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CVD growth of monolayer MoS₂: Role of growth zone configuration and precursors ratio

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Single-layer, large-scale two-dimensional material growth is still a challenge for their wide-range usage. Therefore, we carried out a comprehensive study of monolayer MoS₂ growth by CVD investigating the influence of growth zone configuration and precursors ratio. We first compared the two commonly used approaches regarding the relative substrate and precursor positions, namely, horizontal and face-down configurations where face-down approach is found to be more favorable to obtain larger flakes under identical growth conditions. Secondly, we used different types of substrate holders to investigate the influence of the Mo and S vapor confinement on the resulting diffusion environment. We suggest that local changes of the S to Mo vapor ratio in the growth zone is a key factor for the change of shape, size and uniformity of the resulting MoS₂ formations, which is also confirmed by performing depositions under different precursor ratios. Therefore, to obtain continuous monolayer films, the S to Mo vapor ratio is needed to be kept within a certain range throughout the substrate. As a conclusion, we obtained monolayer triangles with a side length of 90 µm and circles with a diameter of 500 µm and continuous films with an area of 850 µm x 1 cm when the S-to-Mo vapor ratio is optimized.

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1. Introduction

Owing to the weak van der Waals bonds between the layers of a variety of solids such as graphite, hexagonal boron nitride, black phosphorus, transition metal dichalcogenides (TMDCs) and many others, it is now possible to form one-unit-cell thick two-dimensional (2D) materials with extraordinary properties since the discovery of graphene.1–3 In addition to the peculiarity of such individual mono-layers, either mechanically exfoliated or grown on a substrate, importance of this remarkable achievement provides the ability of bringing any number and any combination of these materials together and designing novel heterostructures. Such designed stacks of 2D materials give rise to new perspectives for tailor-made material properties unattainable otherwise.1,2 However, success of this revolutionary idea depends on large scale growth of individual layers that will be transferred or epitaxially grown on top of each other in a specified sequence to form the designed heterostructures. In this respect, chemical vapor deposition (CVD) is currently accepted as the most promising technique to form large and uniform 2D films or flakes with the desired properties. However, in spite of the recent advances regarding the growth of different 2D films and flakes using CVD, we are still only at the verge of understanding the growth mechanisms in terms of seed formation, nucleation and thermodynamics aspects. For example, an oxi-chalcogenide nanoparticle encased by fullerene TMDC shell (MoS₂ or MoSe₂) is the first entity formed during the growth and act as a nucleation center suggesting a step-by-step growth of the monolayer flakes.3,4 Moreover, thermodynamics calculations reveal that growth is controlled by the slowest diffusing precursor which is Mo rather than S in MoS₂ growth and predicted phase diagram provide a specific window that comprise a sulfur rich atmosphere (a larger sulfur mole fraction than 0.67) between 734 to 2004 K at 1 atm.4,5 Furthermore, commonly observed shape evolution of flakes throughout a single substrate is attributed to the S to Mo ratio, which is not constant along the reaction chamber (in general, a quartz tube) and this experimental data is modeled successfully to determine size and shape of the 2D flakes.5,6 Another issue, vertically standing flakes, which are reported in different articles, are investigated by transmission electron microscope (TEM) and the underlying mechanism is suggested to be related with the compression and extrusion between the MoS₂ islands.7–10

Despite the somewhat slow progress to discover the growth mechanism of the 2D materials particularly of TMDCs (e.g., MoS₂, WS₂, MoSe₂ monolayers) in CVD, their promising performance in electronics (mobility of 200 cm²/V·s, 10⁸ on off ratio for MoS₂ transistors) and possible application areas in optoelectronics (solar cells, photodetectors, light emitting diodes), hydrogen energy and emerging new areas such as valleytronics and piezotronics, urges the grain size or flake size controlled, chemically and structurally uniform monolayer films and flakes.11–16 For this purpose, it is of importance to control CVD growth of monolayer TMDCs with the intended properties.17 Therefore, these approaches are, although not limited to: using aromatic molecules as seeding promoters, using substrates such as mica, sapphire, and GaN for lateral and epitaxial growth, incorporation of H₂ or O₂ to the carrier gas for a larger flake size up to 320 µm, plasma treatment of the surface for higher surface coverage, changing the position of the substrate with respect to the precursors, and usage of different Mo precursors such as MoO₃, MoCl₅, and Mo(CO)₆.9,18–25 Any growth procedure, found to be beneficial for 2D MoS₂ growth, is likely to be applicable to other TMDCs due to the similarity in the growth mechanism making MoS₂ a prototypical material shedding light on the growth of other TMDCs. Therefore, in this research work, we have changed various critical CVD (as shown in Fig. 1) process parameters and systematically investigated the resulting MoS₂ formations.

First of all, we follow two different approaches regarding the position of the substrates with respect to the precursors in our CVD furnace: horizontal and face-down as illustrated in Fig. 2. These approaches are employed under identical growth conditions in order to compare flake size, composi-
tion and growth pattern as illustrated in Fig. 2. Furthermore, we study the effect of substrate holder boat geometry (as shown in Fig. 2) and S-to-MoO$_3$ ratio to find the optimum growth conditions.

2. Experimental methods

In this work, we use MoO$_3$ and S as precursors in an atmospheric pressure CVD system to grow MoS$_2$ monolayers on Si/SiO$_2$ substrates. A schematic drawing of the CVD system (not scaled) is given in Fig. 1. The system includes the following parts: a quartz tube with a diameter of 8 cm and a length of 140 cm, separately controlled two 25 cm long split furnaces, two mass flow controllers calibrated for N$_2$ and H$_2$ and stainless steel flanges at both end connected to a chiller operating at 5 °C. In addition, split furnace is mounted to the tracks (or rails) as illustrated in Fig. 1 that makes system mobile allowing for the ability of controlling the sulphur evaporation rate and growth time by shifting the furnace toward or away from the sulphur. Furthermore, since the furnace can be moved away from the reaction zone when needed, faster cooling rate can be obtained, which prevents excess evaporation of MoO$_3$ and film deterioration during the cooling step.

In this work, we adopt and further improve the growth procedure that we described previously. In the first part of the procedure, MoO$_3$ precursor is put in the quartz boat that also contains the substrates (see Fig. 2). Boat is positioned 16 cm away from the S powder, which corresponds to the inlet of the first zone (see Fig. 1 for the S and Mo zones). 400 sccm of N$_2$ flow is used in all of the experiments. The inner temperature of the reaction zone is measured with a 150 cm long temperature probe where it is adjusted to 700 °C with a heating rate of 10 °C/min to minimize the temperature overshooting. Sulphur melts at 150 °C and at this stage the furnace is shifted right (4 cm away from the S boat) and left there until the furnace reaches 670 °C (corresponds to 700 °C inner temperature). Afterwards, the furnace is shifted to left side by 6 cm, where S zone is subjected to a sudden temperature burst. Depending on the experiment type, all the S is evaporated from the quartz boat within 5 to 10 min, which is recorded as growth time of the experiment.

Using the described CVD system and procedure, we designed three experimental sets. The configurations of the three experimental sets and the used substrate and quartz boat sizes are presented in Fig. 2. In the first set (set-1) [Fig. 2(a)], 1 cm$^2$ substrates are positioned horizontal. In the second experimental configuration (set-2), MoO$_3$ powder is placed in a quartz cylinder that has a height and a diameter of 2 cm. The substrate is placed on this cylinder and MoS$_2$ is formed on the downward facet of the substrate [see Fig. 2(b)]. Precursor amounts are kept the same with set-1 to be able to understand the effect of the growth geometry. In the third experimental set-up (set-3), the same boat in set-1 is used with the “face-down” configuration that was applied in set-2 [Fig. 2(c)]. Using this configuration, we systematically investigate the influence of S to MoO$_3$ ratio (R). It should be noted that S deposits at the colder parts of the quartz tube during the growth. Therefore, we clean quartz tube thermally to remove sulphur deposits to prepare the CVD for a new run.

The grown structures are analyzed by using µ-Raman and photoluminescence (PL) spectroscopy. Optical microscopy (OM) and scanning electron microscopy (SEM) are also used to extensively investigate the morphology of the samples.
3. Results and discussion

3.1 Set-1: Horizontal growth

Figure 3 shows the Raman and PL spectra for set-1 when the distance between the substrate and MoO₃ precursor changes from 2.5 to 11.5 cm. Raman finger-prints of the α-MoO₃ (precursor used in this study) and intentionally grown monoclinic MoO₂ (m-MoO₂) are also demonstrated in Fig. 3(a). These two spectra are labeled as “α” and “m” as shown in Fig. 3(a) and vibrational assignments of these peaks can be found in elsewhere.24,27,28) We use these two spectra as reference to determine the presence of mo-oxide in the samples.

From 2.5 to 11.5 cm, we observe Raman finger-prints of MoS₂ (E₁²g and A₁g).29) However, only in the spectrum of the first sample (2.5–3.5 cm away from the precursor) m-MoO₂ is observed besides the MoS₂ phase. Presence of m-MoO₂ disappears when the distance between substrates and precursor is increased above 3.5 cm. Raman peak difference of the E and A peaks (26 cm⁻¹) of the first and second samples indicate multilayer MoS₂ while this difference decreases to 20 cm⁻¹ for the substrates between 5.5 and 9.5 cm indicating formation of monolayer MoS₂.29,30)

When bulk MoS₂ is thinned down to monolayer, its band-gap structure transforms from indirect (1.2 eV) to direct (1.8 to 1.9 eV) band-gap. Bulk MoS₂, therefore has a negligible quantum yield (QY) as a result of the phonon assisted process [see Fig. 3(b), PL line of sample, 2.5 cm away from the precursor]. On the other hand, monolayer and few layer MoS₂ (from 2 to 6 layers) has significant PL intensity, where QY decreases as the layer number increases from 1 to 6.31) This means that the monolayer MoS₂ demonstrates brightest PL (or highest intensity).31,32) On the other hand, PL response of the few-layer MoS₂ (an indirect semiconductor) still demonstrates good PL intensity. The mechanism yielding good PL intensity for the few layer MoS₂ is suggested to be observed due to direct-gap hot luminescence preventing total PL quenching, which is observed in indirect semiconductors such as Si.31,33) PL response measured from the samples demonstrates the highest PL intensity for the samples grown at the distances of 5.5, 7.5, and 9.5 cm [Fig. 3(b)]. Together with the supporting Raman measurements [Fig. 3(a)] 5.5 to 9.5 cm region is therefore determined as the monolayer growth region.

Normalized PL spectrum is shown in Fig. 3(c). The scope of this study is to gain an understanding on the growth of MoS₂ monolayer. Therefore, PL or exciton phenomena will not be discussed extensively here. PL spectrum of the monolayer and few layer MoS₂ are deconvoluted to three and four peaks that arise from radiative recombination of holes and electrons, respectively. In the case of only in monolayer MoS₂, these three peaks are A⁻ (trion), which is a free electron bound to a neutral exciton with a peak center values ranging from 1.77 to 1.85 eV, A exciton (1.83 to 1.92 eV) and B exciton (1.96 to 2.08 eV).34–36) These energy ranges are obtained from the literature and combined in this work for evaluating our data. In the case of the few layer MoS₂, for example from 2 to 6 layers, indirect transition peak with a varying energy between 1.2 to 1.56 eV is experimentally observed.31) With our PL measurement setup, it is unfortu-
nately not possible to measure those indirect transitions that could confirm the multilayer nature of the samples deposited at distances except from 5.5 to 9.5 cm. On the other hand, we are able to observe A\textsuperscript{−}, A, and B exciton peaks. A and B exciton peaks are attributed to the recombinations of electrons and holes in a neutral exciton at K point. Different energy levels of A and B peaks are attributed to the valance band splitting at K point due to the strong spin–orbit coupling.\textsuperscript{33) Peak B therefore indicates recombination at a lower valance band.\textsuperscript{36) Values of these peaks are found by fitting three Lorentzian peaks to the data as previously performed in the literature.\textsuperscript{35,36) Two of the fitted curves are demonstrated in Fig. 3(d) and in Fig. 3(e) as an example.}

\begin{table}[	extwidth] 
\centering 
\caption{Fitting results of the PL curves demonstrated in Fig. 3. VBS is the valance band splitting that is the difference between B exciton peak center and A exciton peak center. R\textsuperscript{2} is the goodness of the fit.} 
\begin{tabular}{|c|c|c|c|c|c|} 
\hline Sample & A\textsuperscript{−} trion (eV) & A exciton (eV) & B exciton (eV) & VBS (meV) & R\textsuperscript{2} \\
\hline 3.5 cm\textsuperscript{a)} & 1.787 & 1.823 & 1.950 & 127 & 0.99739 \\
5.5 cm\textsuperscript{b)} & 1.820 & 1.843 & 1.990 & 170 & 0.99955 \\
7.5 cm\textsuperscript{b)} & 1.843 & 1.868 & 2.038 & 170 & 0.99955 \\
9.5 cm\textsuperscript{b)} & 1.817 & 1.838 & 1.991 & 153 & 0.99954 \\
11.5 cm\textsuperscript{b)} & 1.845 & 1.870 & 2.003 & 133 & 0.99901 \\
\hline 
\end{tabular} 
\end{table} 

Figure 3(e) demonstrates the fitted spectra of the 5.5 cm sample (monolayer). In this spectra, A\textsuperscript{−} is at 1.820 eV, A exciton is at 1.843 eV, and B exciton is at 1.990 eV. Therefore, the valance band splitting (VBS) is 170 meV. Figure 3(d) demonstrates the fitted spectra of the sample at 3.5 cm (few-layer). In the few-layer case, A\textsuperscript{−} is at 1.78 eV, A exciton is at 1.82 eV, and B exciton is at 1.95 eV making a VBS of 127 meV. Results of all the fitting data are given in Table I. Peak centers of A, B excitons and A\textsuperscript{−} are within the range of the indicated value. At the distance of 11.5 cm, we realize a surface with (seed-like) MoS\textsubscript{2} particles starting to form monolayers but these structures could not be completed to form monolayers. Raman spectra of this sample demonstrates few-layer MoS\textsubscript{2} and its relatively high PL intensity indicate that it has a layer number between 2 and 6. We believe that beyond a certain distance, lower Mo and S supply just results in seed-like growth. Lower precursor concentration does not allow the growth of continuous flakes.

Noticeable PL shift observed in A exciton of the monolayers (~40 meV) can be attributed to the stress present at the flakes due to fast cooling step.\textsuperscript{26,37–39} It has been demonstrated that by using Si/SiO\textsubscript{2} substrates and CVD growth, as-grown layers possess a tensile stress.\textsuperscript{38,40} Moreover, it has also been demonstrated that the stress can be revealed after the transfer of the MoS\textsubscript{2} flakes on to a new substrate.\textsuperscript{40} For example, A peak PL position of as-grown layers (not deconvoluted) redshifts 68 meV starting from 1.82 to 1.89 eV. DFT band-gap calculations and supporting experimental PL measurements also demonstrate that the band-gap of the MoS\textsubscript{2} decreases as the tensile stress increase and the PL peak blueshifts with the tensile stress.\textsuperscript{37} Therefore, the optical heterogeneity in our PL samples [Fig. 3(b)] can be attributed to in-situ tensile stress development during the growth (possibly at the cooling step) especially for the monolayer region.

Presence of Mo-oxide and thick MoS\textsubscript{2} between 0–4.5 cm indicates a high Mo concentration gradient. Moreover, emerging monolayer MoS\textsubscript{2} layers beyond 4.5 cm, indicates a specific concentration window for the growth of monolayer flakes.

Figure 4 contains the optical images of the growth pattern of the monolayer MoS\textsubscript{2} (samples ranging between 5.5 to 9.5 cm). MoS\textsubscript{2} monolayers tend to grow at the edges of the substrate in the form of either film [Fig. 4(a)] or separate flakes [Fig. 4(b)]. A growth zone containing film or flakes with a width of 500 to 1500 \( \mu \text{m} \) surrounds the substrates. The common point of these patterns is that the size of the MoS\textsubscript{2} flakes gradually decreases as we go from the edge to the center of the substrate as can be observed from the optical images in Figs. 4(a) and 4(b). Lower left part of the inset of the Fig. 4(b) demonstrates the dark field optical image of the region, where MoS\textsubscript{2} edges seem bright. Upper right inset demonstrates the flake size distribution in this region. As can be seen from this inset, flake size ranges from 1 to 12 \( \mu \text{m} \). More interestingly, when the center of the substrate is investigated with SEM, it is seen that all the surface is covered with particles smaller than 200 nm [Figs. 5(a) and 5(b)]. To the best of our knowledge preferential edge growth of the MoS\textsubscript{2} monolayers on Si/SiO\textsubscript{2} substrates are reported only once. Najmie et al. observed and reported that MoS\textsubscript{2} prefers to grow at the edges, around dust particles, rough surfaces and scratches.\textsuperscript{41} The reason of this behavior is proposed as edge based catalytic behavior that reduce the energy barrier of the nucleation.\textsuperscript{42} This proposal of the
Najmei et al. depends on the preferential growth of graphene around scratches of Cu film and energy calculations.\(^{42,43}\) Edges of the diced wafer, could potentially have higher roughness than center of the substrate, which supports the proposal. On the other hand, large area epitaxial growth of the MoS\(_2\) requires atomically flat lattice matched substrates such as sapphire as demonstrated by Dumcenco et al.\(^{44}\) Therefore, this contrary result to the proposed mechanism might indicate other factors governing the edge growth. As will be explained in the next sections, our results represented by set-2 and set-3 also indicate the existence of other effective mechanisms.

### 3.2 Set-2: Face-down growth-1

As shown in Fig. 2(b) this configuration, there is a 2 cm vertical difference between the position of the precursor and the substrate. Substrate touches the quartz boat as shown in Fig. 6(a). With this configuration, we obtain flakes that are radially distributed over the substrate [see, for example, Figs. 6(a)–6(c)]. Center of the substrate contains small flakes and these flakes gets larger when we get closer to the edges of the substrate. As mentioned before, we shift furnace to the left side (onto the Sulphur) when the growth zone reaches 700 °C. If we do not move the furnace to the left at growth temperature and we wait at this temperature for 10 min, and then shift the furnace onto the sulphur, we get much larger flakes up to 90 \(\mu\)m [Fig. 6(f)] and a ring like film formation with a width of 850 \(\mu\)m is obtained as shown in Fig. 6(e). It is known that the film formation occurs in TMDCs by the growth of individual flakes and their coalescence or merging.\(^{41,45}\) Therefore, 10 min extra growth time initiate a slower growth process (little S vapor can reach the substrate) and the flakes grow larger till they merge to form a continuous monolayer film.

Raman investigation of the samples from this configuration only gives multilayers of MoS\(_2\) at the center of the substrate and the rest of the flakes and film are monolayer MoS\(_2\) [Fig. 6(d)]. Moreover, a radial shape evolution can be tracked around the ring like film as demonstrated in Fig. 7(a) to Fig. 7(d). SEM images given in Figs. 7(b)–7(d) are taken from left to right of the red box illustrated in Fig. 7(a), respectively. As mentioned before, the shape evolution is an indication of different Mo to S ratios locally distributed over the surface of the substrate.\(^{5,41}\) In these experimental conditions, we may assume a constant sulphur concentration due to the large distance between sulphur source to substrate.

![Fig. 5](image.png)

*Fig. 5.* (Color online) SEM images of the substrate centers demonstrating particles below 200 nm. (a) 5000x (scale bar is 2 \(\mu\)m) and (b) 50000x (scale bar is 200 nm).

![Fig. 6](image.png)

*Fig. 6.* (Color online) SEM images and Raman spectra characterization of set-2, (a) schematic representation of the growth zones on the substrate, (b) 100x SEM image for growth duration of 5 min (no baking), (c) 5000x SEM image demonstrating MoS\(_2\) flakes, (d) number of layer characterization obtained by Raman spectra from the center of the substrate (#1) to the outer rim of the sample (baking duration of 10 min, growth duration of 5 min), horizontal lines indicate number of layers, (e) 100x SEM image of the sample with 10 min bake demonstrating one part of the ring structure, and (f) 5000x SEM image of the flakes of the ring structure.
Moreover, diameter of the quartz holder is 2 cm, which decreases the possibility of sulphur concentration difference between points of sulphur-in and sulphur-out [see Fig. 2(b)]. Therefore, the varying concentration precursor through the substrate can be suggested as Mo. To understand the deposition uniformity and film formation, it is necessary to review the basic evaporation theory discussing about a surface source and its evaporation sphere. In this model, the substrate is assumed to be positioned above the source. Our growth geometry is in accordance with the model. According to the kinetic theory driven from the surface source model, center of the substrate subjects to the highest Mo concentration, and the Mo concentration decrease radially from center to the edge of the substrate. Therefore, at specific growth zones demonstrated in Figs. 6(e) and 7(a), this configuration provides an appropriate Mo concentration regime, which allows the seeds to grow laterally. This explains the reason behind the thicker center [Fig. 6(d)], shape evolution and more critically why there is a ring shape monolayer film and flakes around this region. However, the model does not answer the origin of size evolution or nucleation density variation from center to the edge. These can be attributed to the neglected factors such as a dynamic gas flow environment and sulphur poisoning of the precursor. Especially, sulphur gas reacts with the solid MoO₃ powder and turning it into the MoS₂ powder during the growth that may decrease the evaporation of Mo from the precursor dynamically during the growth.

### 3.3 Set-3: Face-down growth-2

In this growth scheme [Fig. 2(c)] face-down approach is utilized with a larger boat and with a larger substrate aiming to have larger growth zones. When the same parameters used with set-1 and set-2 (1–1.5 mg MoO₃ and 150 mg Sulphur), we observe a much larger ring shape growth pattern (not shown in the paper). Besides changing the growth geometry only, we change S to MoO₃ ratio and find that it is also a critical factor determining the quality and size of 2D MoS₂ formations. Our results are summarized schematically in Fig. 8, showing the change in bond structures (from the Raman scattering spectra analysis), morphology, and flake sizes (from confocal microscopy and SEM images) as a function of S/MoO₃ ratio. As depicted in Fig. 8, when a low S/MoO₃ ratio is used, we start to observe Raman signatures from oxide phases, which degrades the film quality. This is also in alignment with the current literature. On the other hand, when this ratio exceeds 150, the triangular flakes become invisible and circular flakes appear. Similarly, the morphology and the maximum flake sizes also change depending on the precursors ratio.

The optical microscopy images showing these morphologies are presented in Figs. 9(a)–9(d). Each confocal optical image includes μ-Raman and photoluminescence spectra in the insets indicating monolayer growth of MoS₂. In Fig. 9(a),

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**Fig. 7.** (Color online) Shape and size evolution of films and flakes from the inner to the outer part of the ring-like structure: (a) general view, (b)–(d) size evolution from the left to the right of the marked rectangle in (a).

**Fig. 8.** (Color online) MoS₂ flake and film characteristics as a function of S/MoO₃ precursor ratio.
at some parts, we observe dot like bright features, which are suggested to be nucleation centers (seeds) from which monolayer MoS₂ grows. However, at some parts, there are no bright spots on the flake. This can be understood regarding the TEM studies performed by Cain et al. TEM studies demonstrate that MoS₂ or in general TMDC 2D materials grow first from a spherical seed. Elemental analysis of the seeds demonstrates a core–shell system. Core of the seed (first entity formed during the growth) is an oxide rich Mo–O–S phase. This seed is then gradually sulfurized to form fullerene like layers around it (MoS₂ layers). Fullerene layers are then spread (or grow) laterally to form flakes suggesting a classical nucleation and growth scheme for the CVD growth. The size of the fullerene like seeds studied by the Cain et al. is around 5 to 10 nm. Such small seeds would not be visible in the confocal image. However, it is interesting to note that some seeds are large enough to be visible in the confocal microscope. This could be explained by the suggestion that some seeds could be formed during an early stage of the growth and enlarge as seeds until the furnace condition is matured for a lateral growth.

The flakes in Fig. 9(b) are in a triangular shape where the flakes do not overlap and do not cause grain boundaries. However, when the density of flakes increase, this leads to flakes to overlap, which results in formation of few-layer MoS₂ due to merging of monolayer flakes. Figure 9(d) exhibits the case of excessive S to MoO₃ ratio where we lose separate triangular shapes and realize merged flakes in a circular shape. 21 cm⁻¹ difference between Raman fingerprints of MoS₂ (E₁g and A₁g) and high intensity PL spectra around 1.83 eV indicate that triangular flakes are single-layer MoS₂ [Figs. 9(a) and 9(b)]. 24 and 26 cm⁻¹ difference between Raman fingerprints of MoS₂ taken from grain-boundaries and center of circular flakes, and low intensity of PL spectra of these points indicate the presence of few layer MoS₂ parts [Figs. 9(c) and 9(d)] while the rest of the film or the circular flake is monolayer.

4. Conclusions
We performed and compared widely-used two growth approaches: horizontal growth and face-down growth with identical growth conditions including S (150 mg) to MoO₃ (1 mg) precursor ratio, substrate temperature (700 °C), atmospheric pressure, and 400 sccm of N₂ carrier gas. In the case of face-down approach, we also changed substrate holder types to control the S to Mo vapor ratio, hence the interaction between these vapors and the substrates. According to our results, face-down approach is found to be more favorable to obtain larger flakes presumably because of higher Mo confinement in the growth zone. In the horizontal growth, it is observed that although all the surface is covered with monolayer MoS₂ formations, either these formations are too small (<200 nm) at the central area of the substrate or they are found at the edges (~10 µm). On the other hand, face-down approach gives much larger flakes (~90 µm) and larger continuous films (850 µm × 1 cm). In this research work using face-down approach, we could control size and shape of the flakes by changing S/MoO₃ ratio, where it is found to be between 66 to 150 to obtain larger and uniform monolayers. In short, we find that the local S and Mo vapor concentrations in the growth zone are of critical importance to control the shape, size and uniformity of the resulting MoS₂ flakes and films.

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