Characterize	• Optical microscopy • Raman spectroscopy • Scanning electron microscopy
Goal	• Continuous thin films of MoS_2

What are transition metal dichalcogenides?

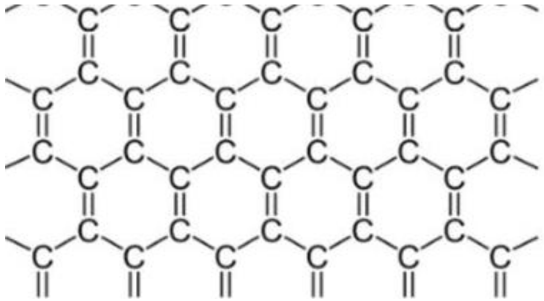
- What are TMDCs?
- Chemical formula = MX_2
- Semiconductors ~ reduced to nanostructures/2D materials
- Nanoscale materials vs bulk materials
- Created via exfoliation, physical or chemical vapor deposition (CVD), sputtering.
- Applications of TMDCs: catalysis, sensor applications, electronic devices, electrochemical reactions, energy storage, fuel cell, and renewable energy technology.



Why MoS_2?

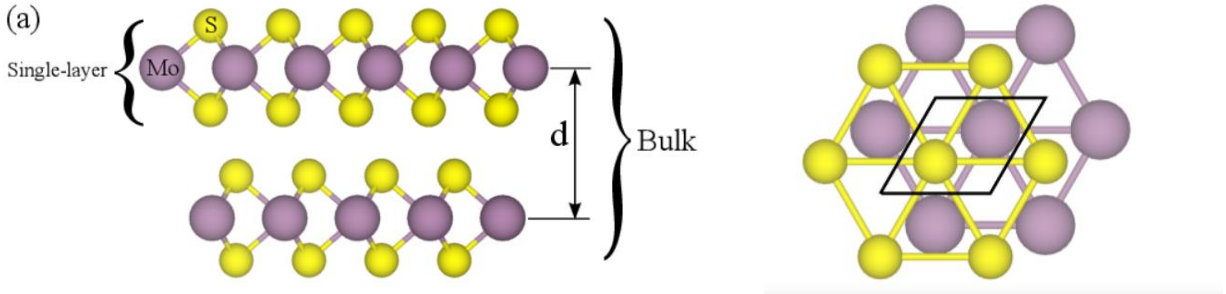
- **<u>Graphene</u>**

- Monolayers discovered in 2004; Nobel Prize in 2010
- Carbon atoms ~ hexagonal lattice
- Mechanical stiffness, flexibility, thermal and electric properties
- Zero bandgap – No optical switching!



- **<u>MoS_2</u>**

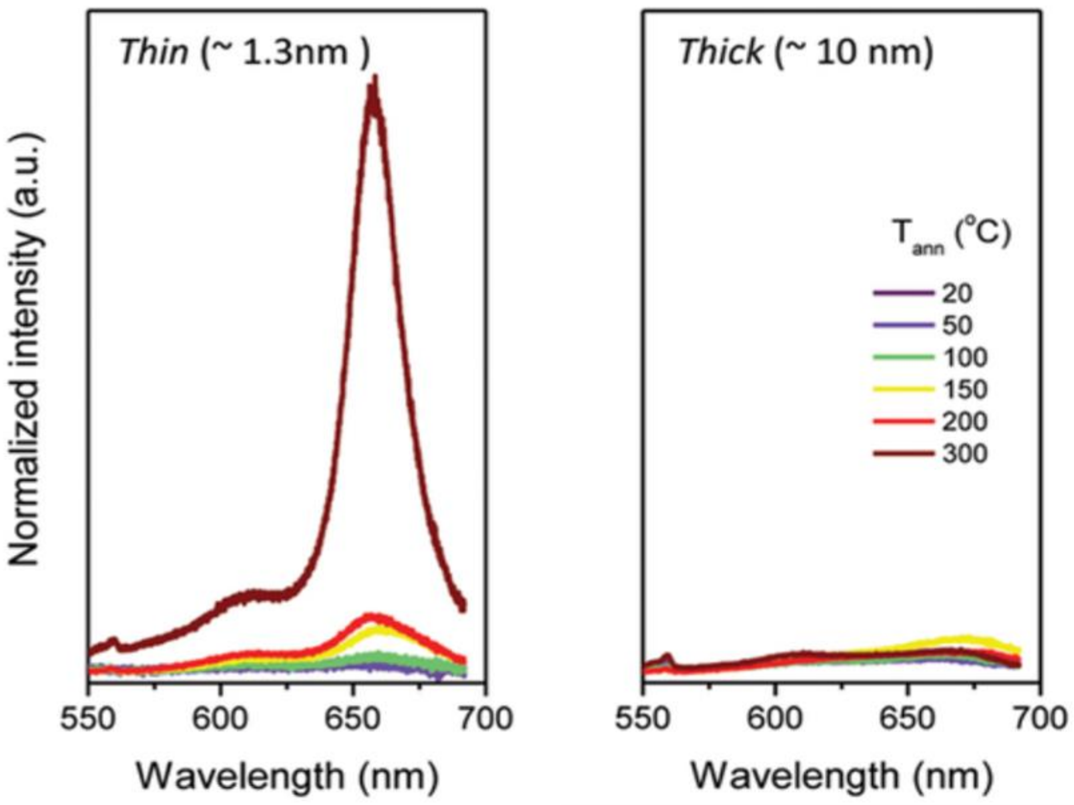
- It behaves similarly to graphene due to its structure and has a tunable bandgap so is a great substitute.
- Allows switching.
- The bandgap is layer dependent.



(Sanchez, Hummer, *et al*. 2015)

Properties and applications of MoS_2

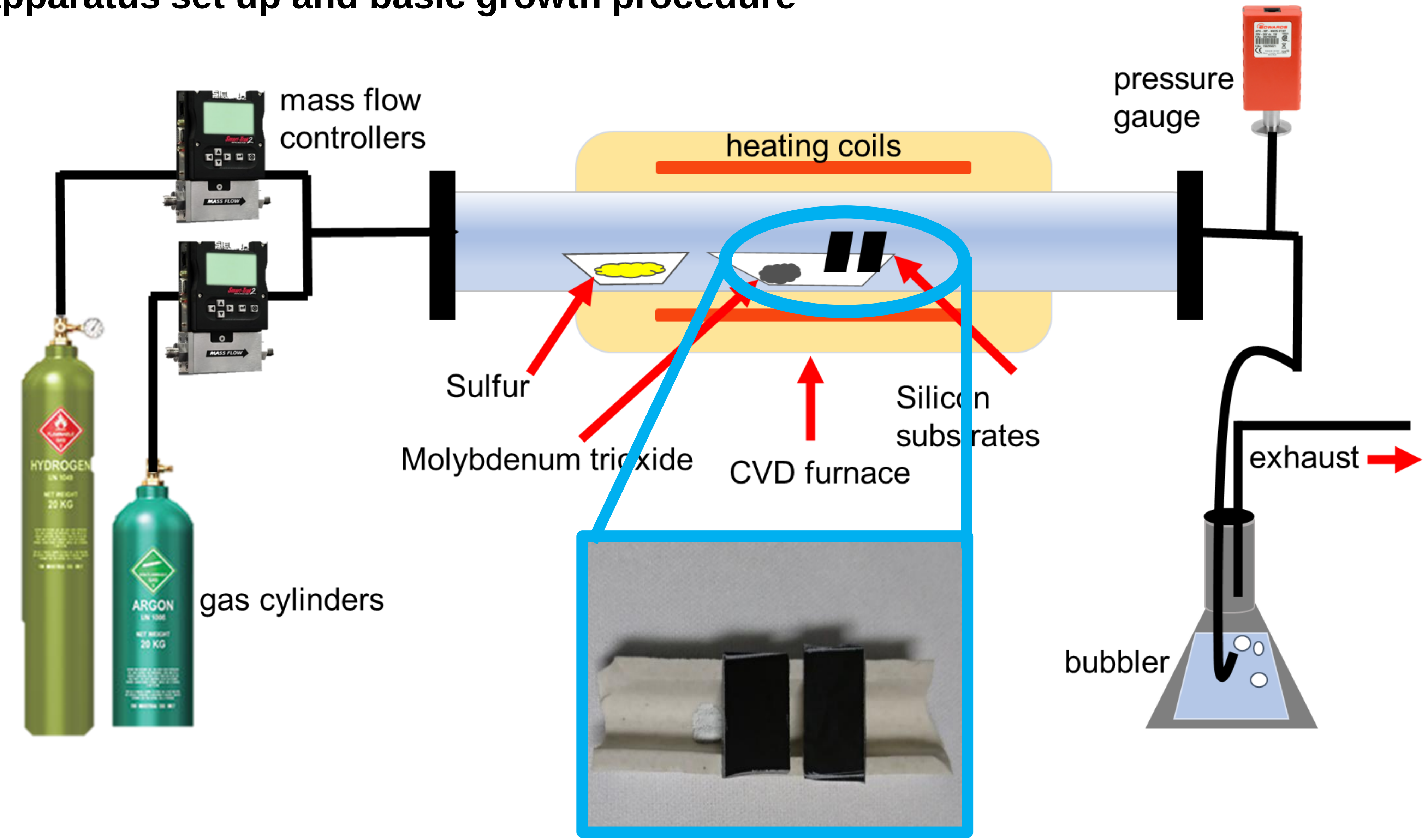
- Shows n type and p type behavior depending on which dopant is used.
- Highly photosensitive and photo responsive due to the direct bandgap in nanoform.
- Recently being explored for optical and electric sensing applications.



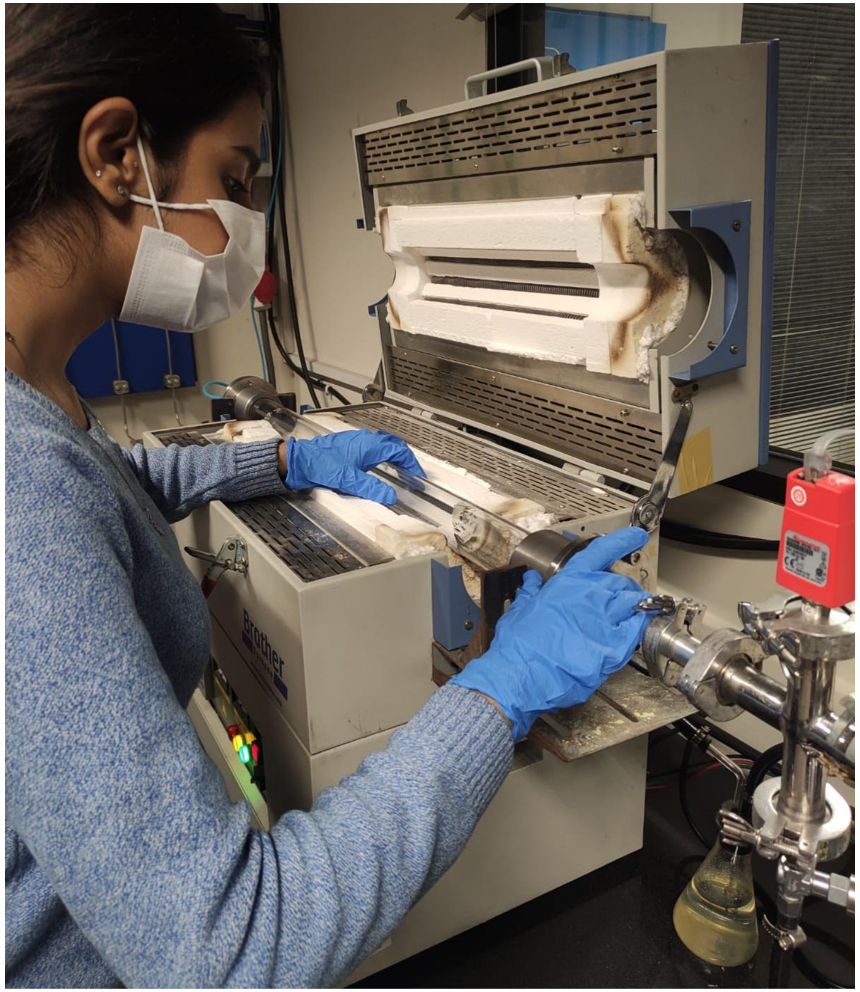
(C. Vidya, *et al.*, 2022)

Chemical vapor deposition (CVD) technique

The apparatus set up and basic growth procedure

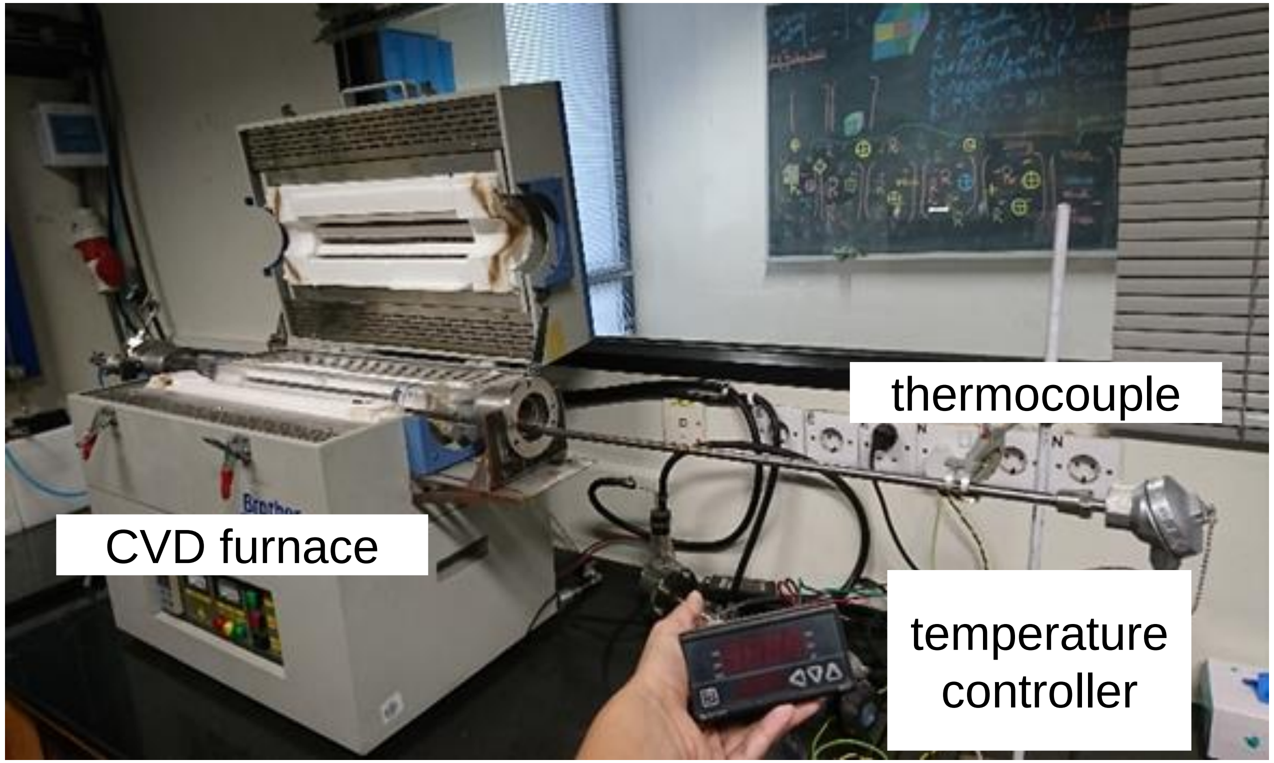


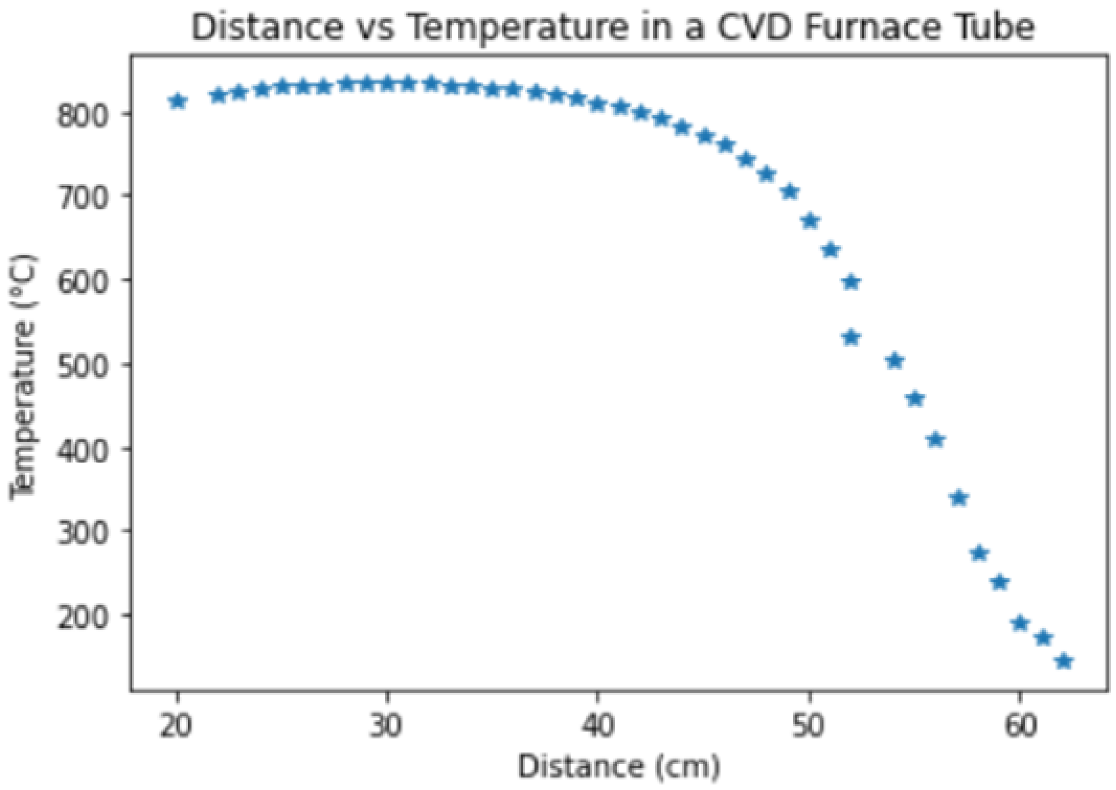
Actual apparatus setup in Spin Physics Lab



Thermal Mapping of the furnace

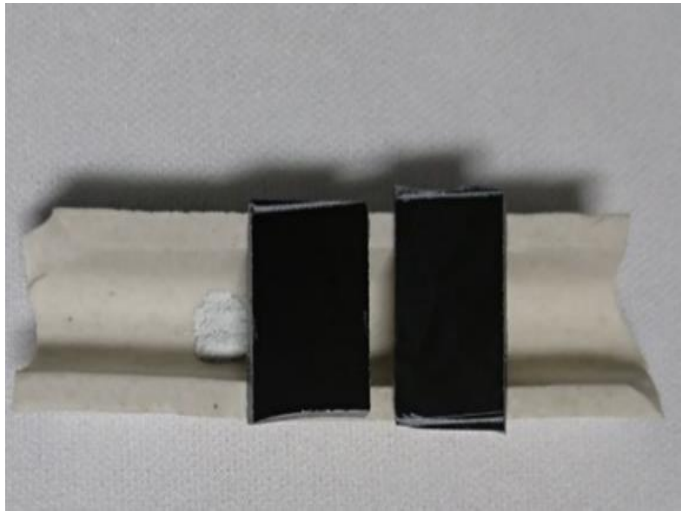
- How do we know where to place precursors and substrates in the tube?



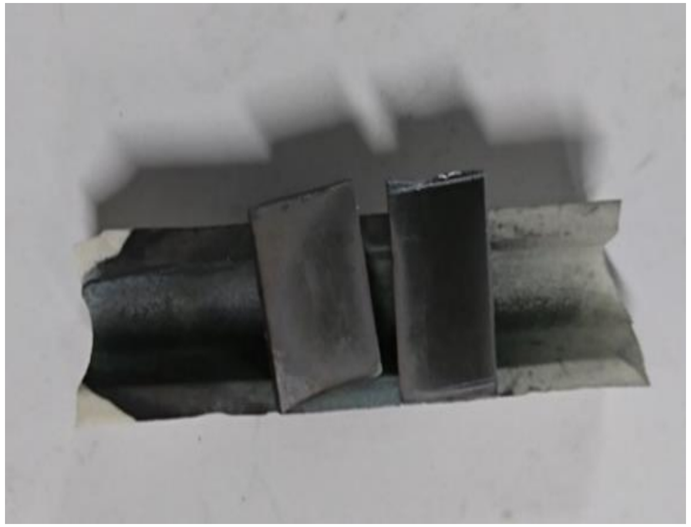


Visual observations of apparatus

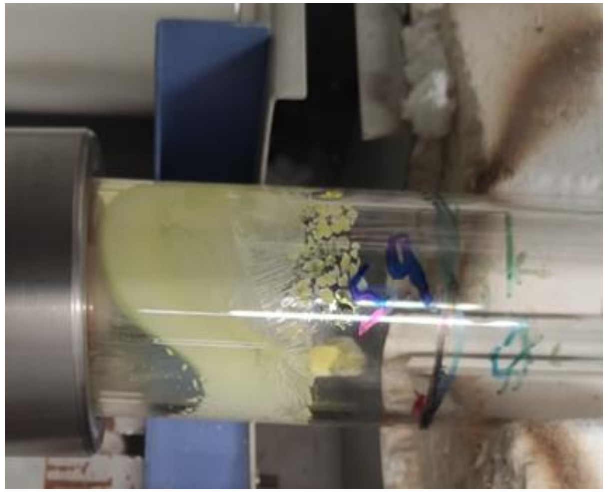
Substrates and precursor before growth



Substrates and precursor after growth



inlet

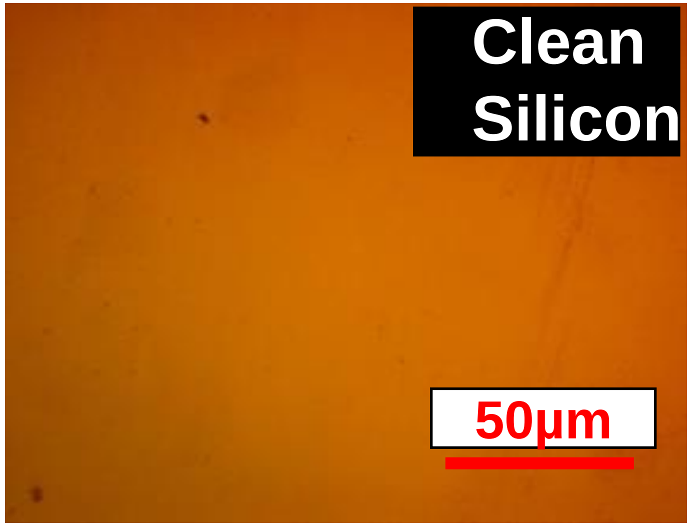


outlet

Characterization Techniques

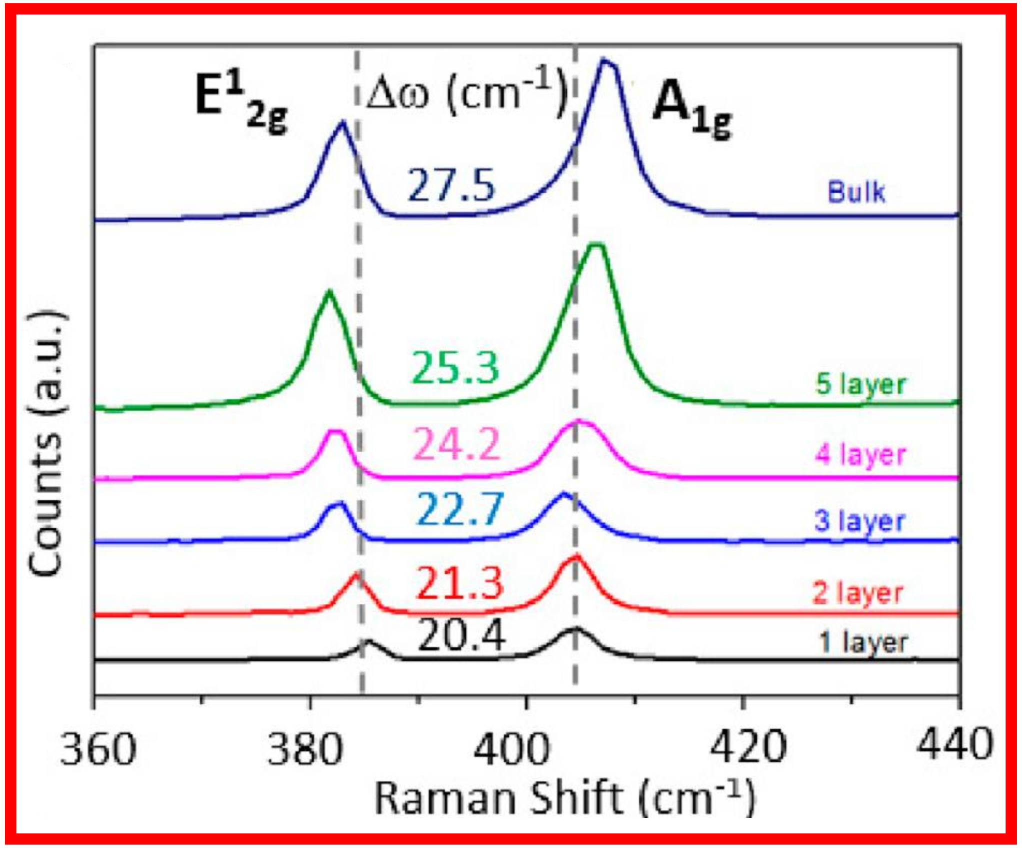
Optical microscopy

- To observe if growth has occurred
- Optical microscopy is performed at 50x magnification.



Raman Spectroscopy

- Noninvasive, nondestructive, vibrational spectroscopy technique.
- Helps identify chemical nature through the scattering produced by the in-plane and out of plane vibrations between the bonds.
- To identify the exact molecule, as the bonds are unique to each chemical makeup.
- MoS_2 has signature peaks E^1_{2g} and A_{1g}



(Tummala, Lamperti *et al.* 2020)

Scanning electron microscopy

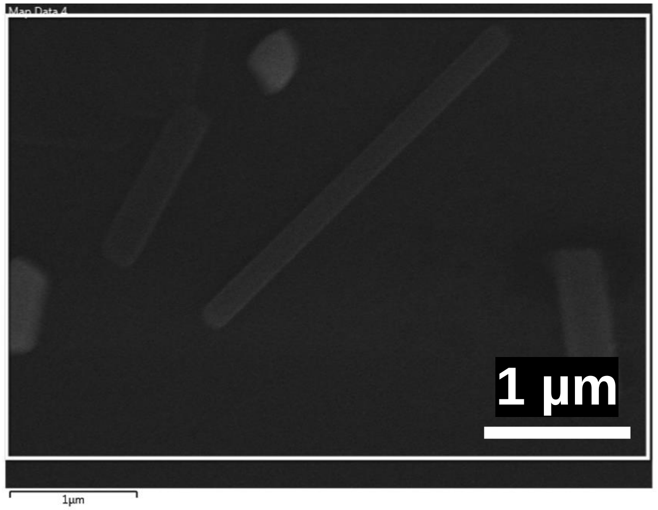
Topography
- Appearance and surface features like texture

Crystallography
- How the atoms or flakes are arranged in the film

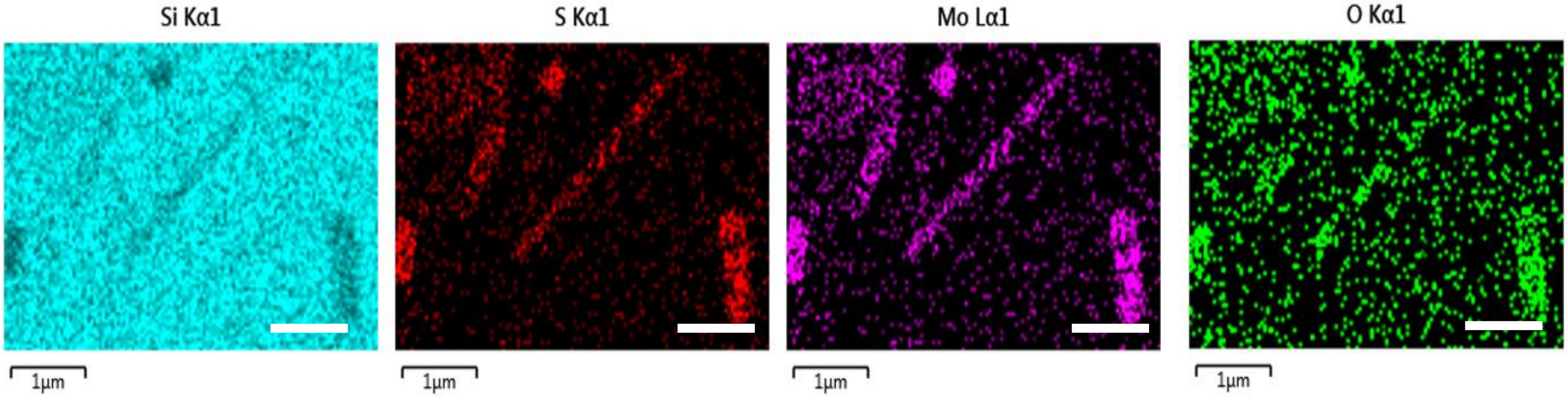
Morphology
- The size of the particles produced

Composition
- The elements that have played part in making the film and their respective compositions and ratio

Energy Dispersive X-ray Spectroscopy (EDX)

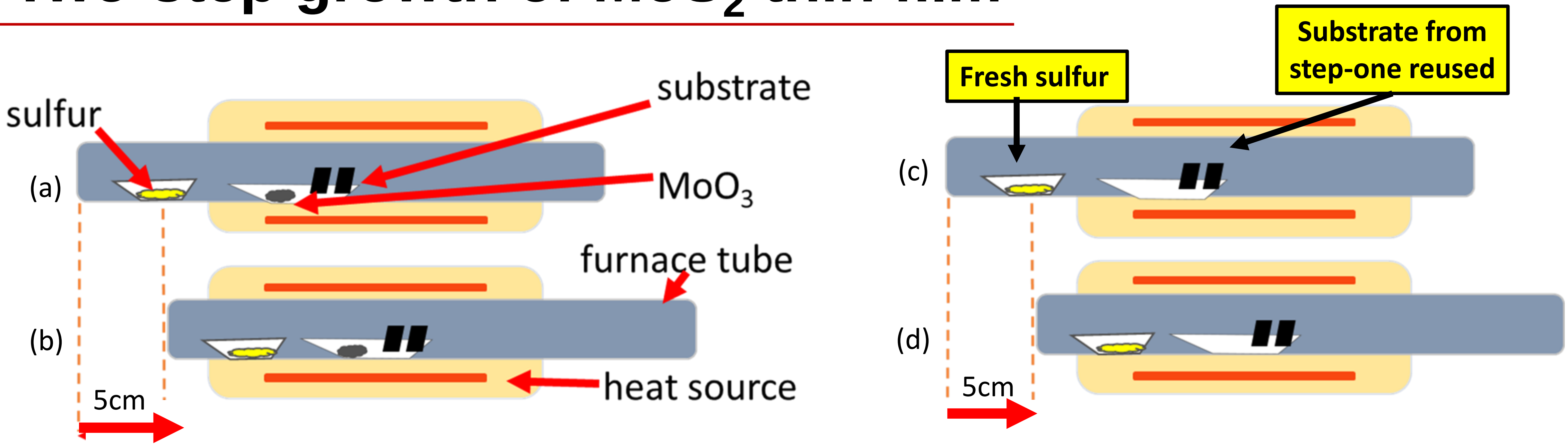


- Used with SEM to analyze the chemical composition of materials.
- A focused beam of electrons is scanned over the surface to produce an image, triggering and detecting X-ray emissions.
- These correspond to atomic levels present in sample, used to identify chemical composition.
- Provides detailed information on elemental composition, distribution, and structure.



Synthesis of MoS_2 thin films using a step-wise approach

Two-step growth of MoS_2 thin film



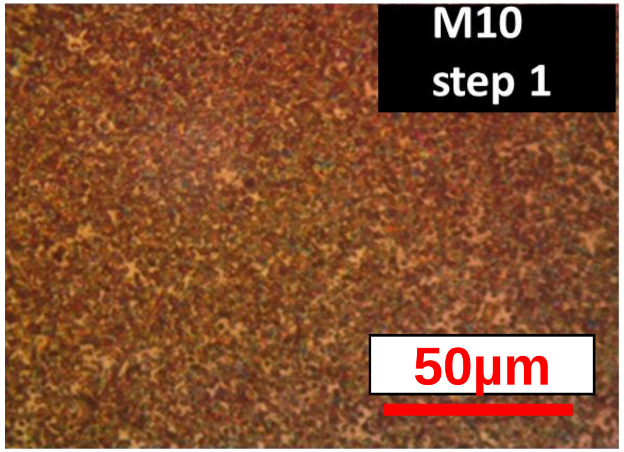
Step 1: $MoO_3 + S \rightarrow MoO_{3-x} + SO_2$

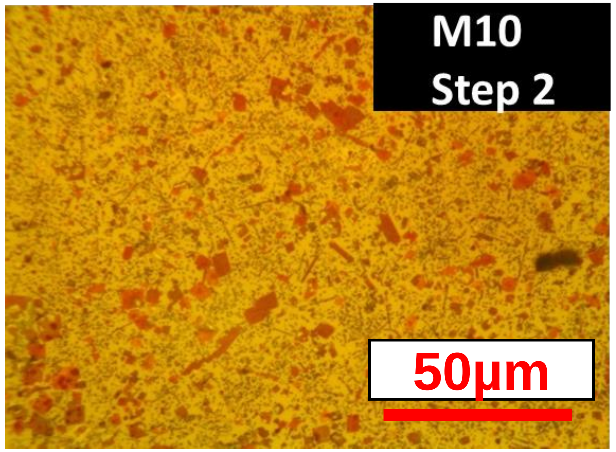
Step 2: $MoO_{3-x} + S \rightarrow MoS_2 + SO_2$

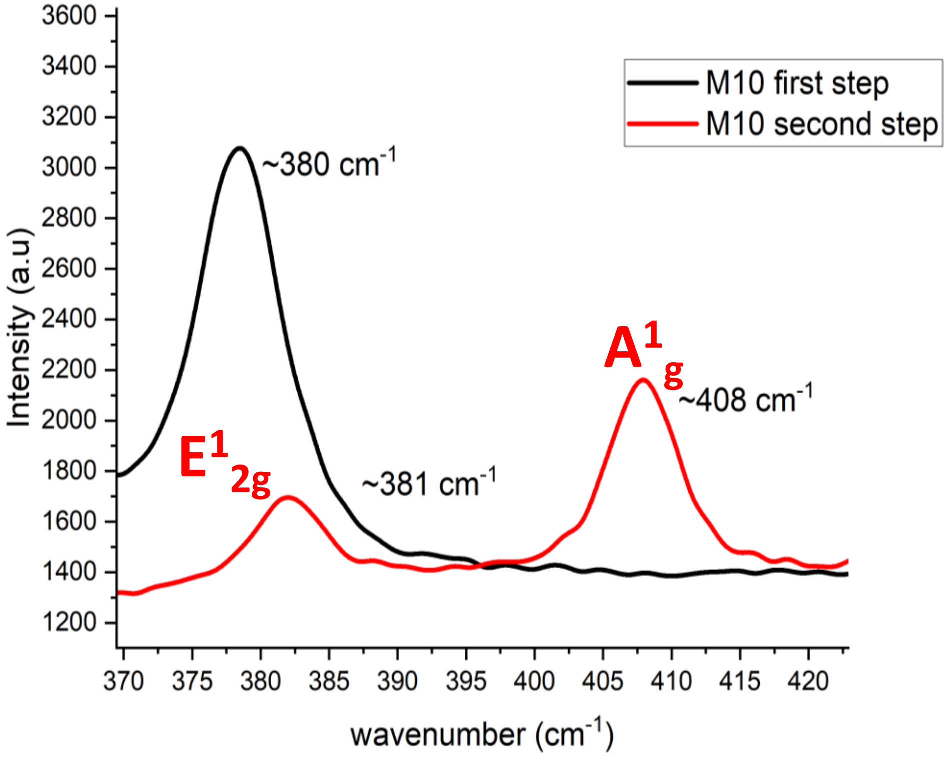
The schematic above shows the step-wise process to produce a thin film of MoS_2 along with the displacement over which the tube is physically moved.

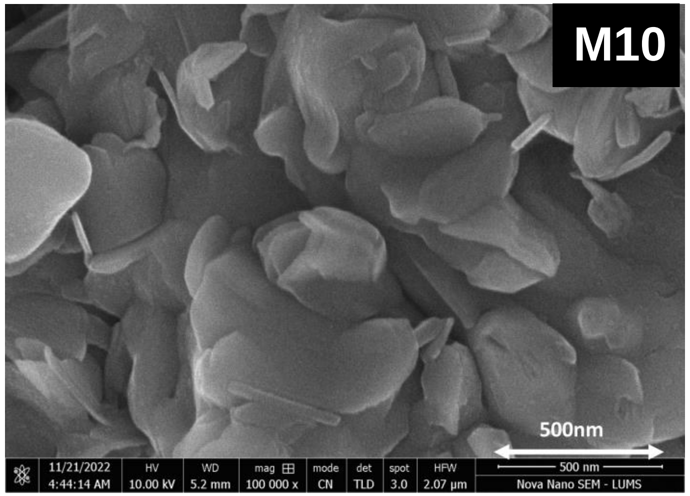
(Wang, W., *et al*., 2018)

Data obtained from two-step growth









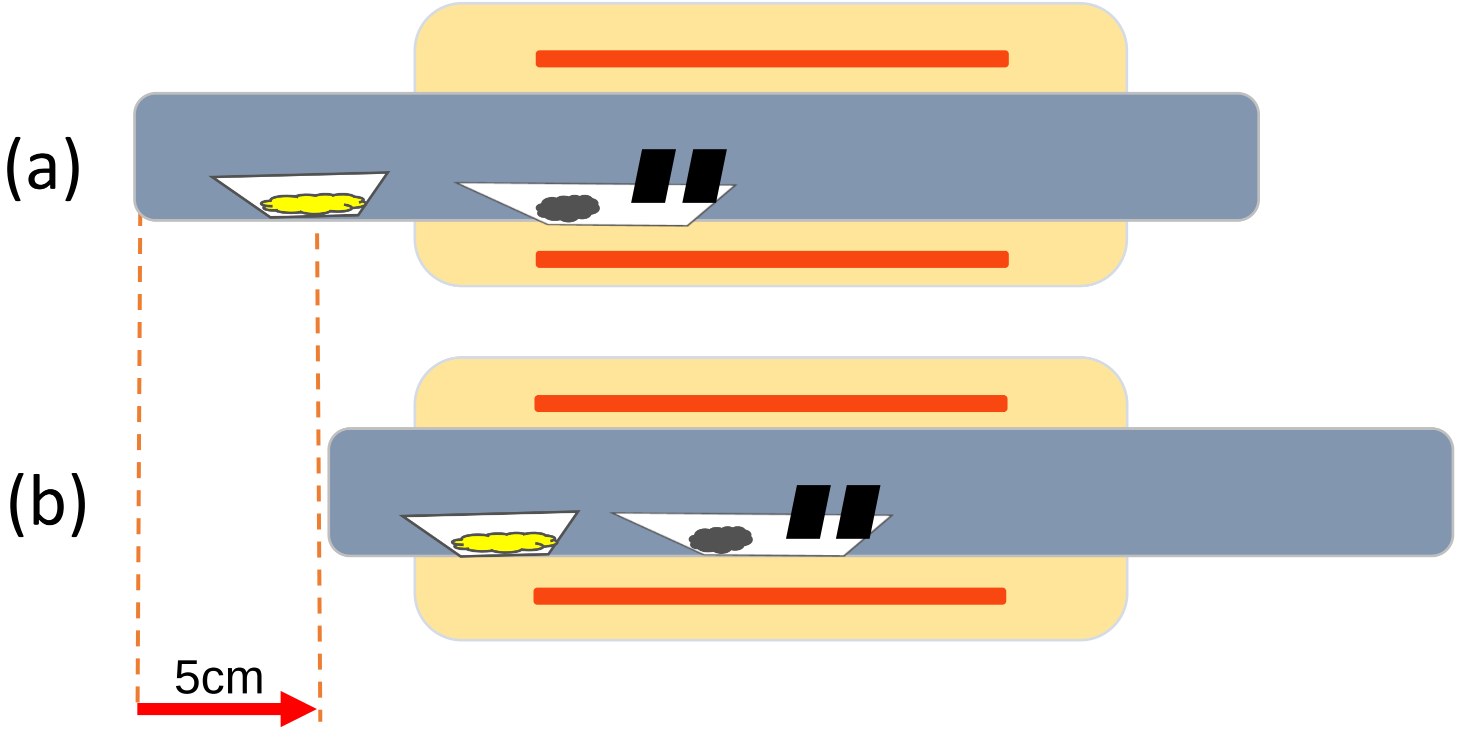
Optimization of parameters for two-step growth

	M10	M12	M10 (sulfurized)	M12 (sulfurized)
Substrate	Si	Si	Si	Si
MoO_3 (mg)	35	25	0	0
S (mg)	1.5	1.5	3	3
Set temperature (°C)	800	800	800	800
Growth temperature (°C)	799	799	750	750
Gas	Ar	Ar	Ar	Ar
Working pressure (torr)	1.8	1.8	1.8	1.8
Gas flow (sccm)	400-150	400-50	100-70	200-100
Growth time (min)	30	30	30	30

First target achieved!

- Next, we challenged ourselves to produce MoS_2 in one step for efficiency.

One-step growth of MoS_2 thin film

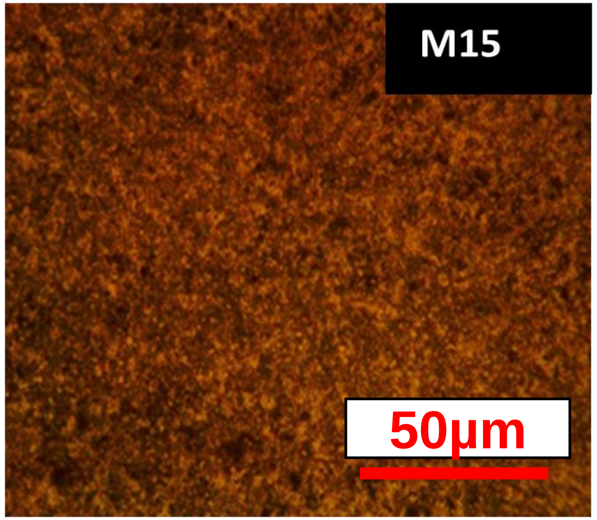


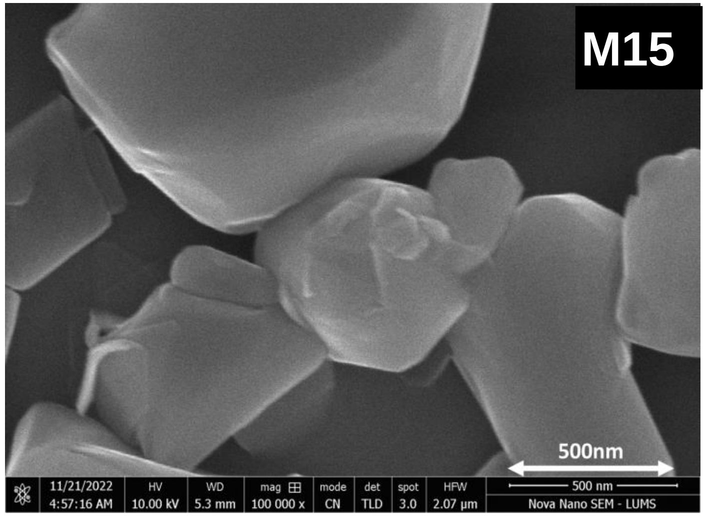
$$MoO_3 + S \rightarrow MoS_2 + SO_2$$

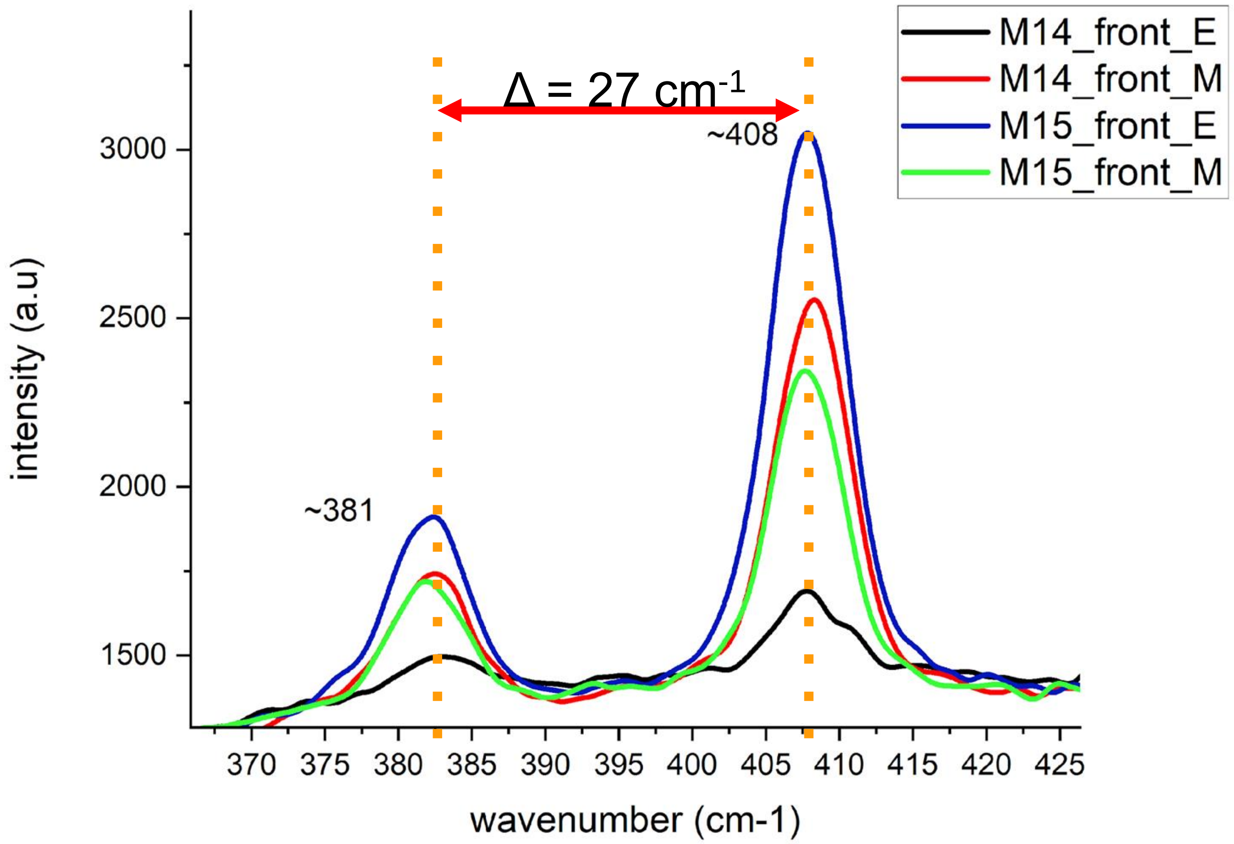
- Only the parameters were slightly altered, the process remained the same to produce the two-step method results.

(Wang, W., *et al*., 2018)

Data obtained from one step growth







Optimization of parameters for one-step growth

	M14	M15
Substrate	Si	Si
MoO_3 (mg)	26	26
S (g)	6	6
Set temperature (°C)	800	800
Growth temperature (°C)	810	810
Gas	Ar	Ar
Working pressure (torr)	1.8	1.8
Gas flow (sccm)	100-70	100-70
Growth time (min)	30	30

Second target achieved!

- MoS_2 thin films were produced multiple times using this set of parameters.
- It was found to be more efficient as lesser energy, precursors and time were utilized.

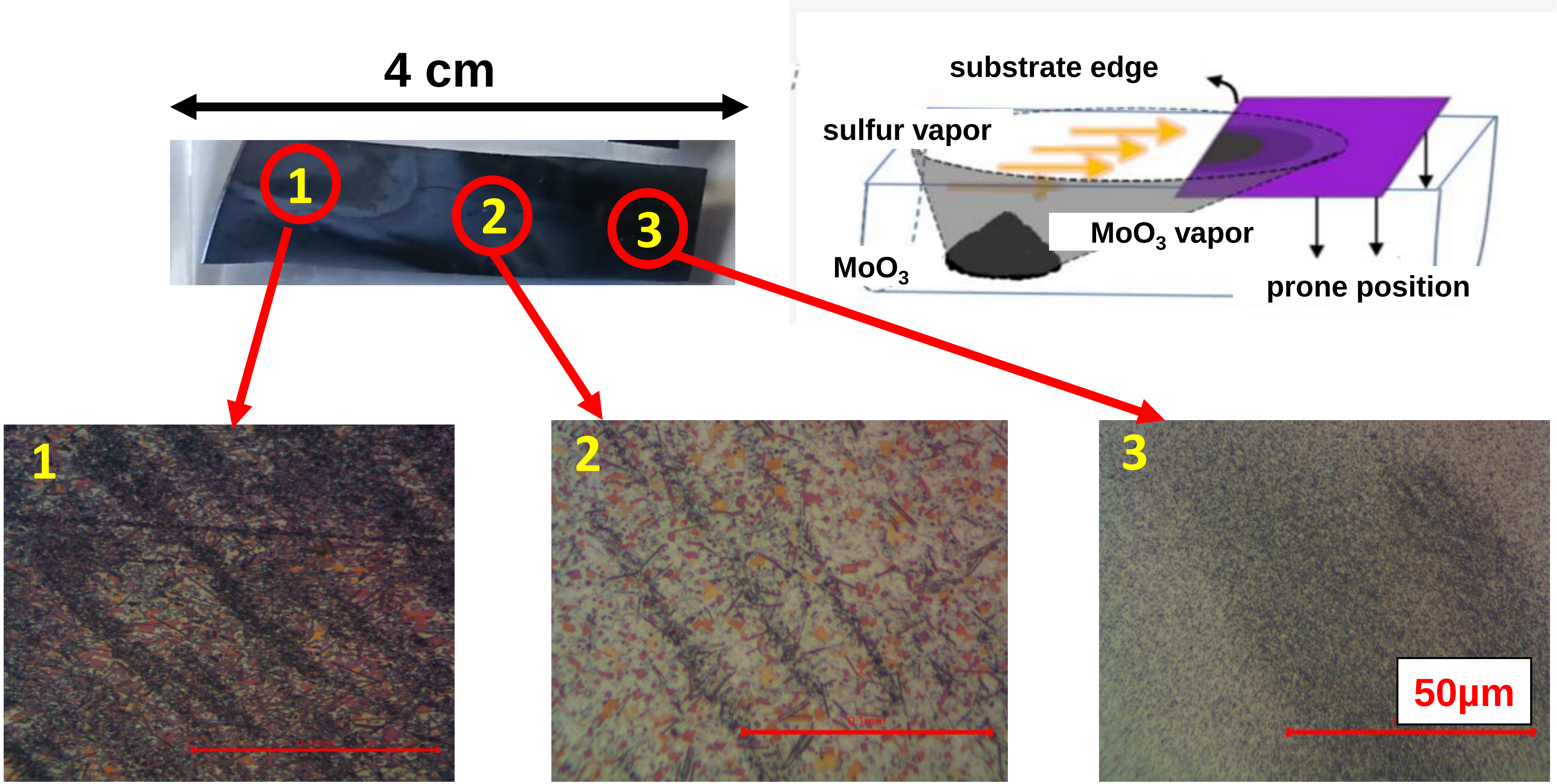
Optimization of parameters to reduce the number of layers grown

Mass of precursor, position and orientation of the substrate

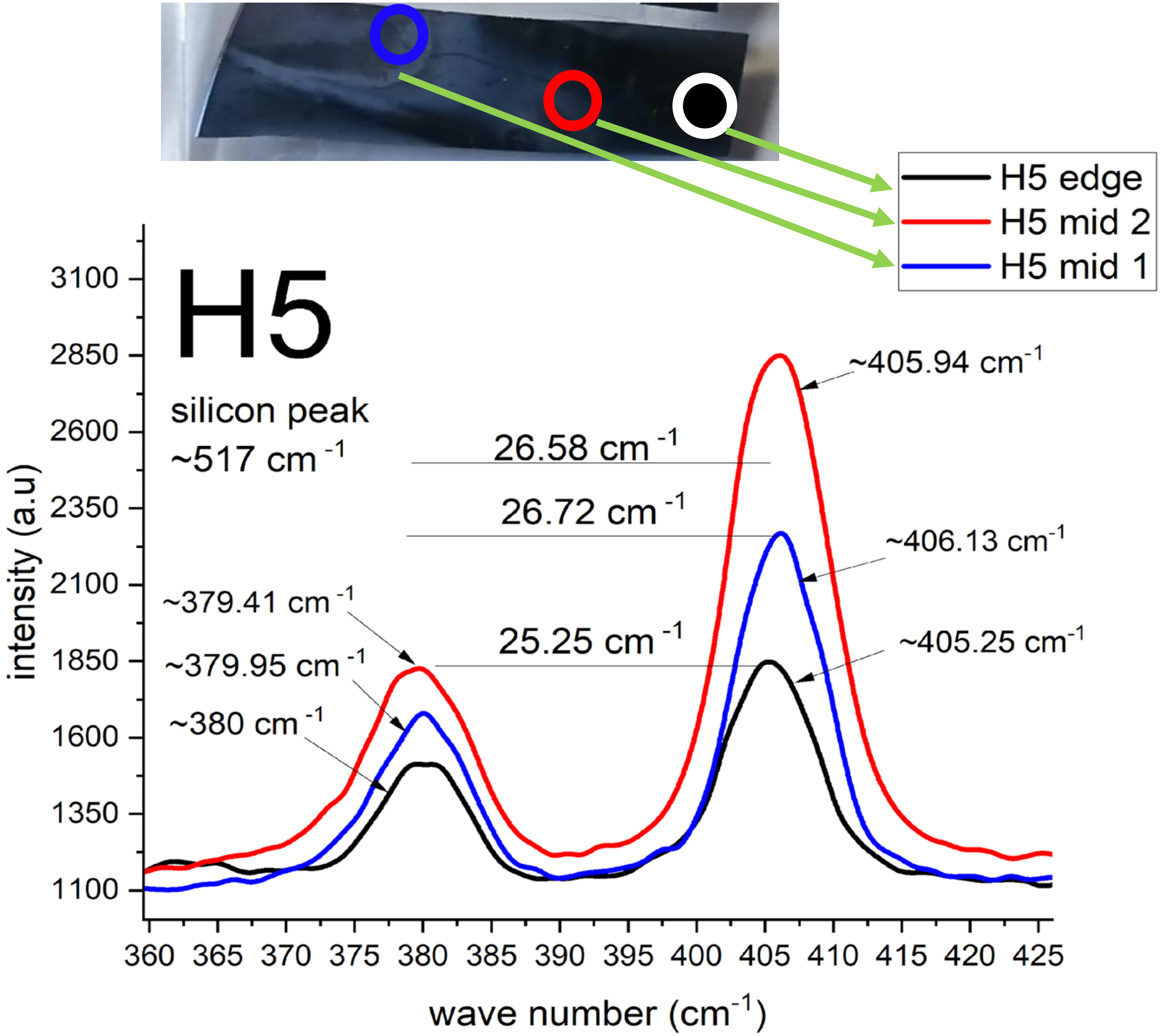
	H1, H2	H3, H4	H5, H6	H7,8,9
Substrate	Si	Si	Si	Si
MoO_3 (mg)	13.8	8.3	5	7
S (g)	6	4	4	6
Set temperature (°C)	800	800	800	800
Growth temperature (°C)	832.6	832.6	832.6	825.3
Gas	Ar	Ar	Ar	Ar
Working pressure (torr)	2.1	2.1	2.1	2.1
Gas flow (sccm)	100	100	100	100
Growth time (mins)	15	15	7	10

- Reduced mass of precursors.
- Position and orientation varied.

Effect of precursor to substrate distance

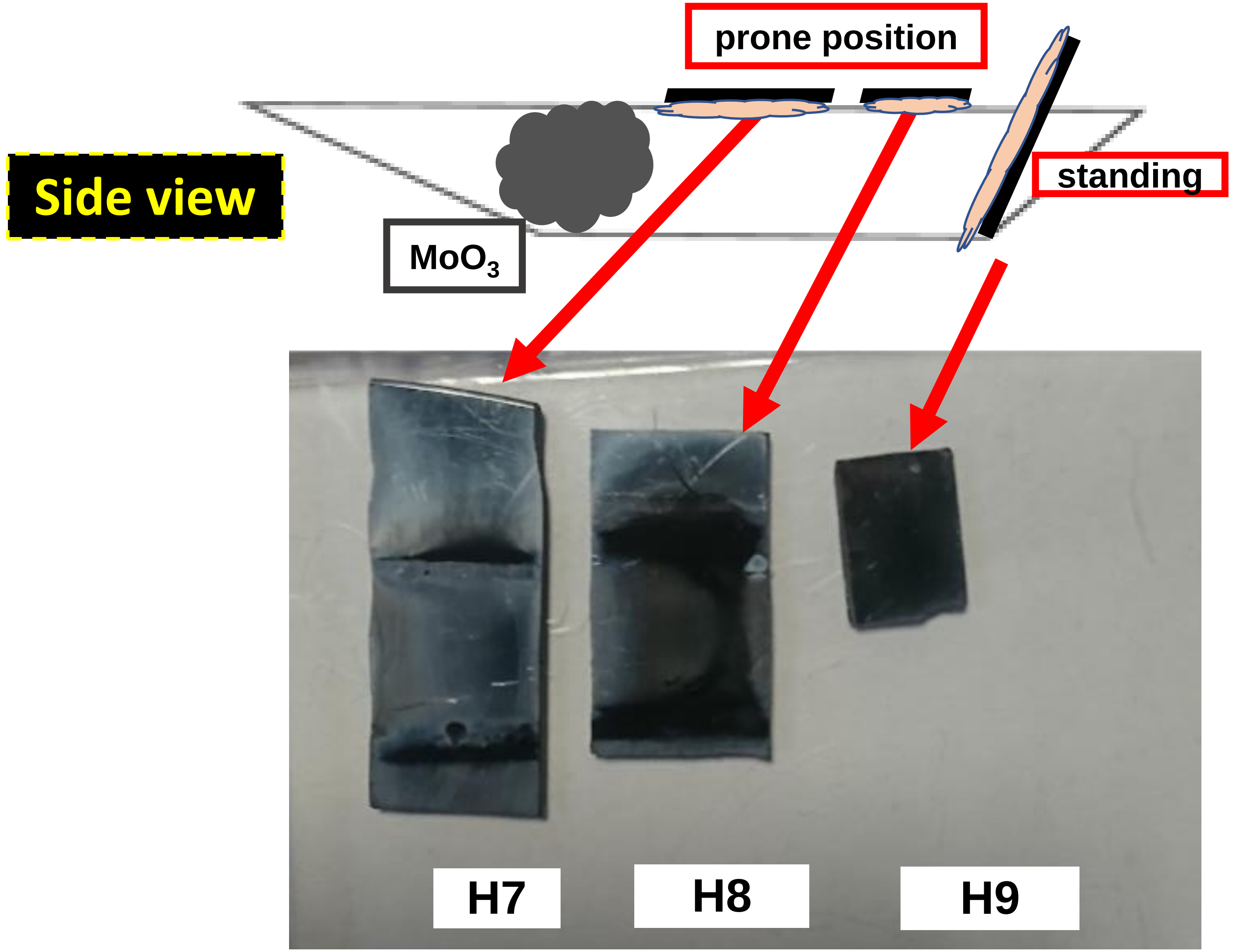


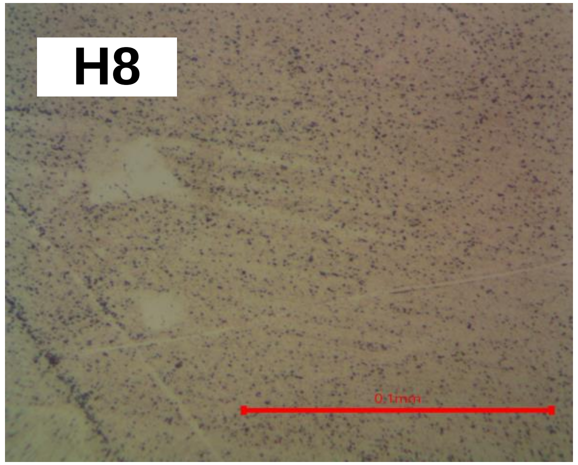
Raman analysis for varying distances from the precursor

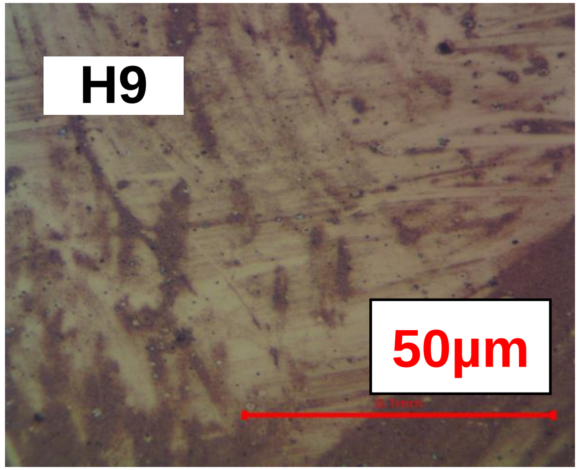


- **<u>First goal of SPROJ B achieved!</u>**
- Peak separation 27cm^{-1} represents bulk, and 25.3cm^{-1} represents **<u>5 atomic layers</u>**, we see this gradient of atomic layers along the length of sample H5.
- As we move further away from the precursor, we see a decrease in peak separation.
- This allows us to conclude that the position of the substrate and its distance from the precursor is vital to the growth of atomic layers.

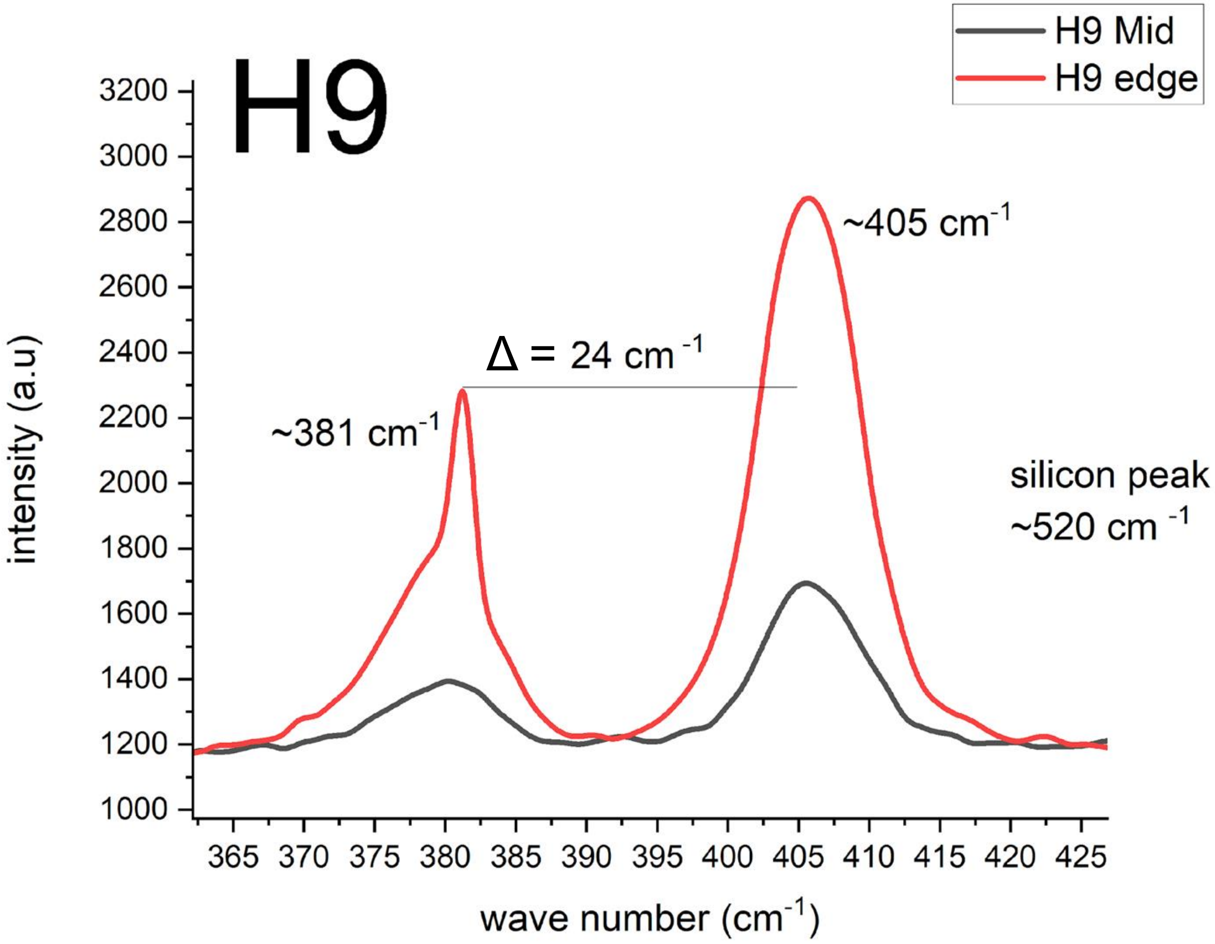
Effect of substrate Orientation







Raman analysis for the change in orientation



- This sample was kept in standing.
- From our reference Raman plot, a peak difference of 24 cm^{-1} corresponds to the presence of **<u>4 atomic layers.</u>**
- First optimization set allowed us to realize that **<u>distance and orientation</u>** of the substrate are vital to the growth of atomic layers.

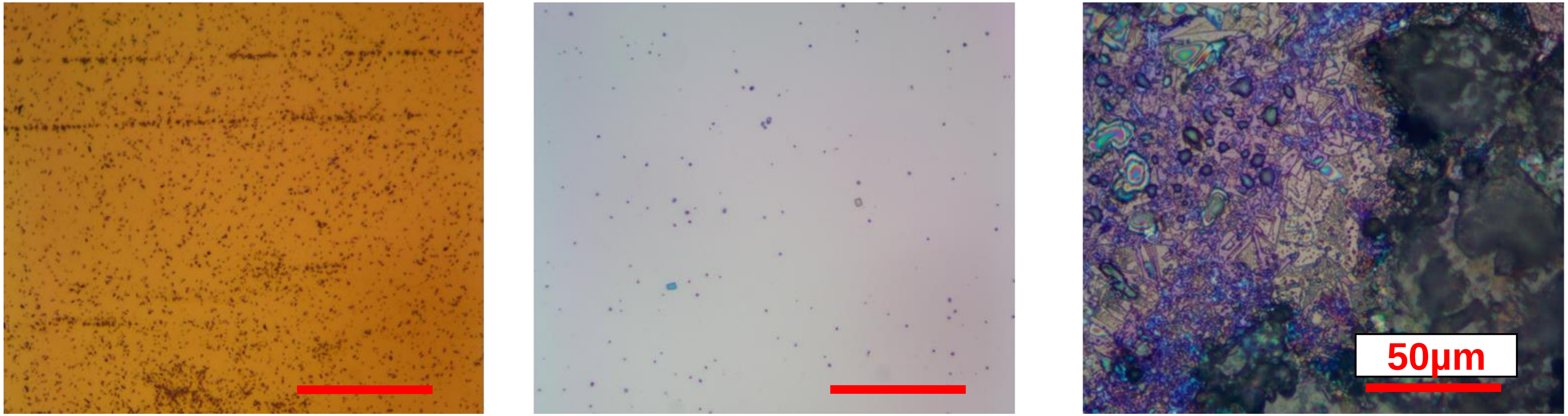
Alkali metal assisted growth of MoS_2 films

Purpose of using alkali metals in assisting growth

	H19	H30,31,32	H33,34,35
Substrate	Si	Si	Si
MoO_3 (mg)	10	5	5
NaCl	15	15	15
S (g)	2.00	2.00	2.00
Set temperature (°C)	800	800	800
Growth temperature (ºC)	800	800	832.6
Gas	Ar	Ar	Ar
Working pressure (torr)	2.1	2.1	2.1
Gas flow (sccm)	100	100	100
Growth time (mins)	10	10	10

- NaCl used: cost effective catalyst.
- Reduces temperature required for growth.
- NaCl changes morphology (can enhance it but may also drastically affect it).

Optical Images of NaCl assisted growth

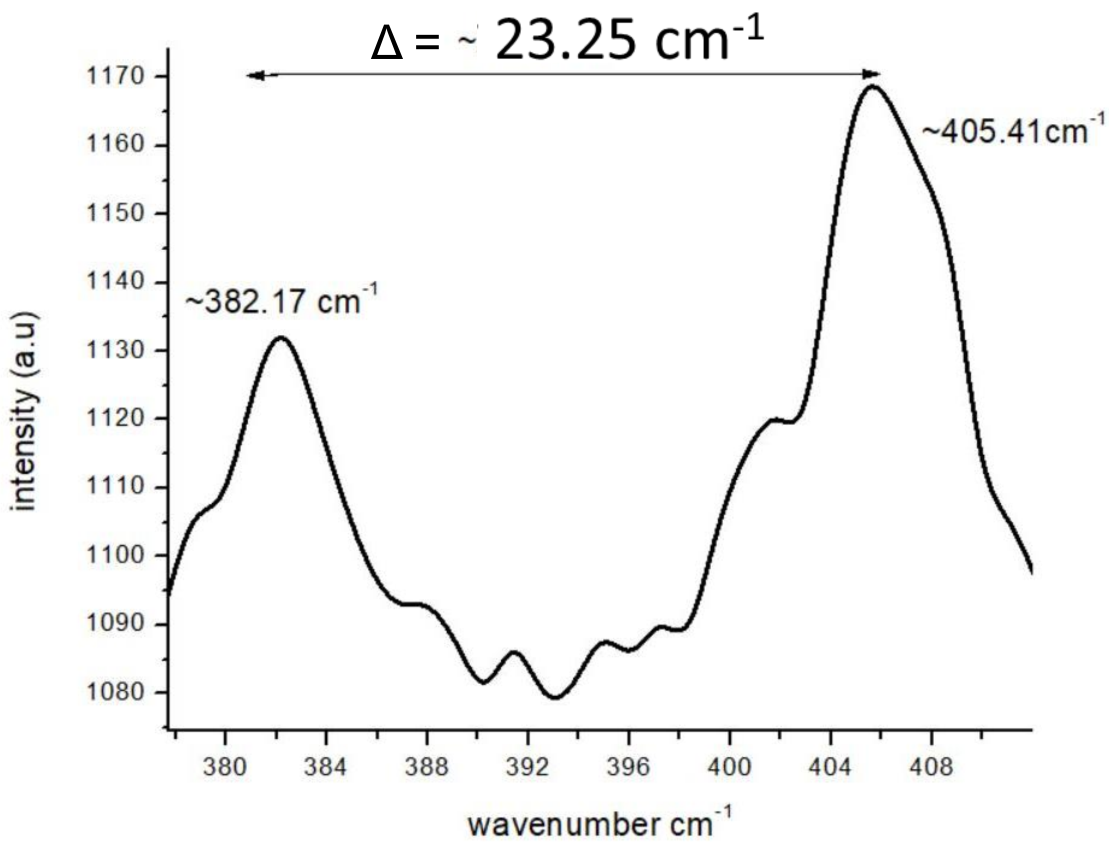


Increasing temperature and increasing NaCl to MoS_2 ratio.

Low NaCl : MoS_2 ratio

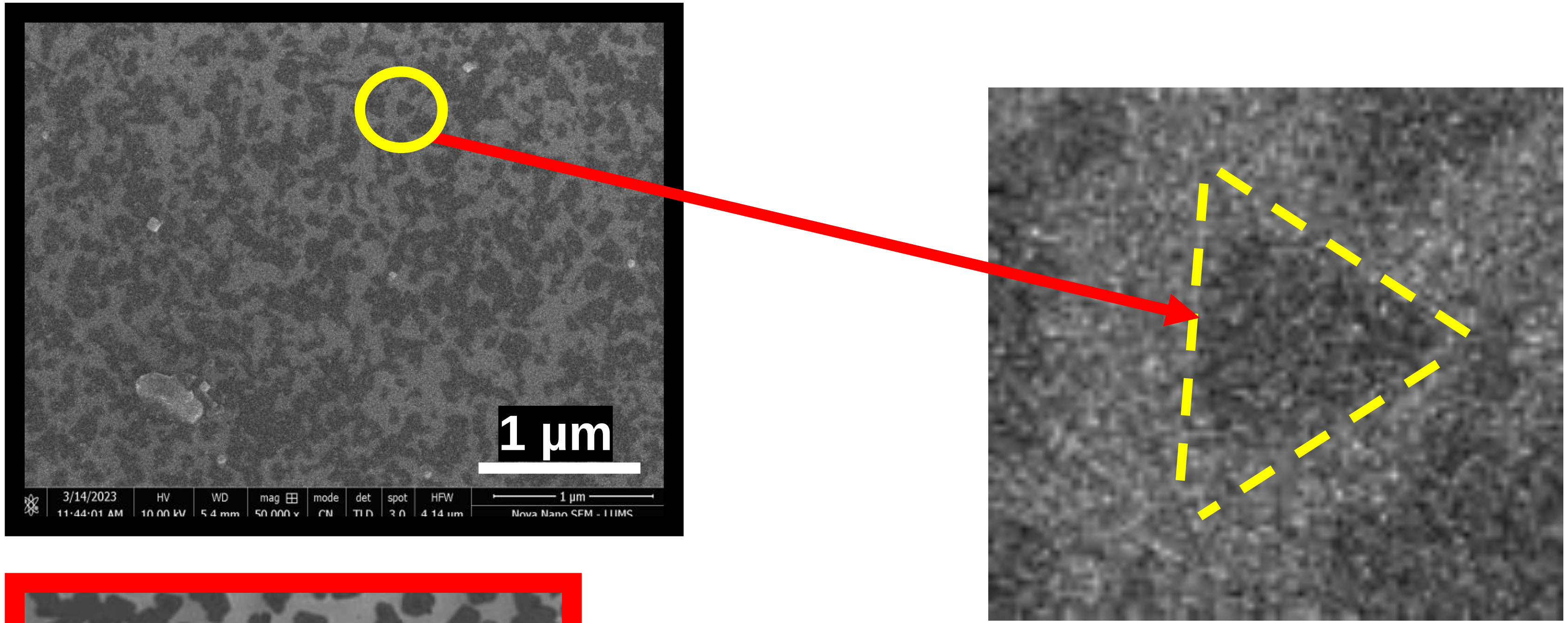
High NaCl : MoS_2 ratio

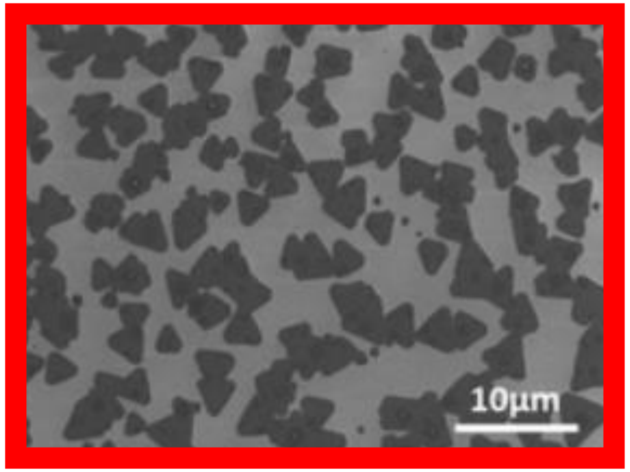
Raman analysis of NaCl assisted growth



- Using NaCl has brought down the thickness towards **3 atomic layers**.
- This can be confirmed by the peak separation of 23.25 cm^{-1} from reference.
- NaCl also improved the growth time by decreasing it.

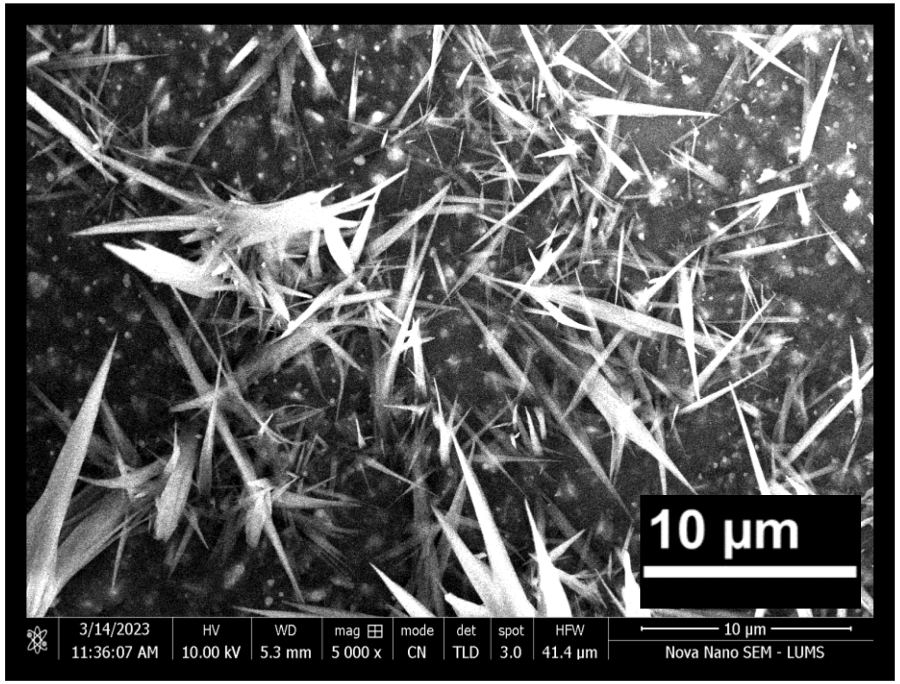
SEM images of films produced with NaCl



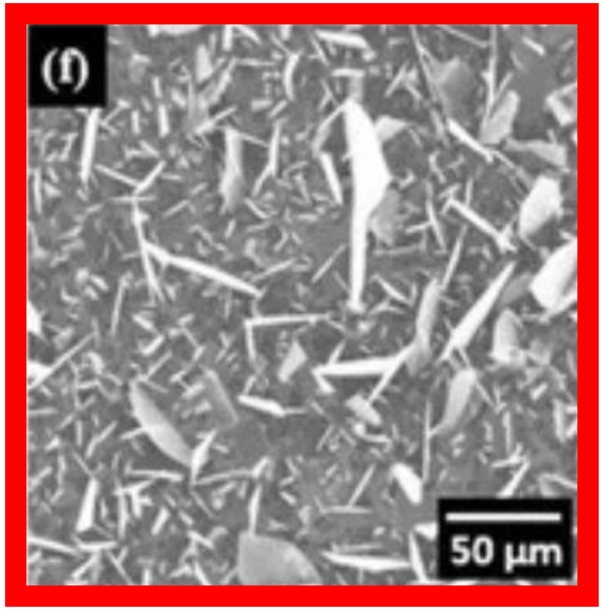


(Wang, Rong et Al. 2014)

- The image shows the film produced with triangular shapes or overlapping triangles.



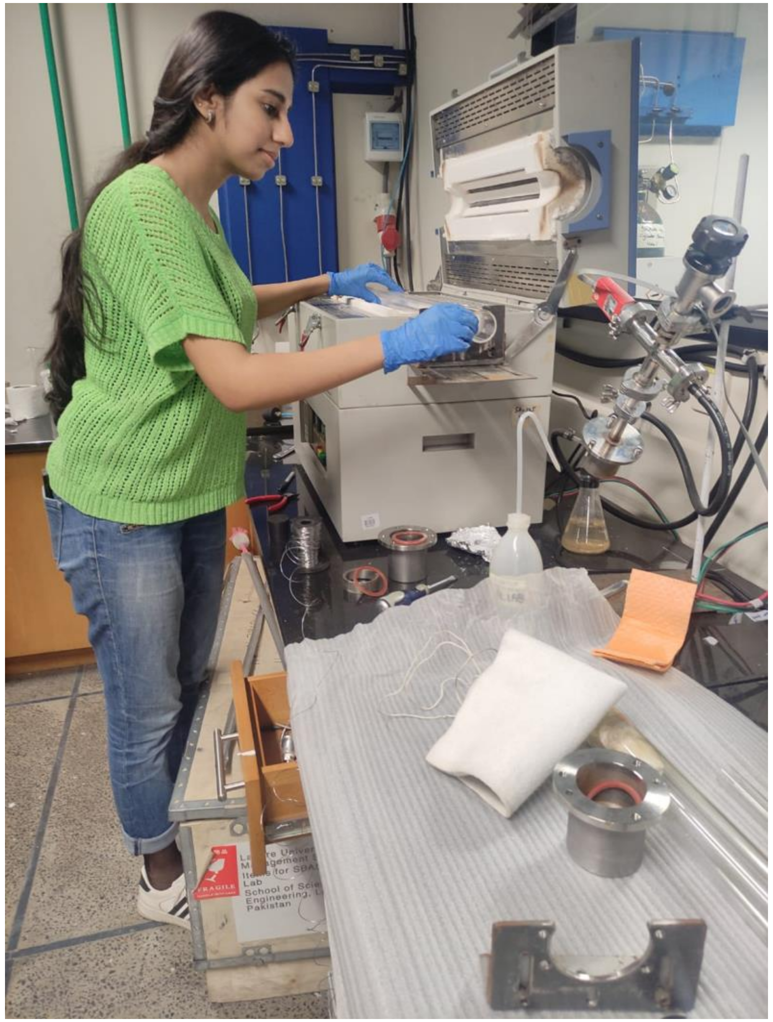
- To the left is a field of vertically standing triangular flakes of MoS_2.
- This is in line with literature which claims that the addition of NaCl alters the morphology.

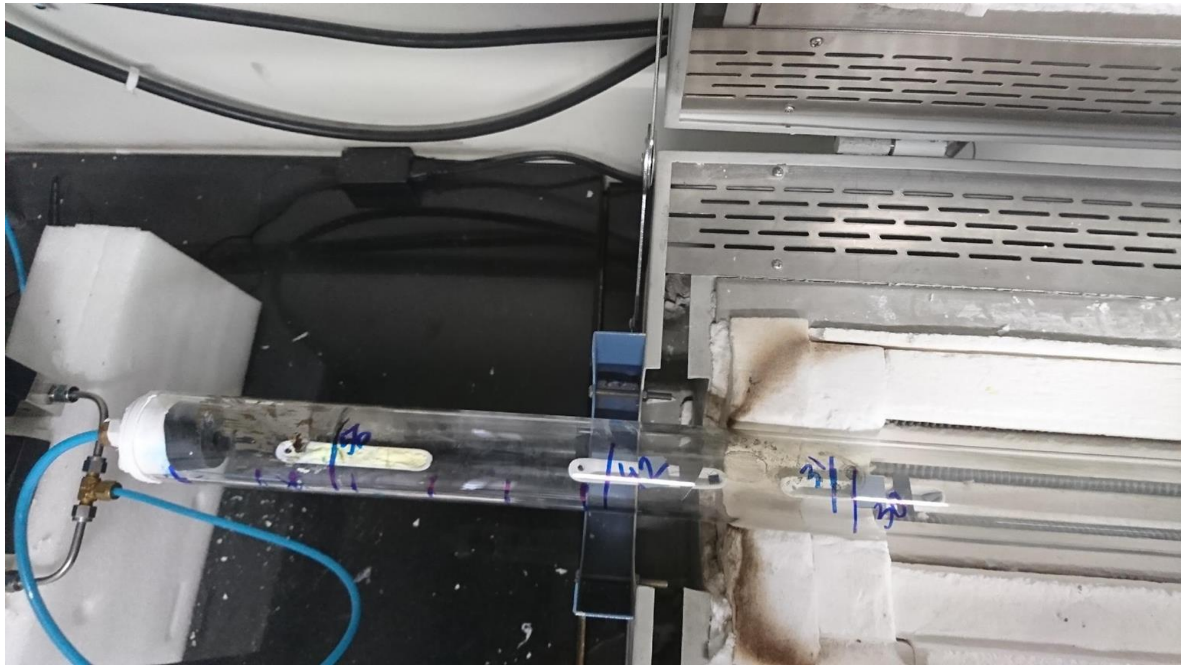


(Jian, Chang, Xu. 2018)

Creating an alternative to a double heating zone furnace

Apparatus altered to create a double zone furnace

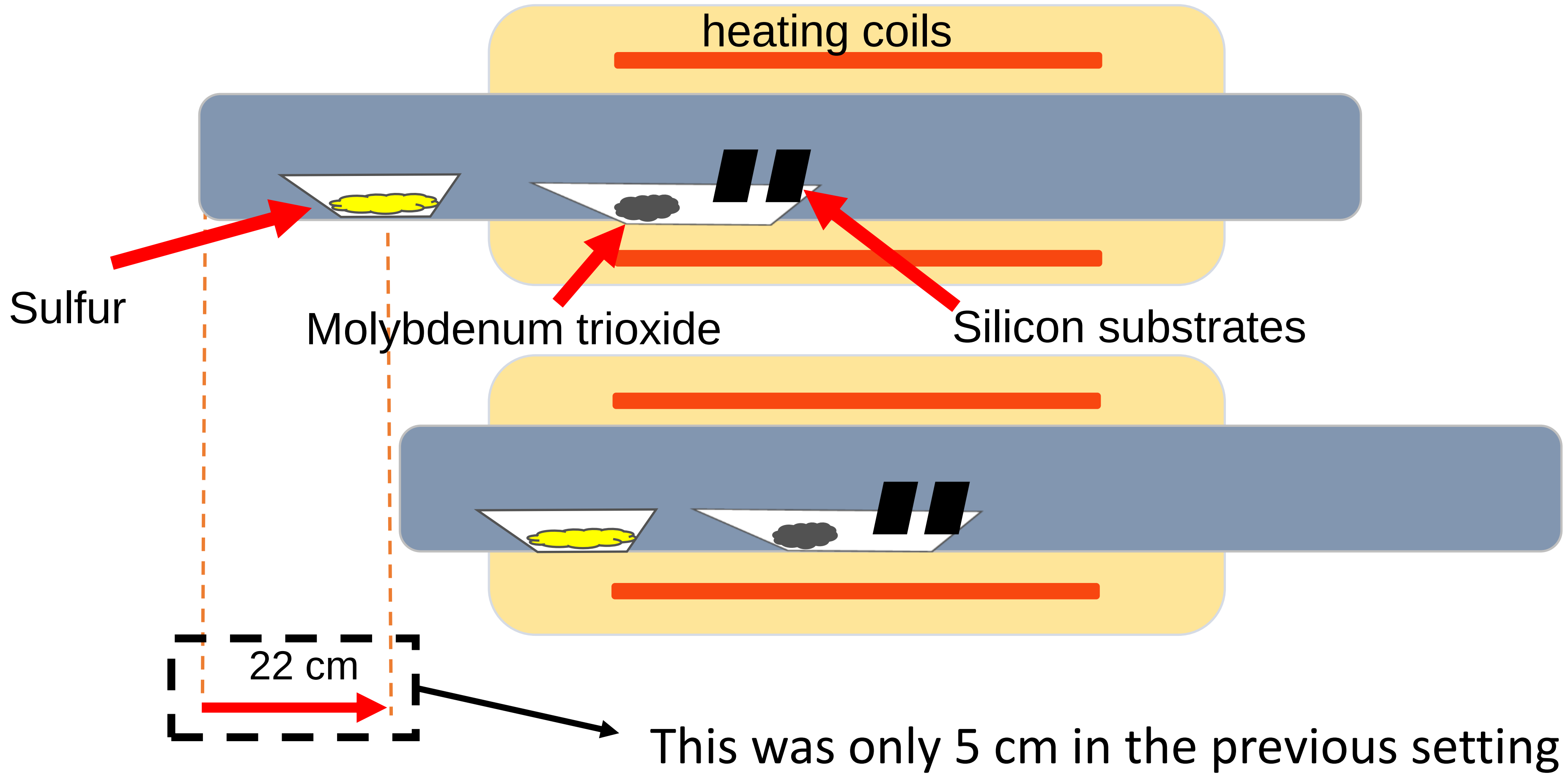




- The tube's end flanges were replaced with a cork and teflon tape combination, this was carefully secured in place.

- These changes allowed us more movement in the tube displacement, which allowed us to create a double-zone like furnace.

Altered apparatus

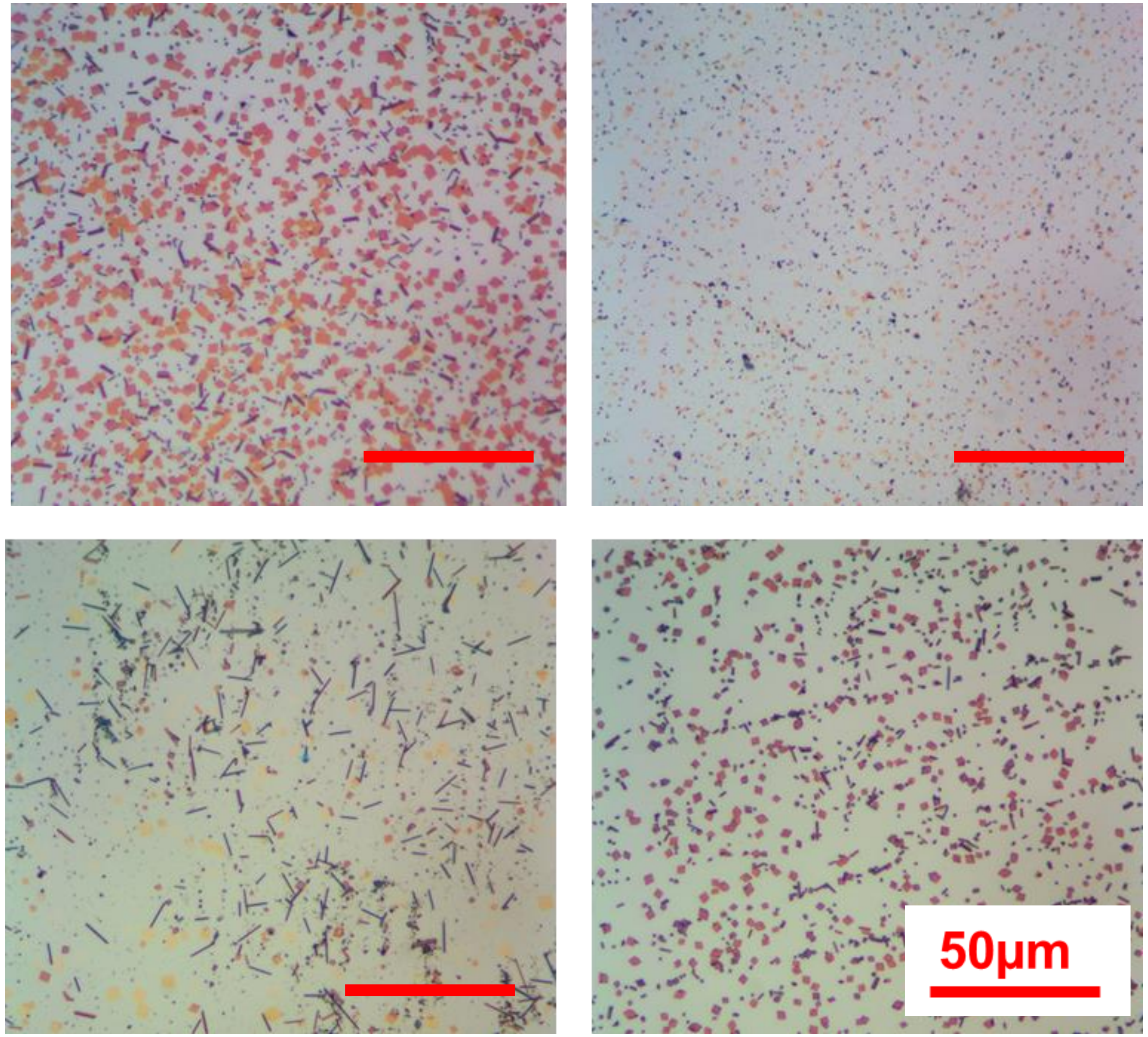


Altered apparatus

	H15	H16	H17,18	H20,H21	H22	H23	H24	H25	H26,27	H28,29
Substrate	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
MoO_3 (mg)	5.00	4.90	2.50	5.00	5.00	5.00	3	0.5	10	8
S (g)	4.00	1.15	2.00	0.4	0.8	0.8	0.8	0.8	1.6	6
Set temperature (°C)	800	800	800	800	800	700	800	800	800	800
Growth temperature (ºC)	832.6	832.6	832.6	832.6	832.6	760	832.6	832.6	832.6	832.6
Gas	Ar	Ar	Ar	Ar	Ar	Ar	Ar	Ar	Ar	Ar
Working pressure (torr)	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Gas flow (sccm)	100	100	100	100-200	100-200	100	100	200-235	235	100
Growth time (mins)	25	7	10	10	7	15	7	7	7	10

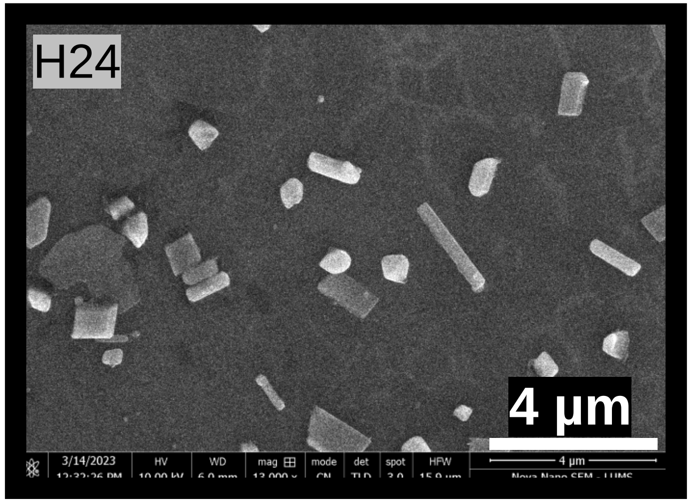
- The precursors were further decreased.
- The displacement of the tube was varied greatly by changes to the apparatus.
- Gas pressure was varied.
- Position of the substrate with respect to the precursor was varied.

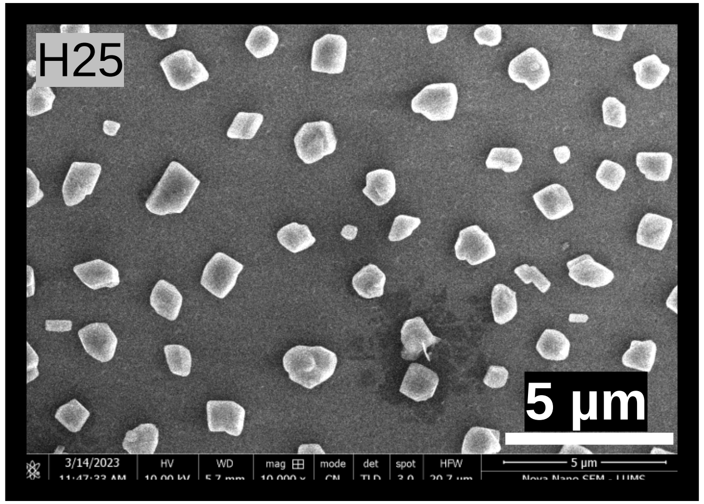
Optical Images

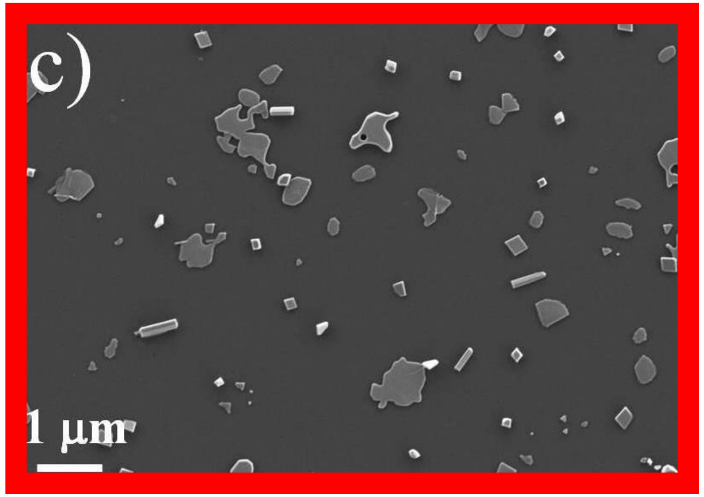


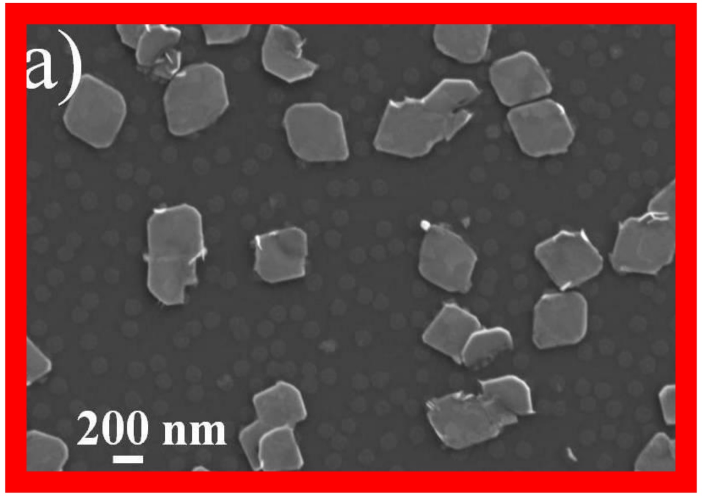
- The images are instantly cleaner and sharper once the double zone is created.
- Rods, squares and quadrilateral shapes are visible with clear outlines.

SEM images and more clues!



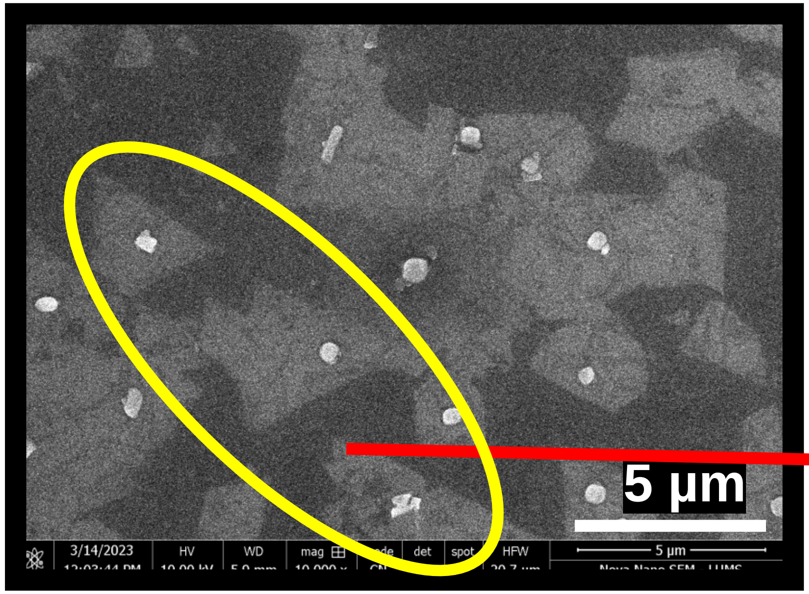


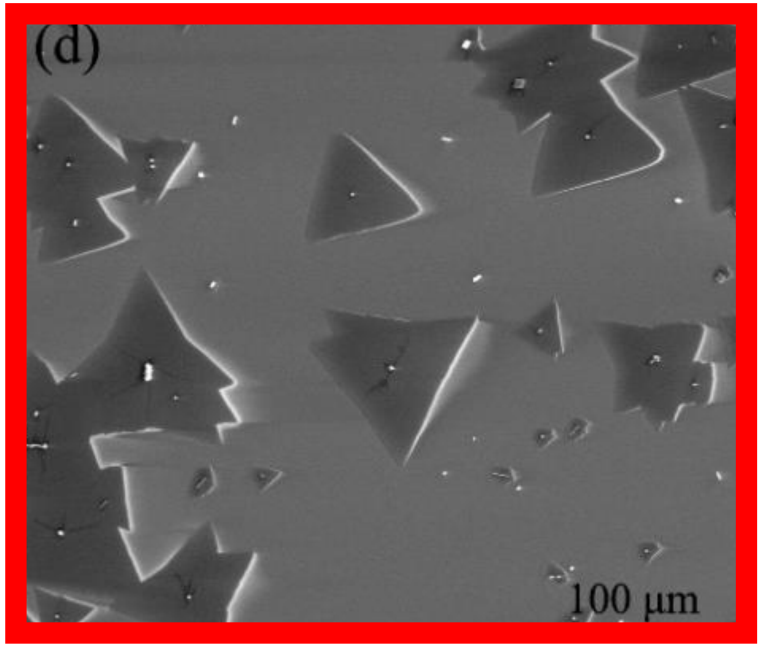


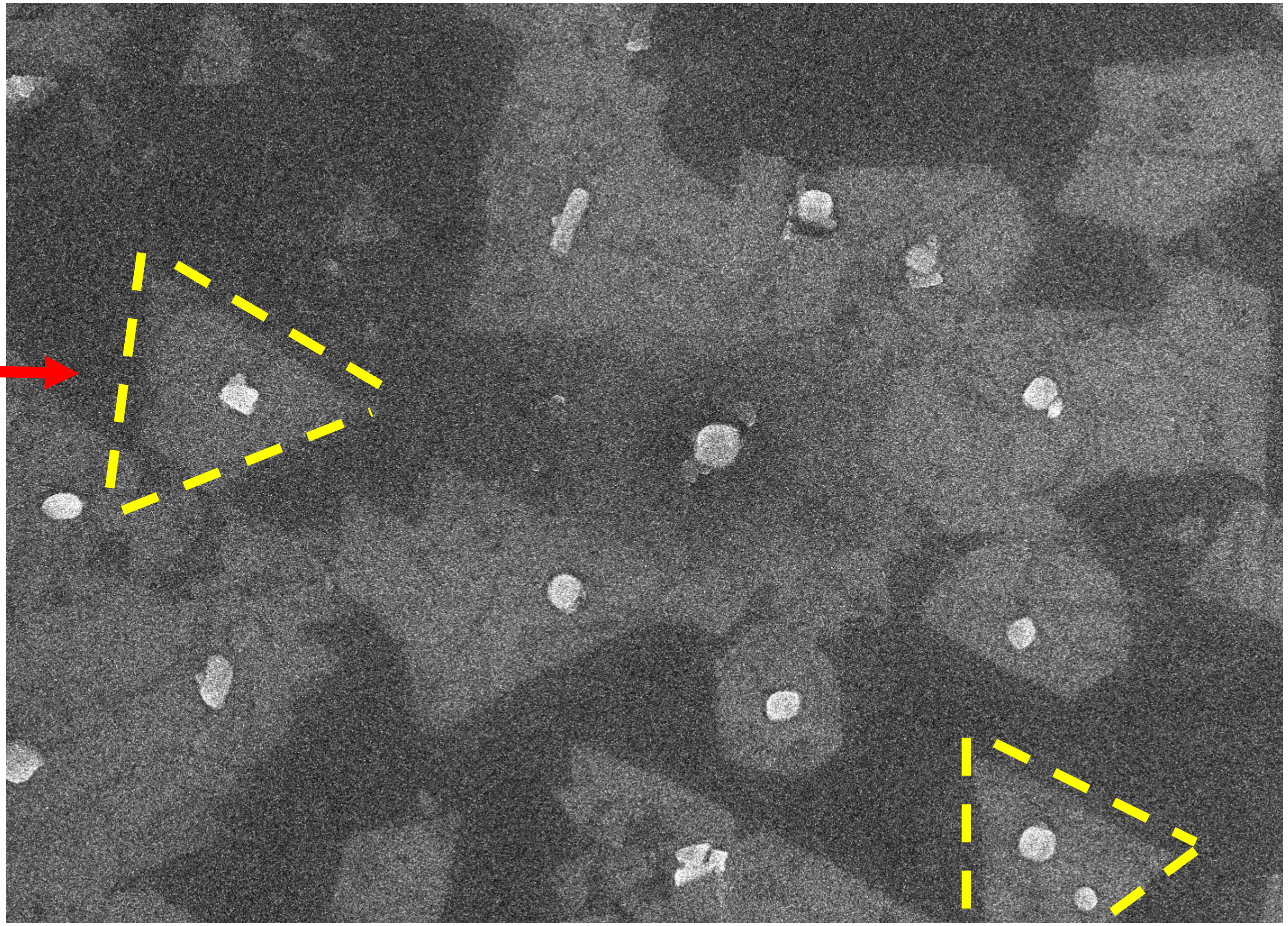


- Rod-like structures and quadrilaterals are visible.
- There appear to be flakes in the background and the foreground.
- The images in the bottom row were taken from a paper that produced MoS_2 the same way as us.

(John, Dhara.)

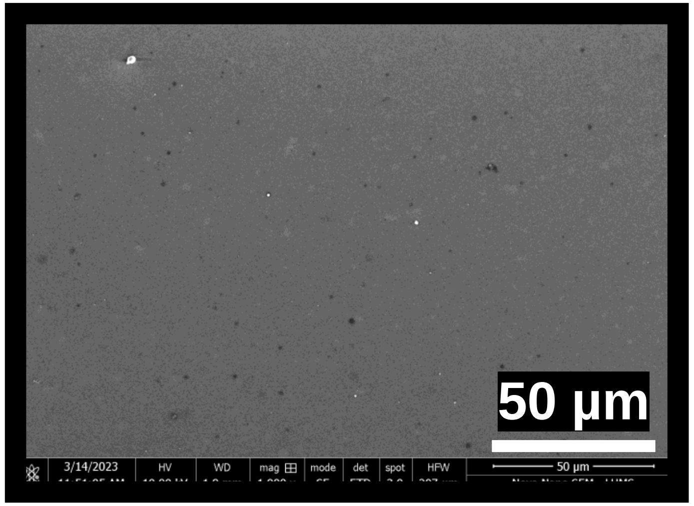


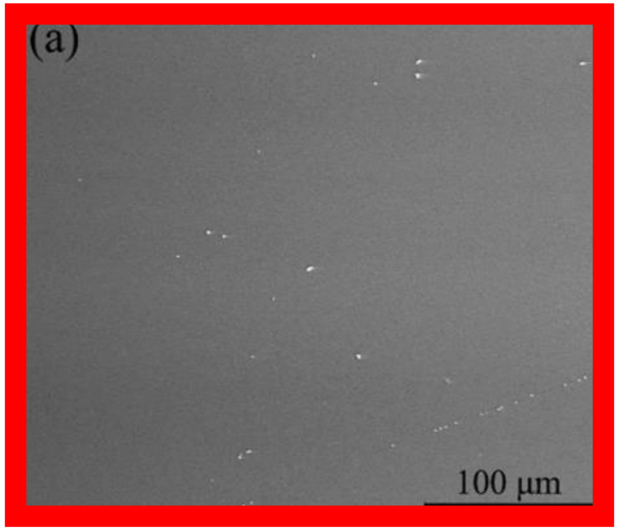




(Jian, Xang, Ju. 2019.)

Towards a continuous monolayer



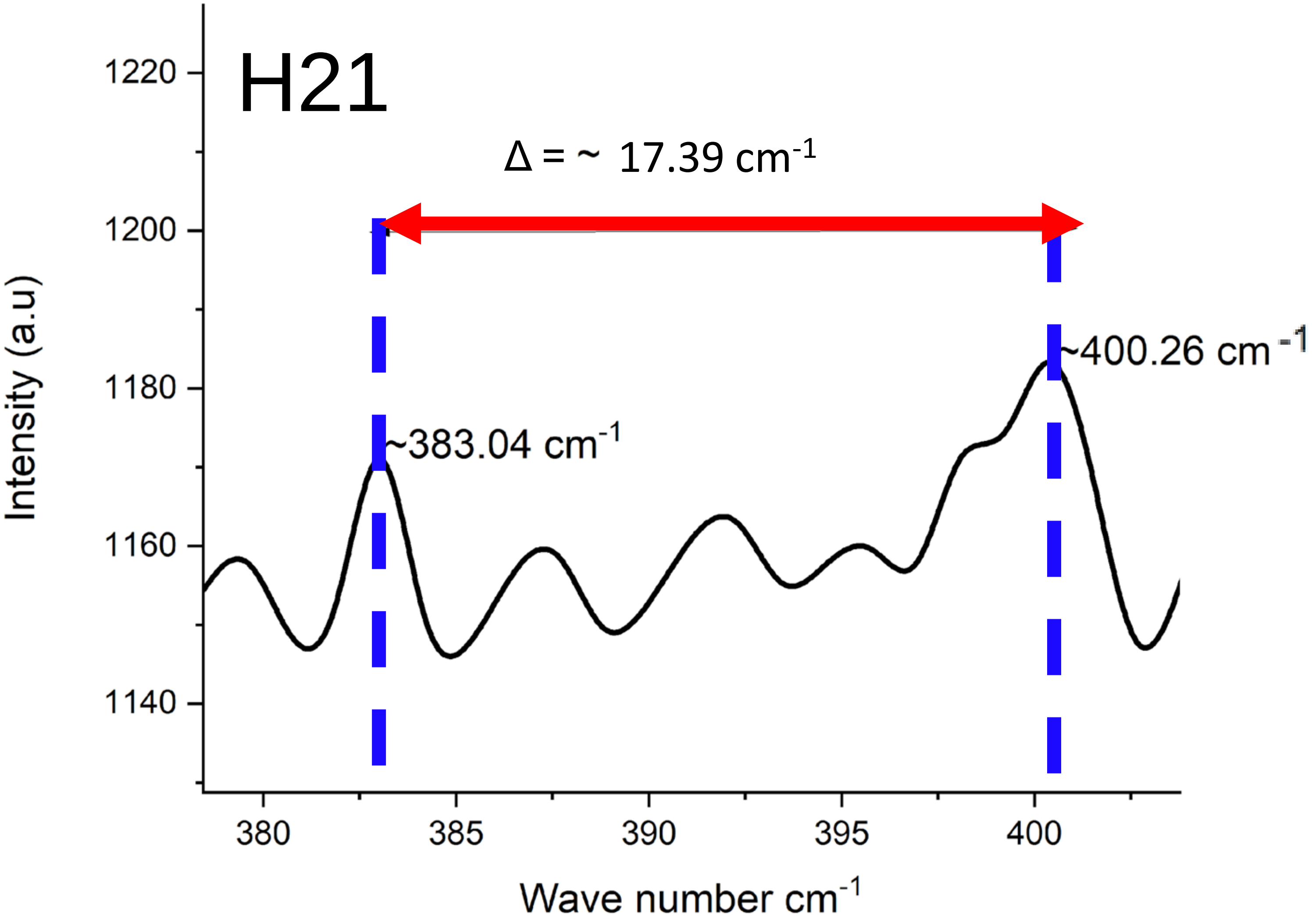


(Jian, Xang, Ju. 2019.)

- The image shows our results for this monolayer which appear to be a continuous film with a few flakes in the foreground

- The reference image for a monolayer taken from the literature shows an almost similar image of a continuous film!

A noisy monolayer!

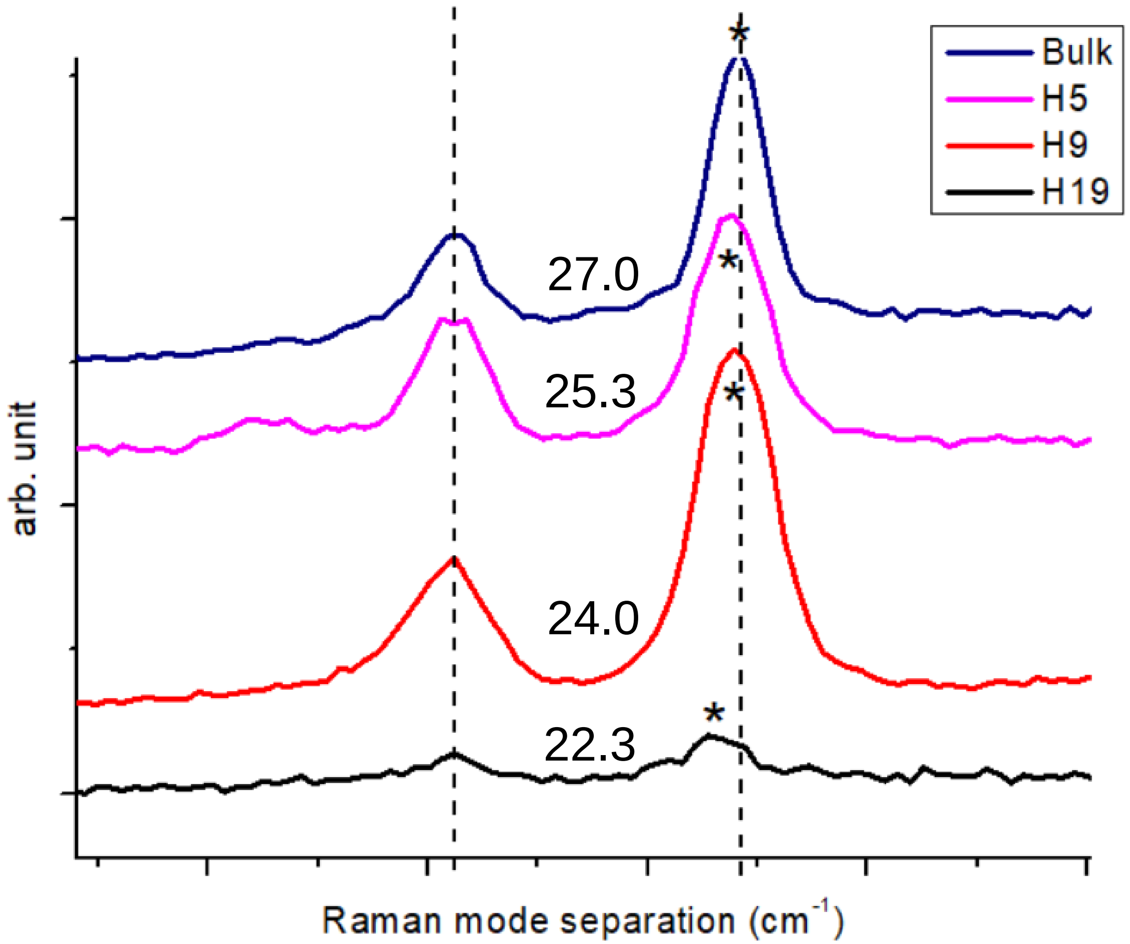


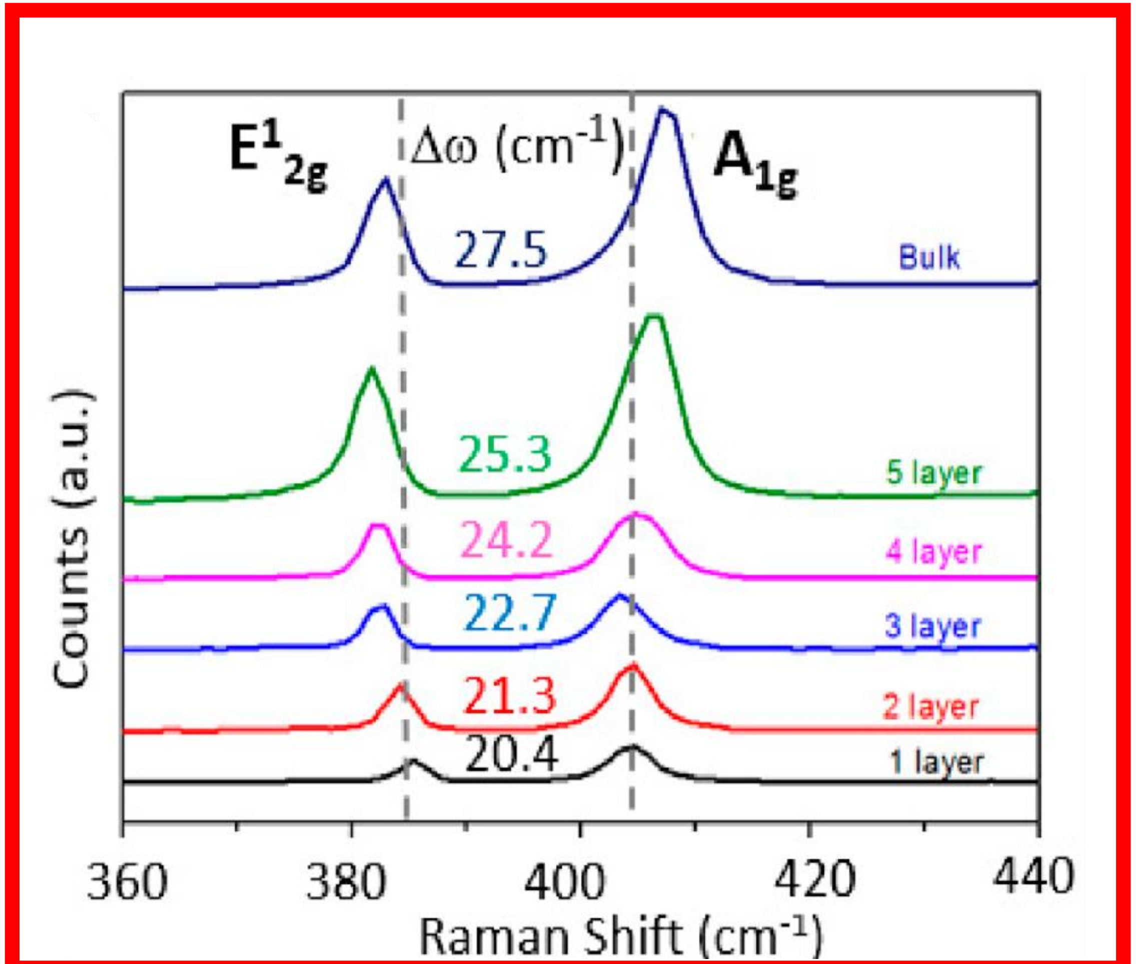
- When deposition on the film is very less, it's detected signal from Raman can become very weak in strength.

  These peaks appeared clearly in the Raman data but became very noisy once plotted.

- **<u>The peak separation of 17.39 cm^{-1} indicates the presence of a monolayer.</u>**

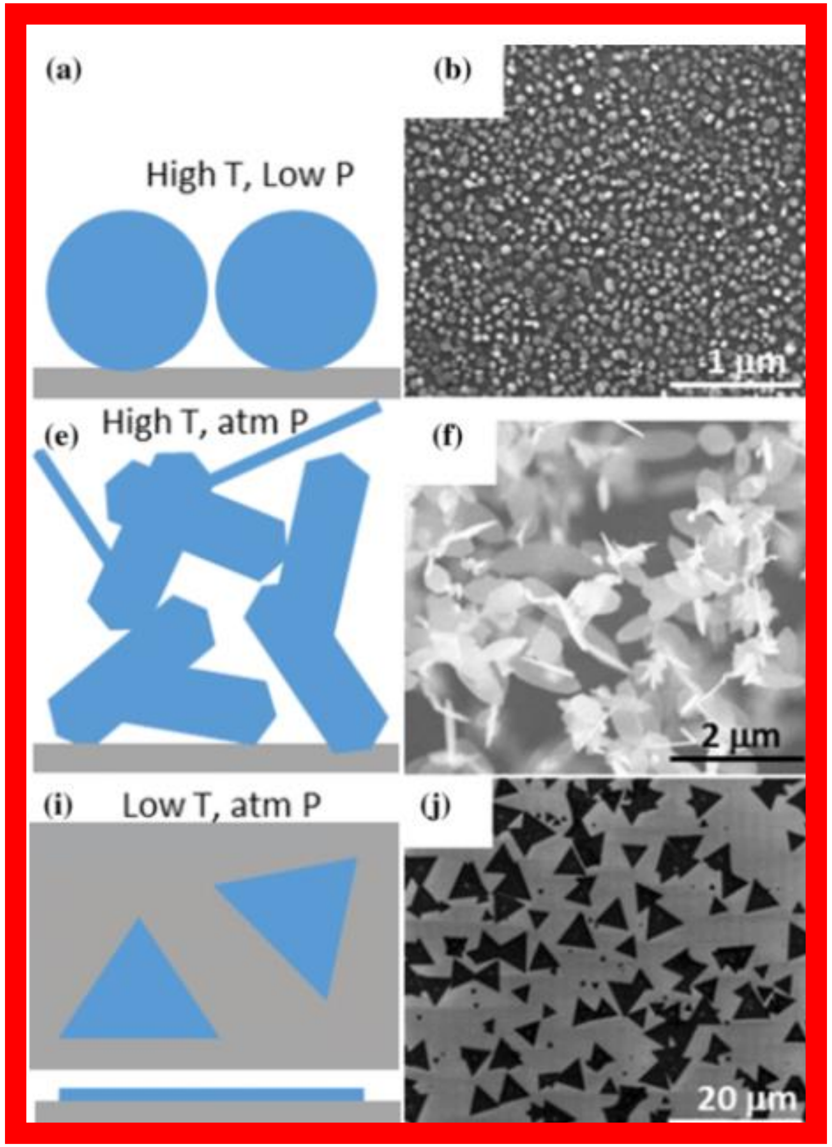
Best results plotted!



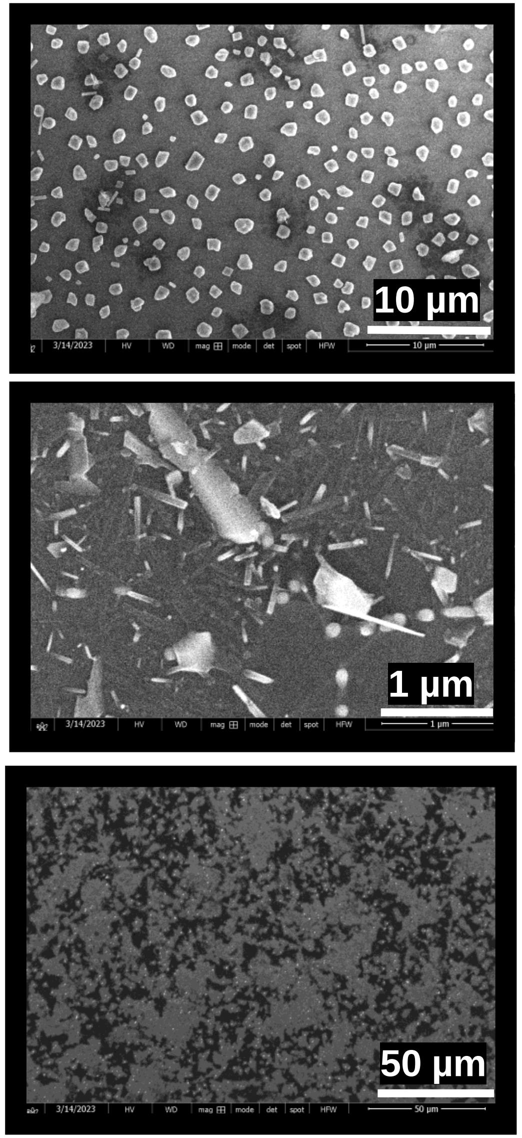


(Tummala, Lamperti *et al.* 2020)

Conclusion and future remarks



Our results



- The reference image shows the effect of temperature and pressure.
- Our results to the right show similarity to the reference image.

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