Large Area Deposition of MoS_2 By Pulsed Laser Deposition With *In-Situ* Thickness Control

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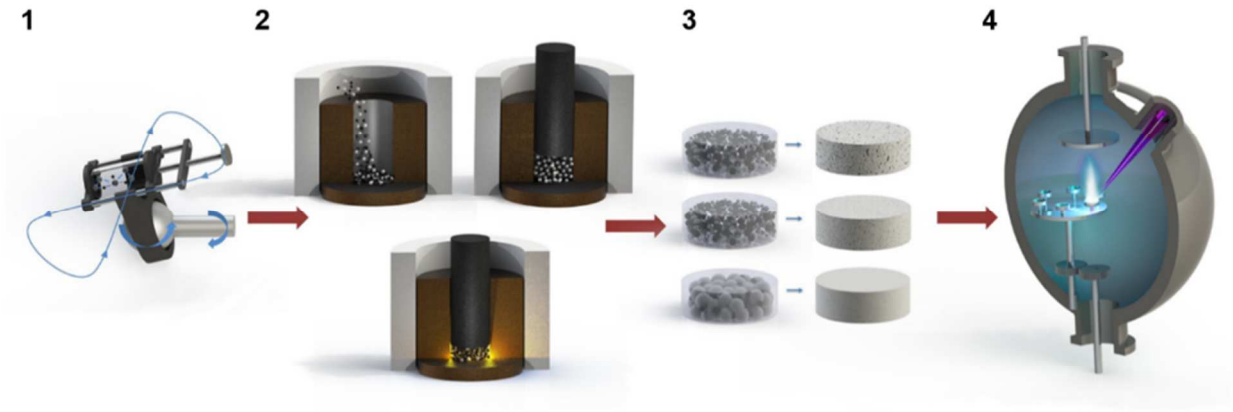

Figure S1. Target fabrication and process flow chart for the fabrication of MoS_2 Thin films.

Target fabrication

Powders of MoS_2 and S were mixed and the hot pressed to create three different targets with different densities as reported in Table 1. Target 100ºC / 2 µm and 75ºC / 2µm were fabricated with the same particle size and different hot press conditions, while target 75ºC / 43µm was fabricated with a larger (43µm) MoS_2 particle size and 75°C for 3 hours with a powder

compression of 18 ton-force. Figure S1. shows the target non-scale particle size. The thin film deposition was carried in separate processes with identical conditions. The films are named with the same nomenclature as the corresponding targets.

Table 1. MoS_2 target fabrication conditions. Targets 100°C / 2 µm to 75°C / 43 µm have a sulfur particle size of 20 µm with variable MoS_2 particle size.

Processing Condition	100°C / 2 µm	75°C / 2 µm	75°C / 43 µm	Commercial
MoS_2 size (µm)	2	2	43	N/A
Milling Process	SPEX milling	SPEX milling	SPEX milling	Commercial brand
Hot pressed condition	100 °C 1h / 25 Ton	75 °C 3h / 18 Ton	75 °C 3h / 18 Ton	N/A
MoS_2:S ratio	1:1	1:1	1:1	1:0
Relative density %	88.1	88.7	99.9	N/A

Precursor costs

PLD:

For the process of 10 min of deposition time the target cost is estimated as follows:

MoS_2 and S powders for targets 75ºC / 43µm, 75ºC / 2µm, 100ºC / 2µm

For each target 11.17 gr. of MoS_2 powder and 2.23 gr. Sulfur powder were used.

- Sulfur (20 µm particle size)

  US$ 125.7 /50 gr. ($2.514/ gr)

- MoS_2 (43 µm particle size)

  US$ 64.15 / 100 gr. ($0.6415 / gr)

- MoS_2 (2 µm particle size)

  US$ 93.6 / 100 gr ($0.936 / gr)

Table 2. Materials cost for MoS_2 target fabrication					
Target	**Sulfur (US$ / g)**	**MoS_2 (US$ / g)**	**Sulfur (g)**	**MoS_2 (g)**	**Target cost (US$)**
100°C / 2 µm	2.5	0.936	2.23	11.17	16.06
75°C / 2 µm	2.5	0.936	2.23	11.17	16.06
75°C / 43 µm	2.5	0.641	2.23	11.17	12.77

CVD

Prices as of April 6 2016

- $Mo(CO)_6$

0.01 sscm per 26 hours = 15.600 cm^3; $MoCl_5$ density is 2.928 g/cm^3; 45.6768 $MoCl_5$ grams were used for a total of $ 565.478 dollars

- $(C_2H_5)_2S$

0.4 sscm per 26 hours =624 cm^3; $1.22 dollars/ ml, for a total of $761.28 dollars

- H_2

5 sscm per 26 hours = 7800 cm^3 ; $4.22 dollars/ lt, for a total of $32.94 dollars

- Ar

150 sscm per 26 hours = 234000 cm^3 ; $4.61 dollars/ lt, for a total of $1078.74 dollars

Powders and thin films characterization (SEM)

The morphology of the MoS_2 thin films and the powders used for the target fabrication, was imaged using Scanning Electron Microscopy (SEM) with an electron microscope Zeiss Supra-40. **Figures S2 a,b,c,d,e,f** show the top view of each thin film and the particle shape of Sulfur and molybdenum disulfide powders. The film produced by target 75ºC / 43 µm had less particles on the surface and it appeared more superficially homogeneous than the other thin films **(Figure S2d)**

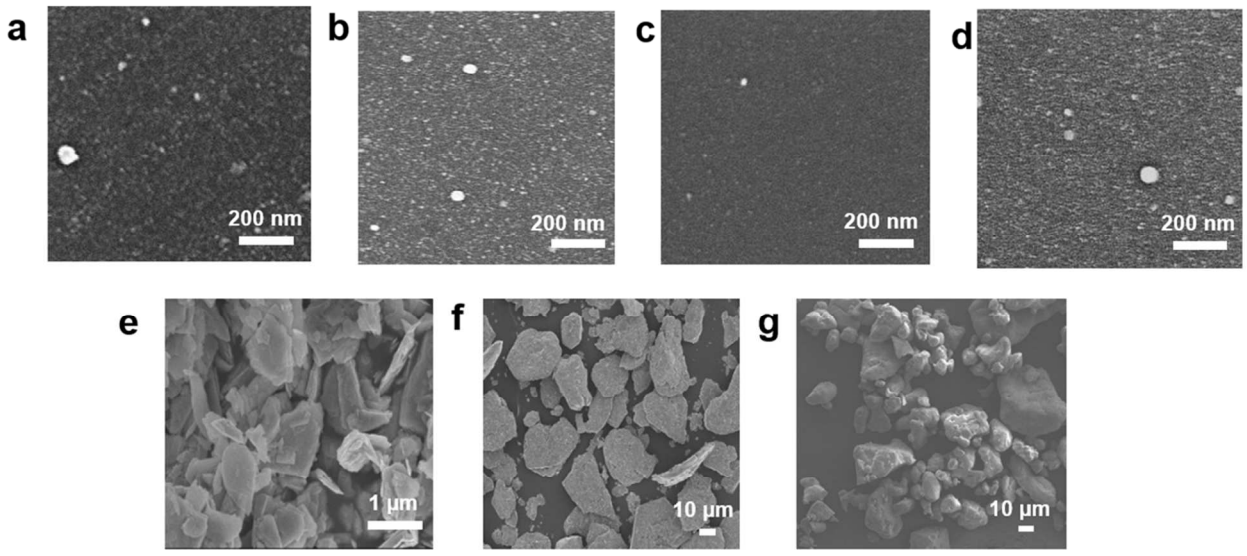

Figure S2. Scanning electron microscopy of thin films (top view) and MoS_2 and Sulfur powders. Figures S2 a, b, c, d show the top view of thin films 100ºC /2 µm, 75ºC / 2µm, 75ºC / 43 µm and T, respectively. Figures S2 e-f show MoS_2 powder of 2 µm and 43 µm. Figure S2 g shows the Sulfur particle size.

Thin film 75°C / 43µm deposited 5.08 cm diameter sapphire wafer

With thin film **75°C / 43µm** being homogeneous and presenting less particle density, it was the ideal candidate to deposit it on a 50.8 mm sapphire wafer. Thin film 75ºC / 43 µm homogenously covered the entire sapphire wafer. **(Figure S3)**

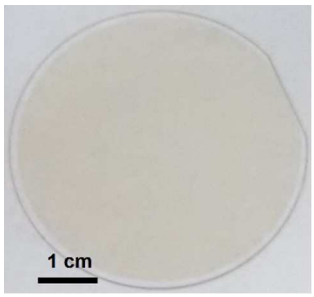

Figure S3. MoS_2 thin film 75°C / 43 µm on a two inches diameter sapphire wafer

Characterization of the samples

The Mo 3d, S 2s, and S 2p regions of the XPS spectra for samples 100ºC /2 µm, 75ºC /2 µm, 75ºC /43 µm and T are shown in **Figure S4** and the deconvolution in **Figure S5**. The Mo 3d spectra consists of peaks at around 229.5 and 232.6 eV that correspond to Mo^{4+} $3d^{5/2}$ and Mo^{4+} $3d^{3/2}$ of MoS_2, respectively. Deconvolution of peaks from samples 100ºC / 2 µm, 75ºC / 2µm, and T revealed additional peaks that were shifted to lower and higher energies with respect to the

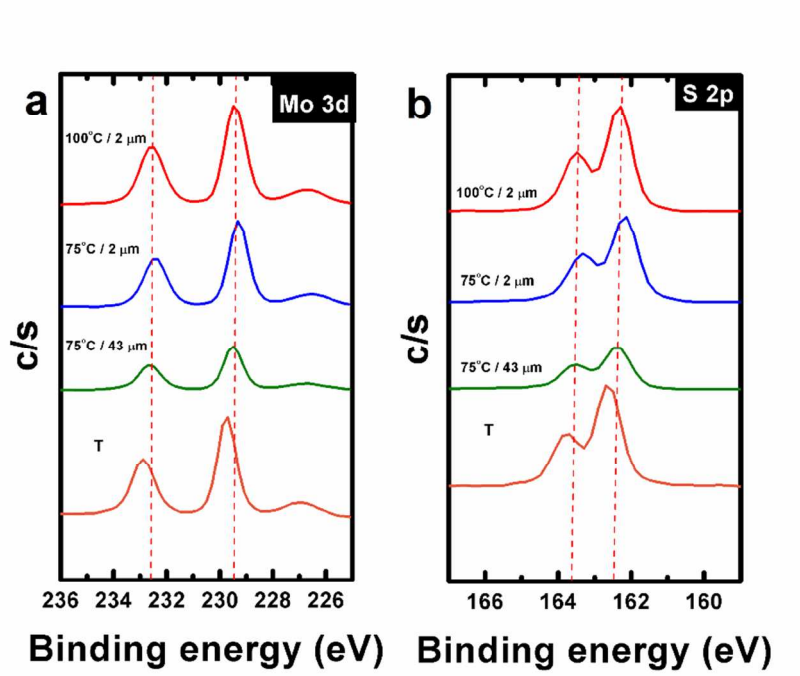

Figure S4. X-ray photoelectron spectroscopy (Fig S4a and S4b) for films deposited on sapphire. For reference, the dashed lines in each figure shows the expected binding energy or Raman shift for a stoichiometric MoS_2. The thinnest film (~1.3 nm, film 75°C / 43 µm) was deposited from the target with the highest density and seems to be the most stoichiometric

actual binding energy value of the MoS_2 peaks. In the S 2p region of the spectra, additional peaks were obtained from the doublet peaks of MoS_2, S $2p^{1/2}$ and S $2p^{3/2}$, which have binding energy at 163.6 and 162.4 eV, respectively. The shifting of these additional peaks suggests the presence of molybdenum oxides, MoS_X (with $X \neq 2$) phase, molybdenum oxysulfides, and free Mo. Furthermore, no peaks were observed between 233 and 236 eV for thin film 75ºC / 43 µm, which indicated that Mo atoms remained unoxidized.

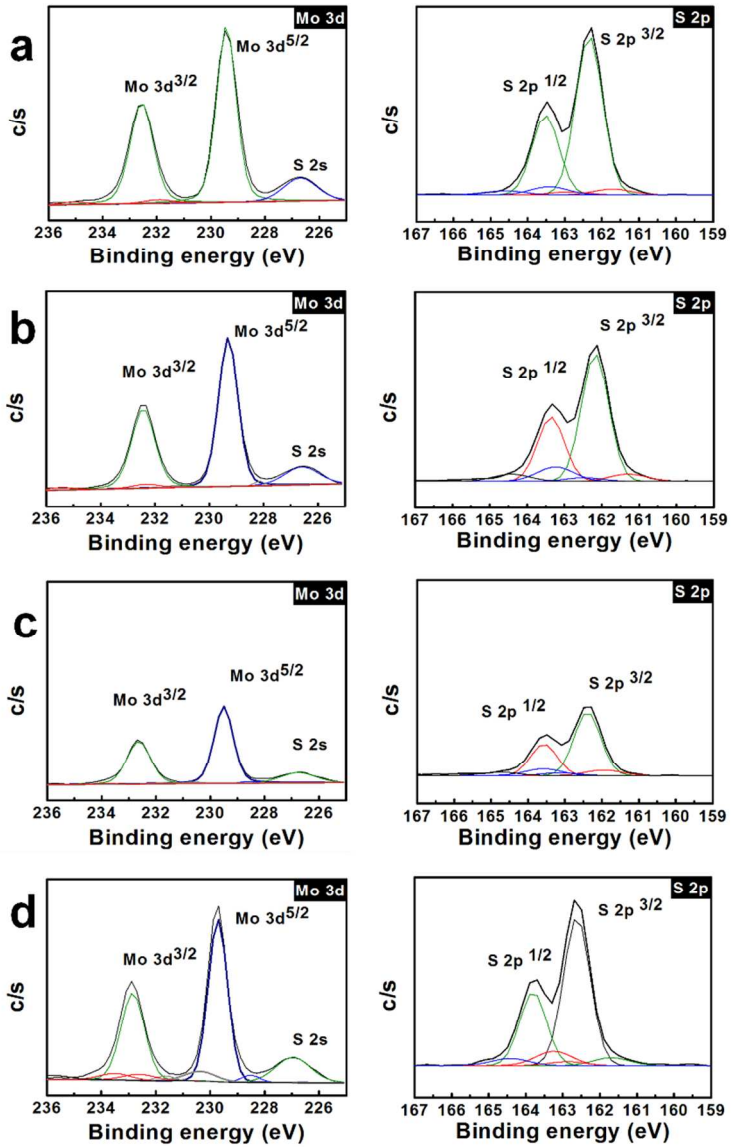

Figure S5. Deconvolutions of XPS spectra for each thin film. Thin film 100ºC /2 µm (a), Thin film 75ºC / 43 µm (b), 75ºC / 43 µm, (c), Thin film T (d). Thin film 100ºC / 2 µm showed binding energy typical of MoS_2 and two bands typical of MoO_3

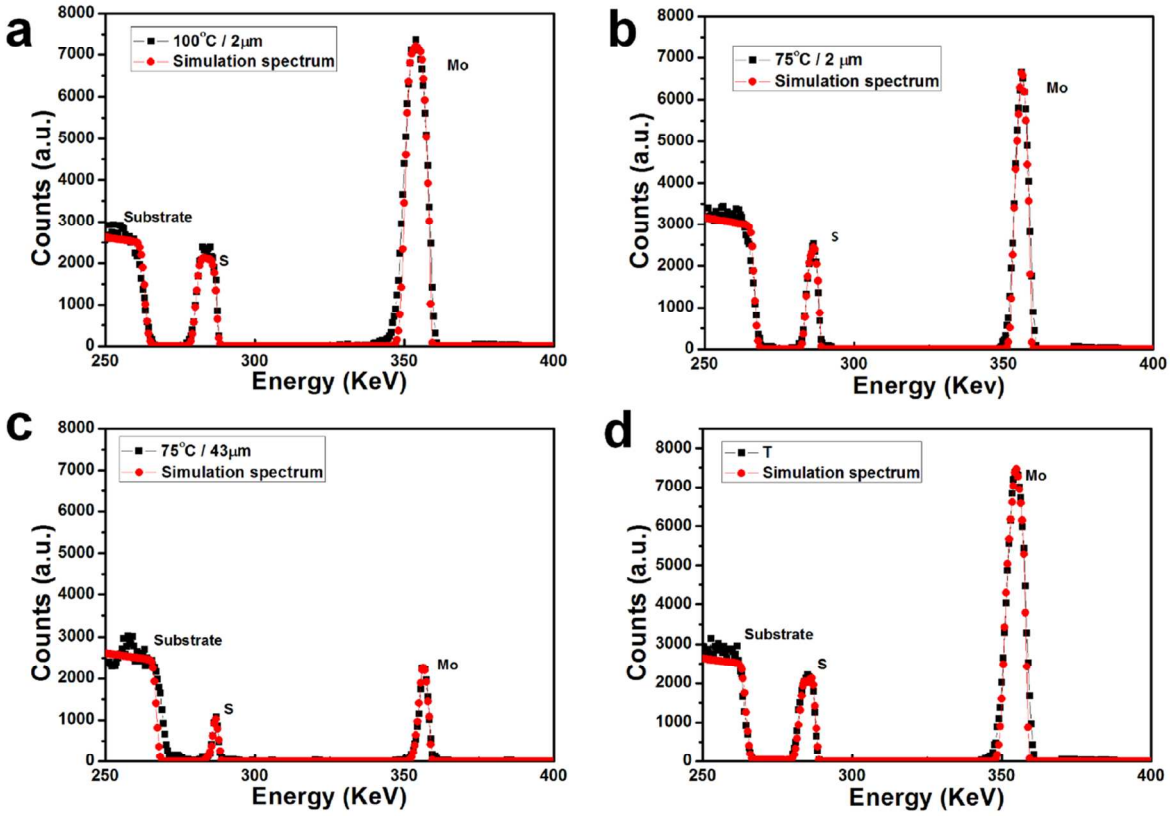

Figure S6 Rutherford Backscattering Spectrometry. RBS spectra (dark line) and simulation spectra (red line) for thin films 100ºC / 2 µm (a), 75ºC / 2µm, (b), 75ºC / 43µm, (c), and T (d).

Electrical Characterization- Circular Transfer Length Method

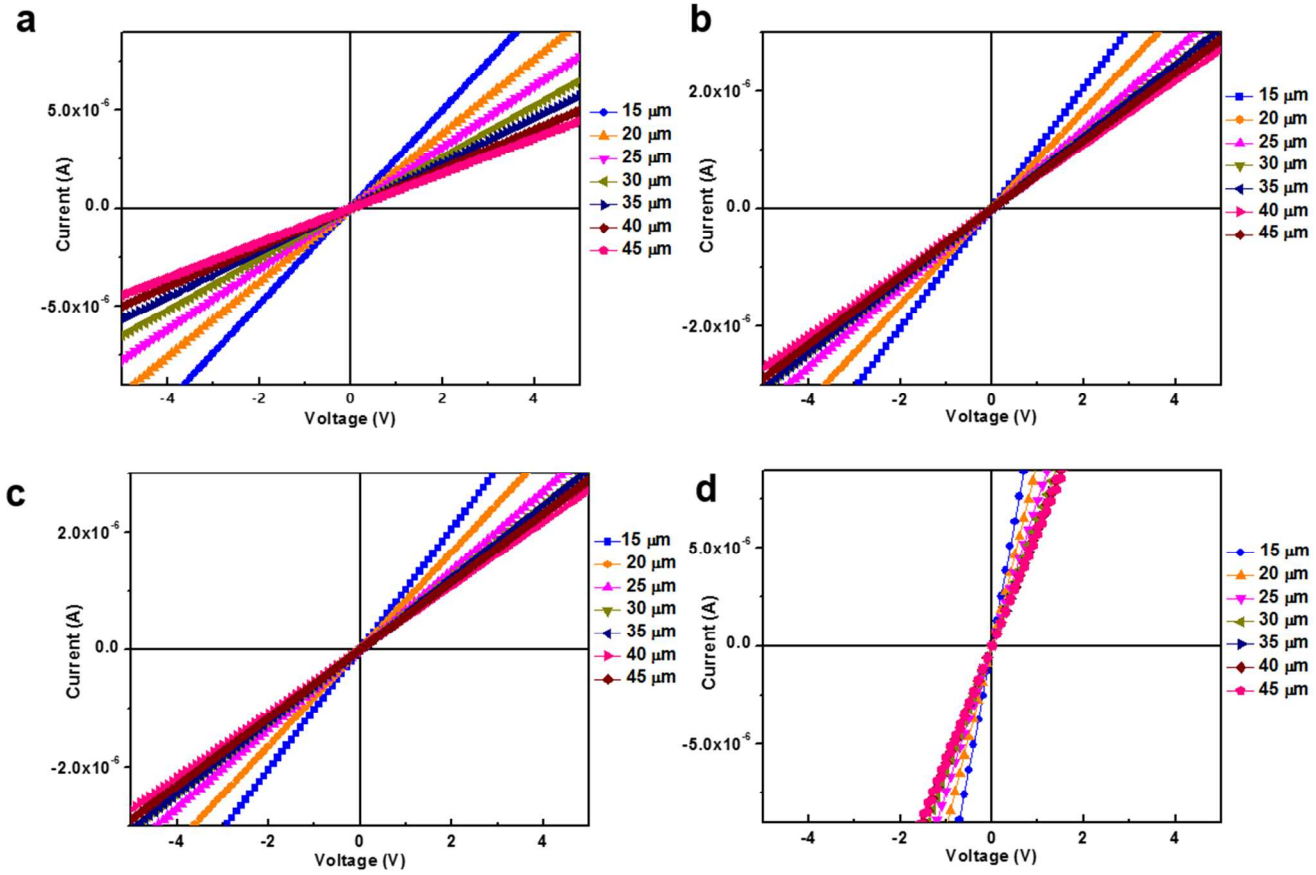

Figure S7. CTLM measurements for thin films. I-V characteristics of (a) Thin film 100ºC / 2 µm (b) 75ºC / 2µm, (c), 75ºC / 43µm, (d) and T.

The CTLM measurements were made on circles from of 15 to 45 microns, since those were the ones that opened easier during the lift off lithography process**. Figure S7** shows the I-V measurements for each sample. The Voltage for the evaluation varied from -4 to 4 Volts. Figure S8 shows the electron microscopy image of the CTLM pattern.

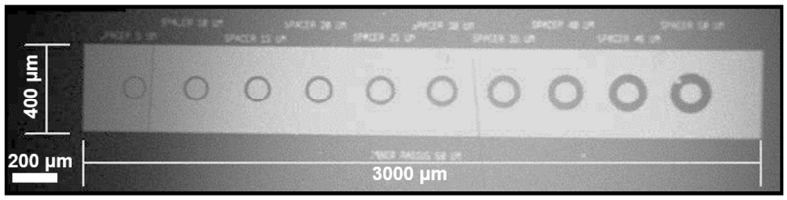

Figure S8. Scanning Electron Microscopy (SEM) image from the CTLM pattern. The light part are the Au contacts and the dark part is the MoS_2 thin film .

Phase Contrast Imaging – Thin film Crystallinity

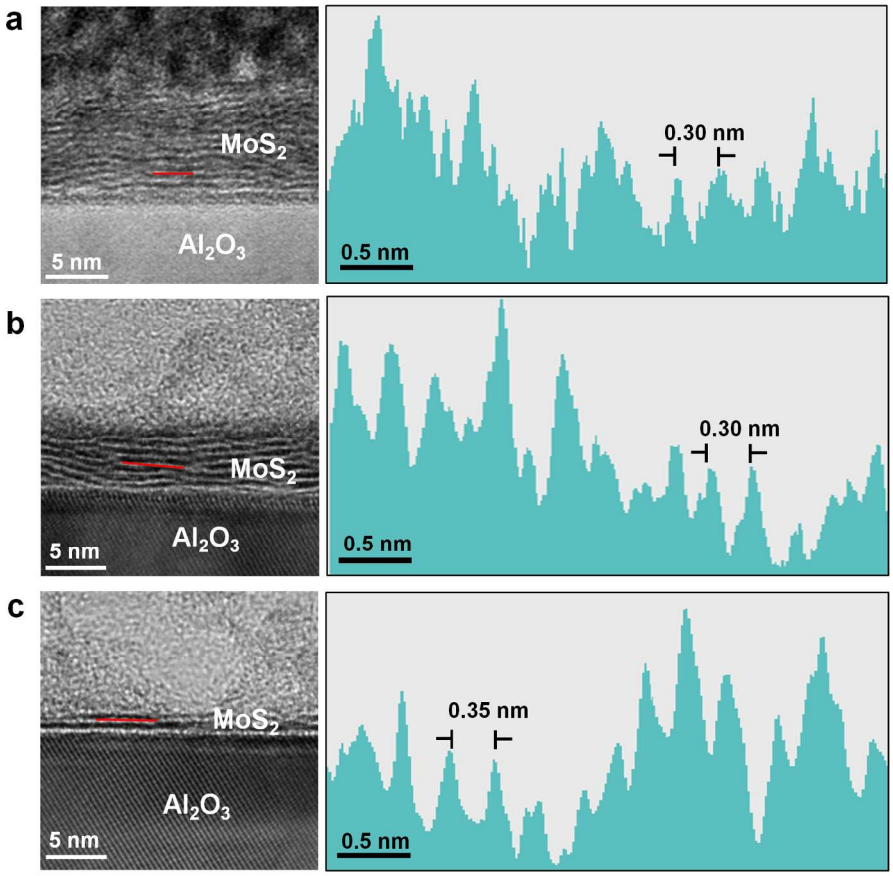

Figure S9. Phase contrast profiling. Cross section of films 100 Thin film 100ºC / 2 µm (b) 75ºC / 2 µm, y (c) 75ºC / 43 µm. The red line shows the location of the profile.

A profile for each thin film was acquired using a Gatan Microscopy Suite software (v. 2.32.888.0). Each line in red **(Figure S9)** shows the location of the profile. From these analyses an atomic arrangement consistent with a crystalline film is evident from the atomic separation results shown in the corresponding profiles. The 0.30 to 0.35 nm interatomic distance experimentally measured match closely the theoretical interatomic separation between Sulfur in MoS_2, which is approximately 0.31 nm. (Stupian and Leung 1987)Evidently, the films synthetized in this work are crystalline.

Grain Size on Graphene

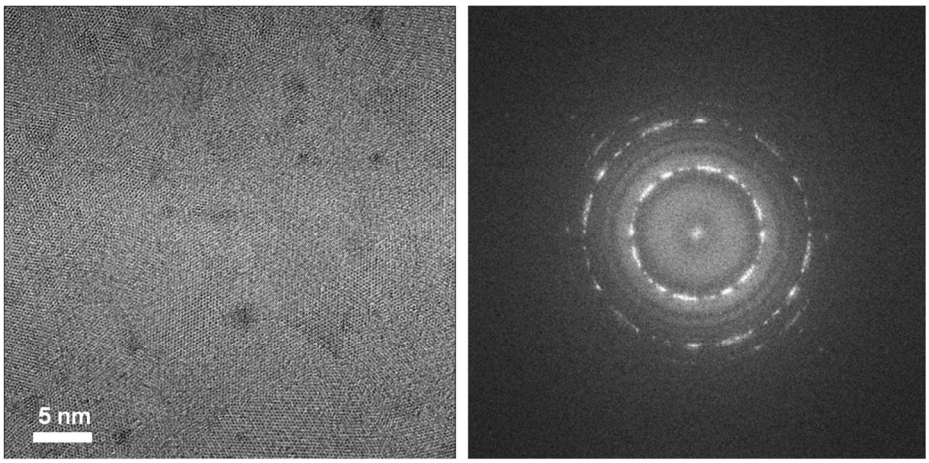

Figure S10. Top view of MoS_2 Grains and MoS_2 on graphene FFT image simulation. The rings and multiple points in the materials shows that the film is polycrystalline.

The grain size of thin film 75ºC / 43 µm was measured on Graphene. On average the grain size was 16.80 nm. Furthermore, the FFT image shows that the film is polycrystalline **(Figure S10)**.

A plain view image of the deposited film on Graphene were obtained using a JEOL JEM-ARM 200F transmission electron microscope operating at 200 kV. The FFT image show demonstrates the polycrystalline nature of the MoS_2 thin film **(Figure S10)**. Grain orientation maps were then created (using the Gatan Microscopy Suite software) from the Fourier spectrum of these images, by moving a mask at discrete angular steps of 5 degrees along a circular path corresponding to the **G** vectors of the MoS_2 reciprocal lattice, and obtaining their inverse FFT. A Sobel and Smooth spatial filters were applied to highlight the grain area, after which the Particle Analysis package was used to identify the grains in the image and obtain their dimensions.(Seyring, et al. 2009) **Figure S11** shows a region of the sample where the MoS_2 grains were found, its grain orientation map, and grain size distribution derived from the above method. On Average the grain size was 16.81 ±6.39 nm **(Figure S12).**

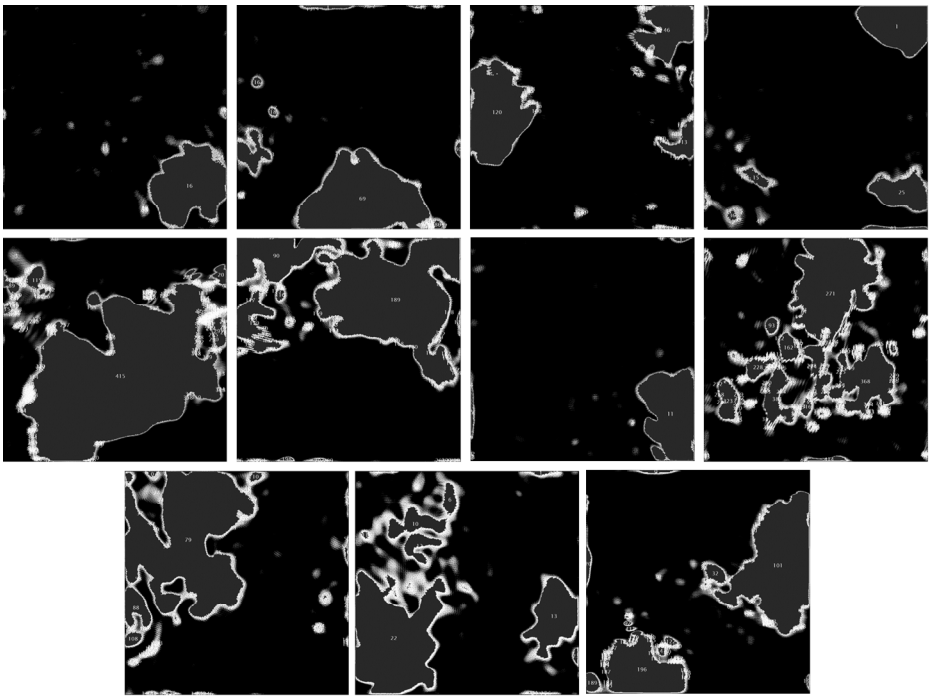

Figure S11. Grain orientation maps for 75ºC / 43 µm on Graphene. The areas in gray represent the grains of MoS_2.

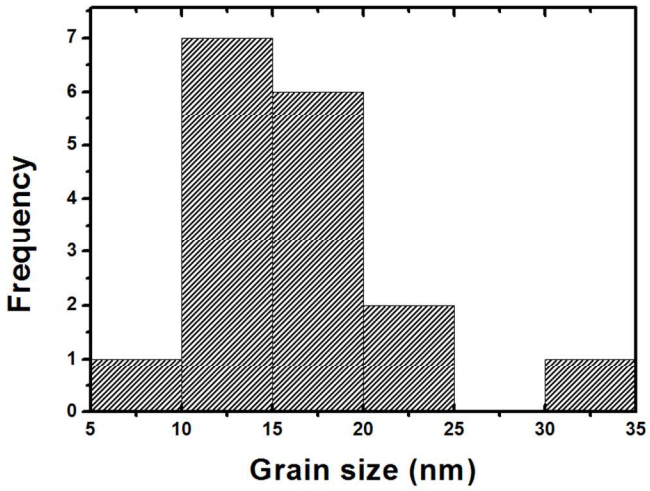

Figure S12. Grain size distribution for thin film 75ºC / 43 µm deposited on Graphene

References

1. Stupian, G. W.; Leung, M. S., Imaging of MoS_2 by Scanning Tunneling Microscopy. *Appl. Phys. Lett.* **1987,** *51*, 1560-1562.

2. Seyring, M.; Song, X.; Chuvilin, A.; Kaiser, U.; Rettenmayr, M., Characterization of Grain structure in Nanocrystalline Gadolinium by High-resolution Transmission Electron Microscopy. *J. Mater. Res.* **2009,** *24*, 342-346.