Analyzing growth kinematics and fractal dimensions of molybdenum disulfide films

Yan Jiang1, Moritz to Baben2, Yuankun Lin1, Chris Littler1, A J Syllaios1, Arup Neogi1 and Usha Philipose1

1 Department of Physics, University of North Texas, Denton, TX 76203, United States of America
2 GTT-Technologies, D-52134 Herzogenrath, Germany

E-mail: yanjiang@my.unt.edu

Received 26 January 2021, revised 9 March 2021
Accepted for publication 11 March 2021
Published 25 March 2021

Abstract

Though the positive role of alkali halides in realizing large area growth of transition metal dichalcogenide layers has been validated, the film-growth kinematics has not yet been fully established. This work presents a systematic analysis of the MoS2 morphology for films grown under various pre-treatment conditions of the substrate with sodium chloride (NaCl). At an optimum NaCl concentration, the domain size of the monolayer increased by almost two orders of magnitude compared to alkali-free growth of MoS2. The results show an inverse relationship between fractal dimension and areal coverage of the substrate with monolayers and multi-layers, respectively. Using the Fact-Sage software, the role of NaCl in determining the partial pressures of Mo- and S-based compounds in gaseous phase at the growth temperature is elucidated. The presence of alkali salts is shown to affect the domain size and film morphology by affecting the Mo and S partial pressures. Compared to alkali-free synthesis under the same growth conditions, MoS2 film growth assisted by NaCl results in ≈81% of the substrate covered by monolayers. Under ideal growth conditions, at an optimum NaCl concentration, nucleation was suppressed, and domains enlarged, resulting in large area growth of MoS2 monolayers. No evidence of alkali or halogen atoms were found in the composition analysis of the films. On the basis of Raman spectroscopy and photoluminescence measurements, the MoS2 films were found to be of good crystalline quality.

Keywords: 2D, materials; fractal dimension; chemical vapor deposition; monolayer

(Some figures may appear in colour only in the online journal)

1. Introduction

Two dimensional (2D) materials possess a layered atomic structure [1–3] and exhibit unique properties of light emission, anomalous lattice vibrations, valley polarization, excitonic dark states and strong light–matter interactions [4–8]. The interest in MoS2 is largely triggered by the fact that its energy band gap becomes direct at the monolayer limit (Eg = 1.85 eV), which makes it promising for electronic and opto-electronic applications [9–11]. In order to successfully exploit the unique attributes of 2D-MoS2 and to integrate them into existing application platforms, it is essential to critically assess the growth recipes and evaluate both qualitatively and quantitatively the quality of the as-grown films.

Recent works have shown that by modifying the growth recipes it is possible to grow wafer-size MoS2 films with various morphologies, such as compact triangles, star-like flakes, and dendrites [8, 12, 13, 14–19]. In order to obtain a specific morphology, there are pronounced differences in the growth processes, such as the use of O2 to enable monolayer growth [20], ambient or low pressure for star-like growth [17, 18, 21–23] and the use of metal-organic precursors for large-area growth [24]. Tuning these morphologies in a simple experimental setup with reproducible results is still a challenge and is one of the objectives of this work. Recent modifications to the growth approach has been the addition of alkali halides like sodium chloride (NaCl) to promote 2D film growth, resulting in monolayers and multi-layers of MoS2.
The films were found to have markedly different morphologies than those grown without NaCl. The ambiguity in these results in terms of the observed morphology change and the possible mechanisms that account for this change remain an issue that warrants further investigation.

Another challenge that impedes establishment of a reproducible recipe is the post-growth film analysis and quantification of the complex film pattern. There are reports of a conventional technique of fractal dimension analysis applied on μm-scale islands of MoS2 [13, 17]. In a recent work, Nie et al. [28] demonstrated the use of kinetic Monte Carlo simulation coupled with first principles calculations to study a specific case of monolayer deposition. No such work has been attempted on large area (cm scale) MoS2 films. Such a study is essential because a quantified film complexity (fractal dimension) can be correlated to the crystallization process, that would provide insights into the growth mechanism.

In this work, we report on a reproducible experimental set-up to achieve controlled film growth of MoS2 monolayers and multi-layers using an atmospheric pressure CVD system. The two major highlights of the growth method are: (i) pre-treating the growth substrate using a NaCl mixture, and (ii) pre-depositing the Mo precursor directly onto the substrate prior to its loading into the CVD system. The advantage of the proposed strategy lies in the fact that it is possible to tune the growth regime by varying the NaCl concentration on the pre-treated growth substrate. At low NaCl concentrations, homogeneously distributed MoS2 monolayers in the form of triangles or three-point stars were obtained with controllable dimensions. At high NaCl concentrations, continuous MoS2 films with multi-layered domains were formed. At an optimum concentration of NaCl, the areal coverage of monolayers peaked at ≈81%.

The morphology, physical dimensions, stoichiometry and crystal quality of the MoS2 films were investigated using optical, scanning electron and atomic force microscopes. The optical quality of the as-grown films was also assessed by means of Raman and photoluminescence (PL) spectroscopy. For better image clarity, contrast imaging was enabled by color threshold, which is a simple technique of segmenting images. The fractal dimensions of monolayers and multi-layers were subsequently determined using a conventional box-counting method. Various morphologies of monolayers and multi-layers with shapes ranging from compact triangles, star-like flakes, circular dendrites, to non-symmetrical fractals covered a 2 × 2 cm² substrate area. Using contrast imaging, (black/white) the evolution of the morphology trend was assessed qualitatively, and the fractal dimensions are determined for a quantitative assessment. Finally, using the thermochemical software FactSage, we relate the evolution of the various morphologies to the time-dependent environment of the precursors in terms of the partial pressures of the gaseous reactants in the growth chamber.

2. Experiment

MoS2 growth procedure. 2D MoS2 crystals were synthesized by a complex reaction involving NaCl, MoO3 and sulfur vapors in atmospheric pressure and at high temperature, in an inert Argon environment. Two different substrates referred to as the precursor and growth substrates were used in this experiment. An Si/SiO2 substrate (2 × 0.7 cm²) was spin-coated at 3000 rpm for 1 min with an aqueous solution of 20 mg ml⁻¹ MoO3/NH₃H₂O (Molybdenum(VI) oxide, ≥99.5%, Ammonia solution 28–30%, MilliporeSigma). This substrate functions as the Mo precursor source, thereby allowing controlled concentration of MoO3 vapors in the growth chamber. A second Si/SiO2 substrate (2 × 2 cm²) that functions as the growth substrate was prepared by spin coating (3000 rpm for 1 min) an aqueous solution of NaCl/NH₃H₂O (Sodium Chloride, ≥99.5%, MilliporeSigma) onto its surface. NaCl solution was added while the sample was stationary prior to spinning. By preparing MoO3 and NaCl in NH₃H₂O, the volatility of the solvent ensured a uniform coverage of NaCl and Mo source on the substrate surface by spin-coating. Reasoning behind putting the NaCl directly on the growth substrate is to ensure a limited and controlled amount of NaCl in the growth chamber and NaCl crystals also serve as the nucleating sites for the film growth. These pre-treated precursor and growth substrates were then placed over an alumina boat, at the center of the high temperature zone of a quartz tube (2 inch diameter) in a 3-zone Carbolute furnace. A series of pre-treated samples with different NaCl/NH₃H₂O concentrations, namely 0.25, 0.5, 1, 2, 4, and 5 mg ml⁻¹ were prepared. Two similar pre-treated substrates were placed on either side of the precursor substrate to enable a study of the carrier gas dynamics on the film morphology. A separate alumina boat containing 30 mg of sulfur powder (≥99%, MilliporeSigma) was placed in the independently controlled low temperature zone, located near the end of the quartz tube. Figure 1(a) shows the corresponding locations of the precursor and growth substrates along with the sulfur source in the three-temperature-zone CVD system. Prior to growth, the tube was purged with argon at an estimated flow rate of 500 sccm. The growth temperature of 800 °C was reached in the main zone of the furnace at a ramp rate of 20 °C min⁻¹ and held constant for 10 min. During this time period, the argon flow rate was maintained at 70 sccm. The temperature of the sulfur powder located at the edge of the secondary zone of the furnace was about 120 °C, well above the melting point of sulfur. Sulfur vapors were carried by the inert gas flow towards the main zone of the furnace where it reacts with the Mo precursor. After 10 min, the furnace was gradually cooled to room temperature [18].

Characterization Details. An Olympus microscope with a maximum magnification of 1000× was used to capture images of the MoS2 films. AFM images were taken using the tapping mode of NanoSurf Mobile S AFM. Raman and photoluminescence spectra were collected from a Nicolet Almega XR Dispersive Raman spectrometer equipped with a 532 nm laser and a TE-cooled silicon CCD array detector with high-resolution gratings. The system is equipped with an Olympus BX51 microscope with motorized stage and spatial resolution down to 1 μm. The spectrometer was used in the backscattering geometry, providing a spectral resolution of approximately 1.0 cm⁻¹ per CCD pixel element.
For PL, excitation from the 532 nm laser was focused on the sample using a 100× objective lens. Scanning electron microscopy (SEM) was performed in field emission mode using a Hitachi SU1510 SEM operating at 10 kV. Energy dispersive x-ray (EDX) spectroscopy was performed on the same system at an accelerating voltage of 20 kV using a Bruker Quanta70 x-ray acquisition system with a Si drift detector. For electron transport measurements an MoS2-based back-gate field effect transistor (FET) was fabricated. Isolated MoS2 monolayers were transferred onto a SiO2 (285 nm dry oxide)/ p++ Si substrate, using a standard wet transfer procedure [29]. Acetone and isopropanol rinses were used to remove any chemical residue. After UV-photo lithography using the MJB3 mask aligner, Au (50nm) contacts were deposited via thermal evaporation to form the source-drain (S/D) contacts. The highly doped Si substrate served as the back gate of the FET. Electrical measurements to characterize the fabricated device were made using the Agilent B1500 semiconductor parametric analyzer.

3. Results and Discussion

The morphometric study unveiled a correlation between the NaCl concentration during the substrate pre-treatment phase and the subsequent coverage of the substrate with MoS2 crystals (monolayers and multi-layers). Two identical growth substrates coated with 0.5 mg ml⁻¹ NaCl/NH₄H₂O were placed on either side of the source substrate which was coated with the Mo precursor of 20 mg ml⁻¹ MoO₃/NH₄H₂O. Figure 1(a) is a schematic illustrating the positioning of the source and growth substrates in the furnace, an arrangement that ensures a controlled supply of the Mo precursor. The experiment had two identical growth substrates in terms of their pre-treatment conditions. By keeping the amount of molybdenum (Mo) and sulfur (S) constant in each run, it was possible to achieve highly reproducible growth results. The NaCl is expected to function as a seeding promoter in the early stages of growth, [26, 30] and its role in this work is discussed in detail in a following section.

3.1. Results

As seen in figure 1(b), the surface of the growth substrate (sample 1) that was placed at the upstream end of the gas flow shows clear optical contrast along the width of the sample. Based on this contrast, the entire surface of sample 1 was divided into two regions, shown enclosed by two boxes marked by red and yellow dashed lines. A magnified view of the boxed regions of sample 1 show that the area encompassed by each bounding box contains a uniform distribution of MoS2, though their areal coverage is very different. The red bounding box region contained a low density of single, compact, triangle shaped MoS2 domains with clearly visible boundaries and lateral sizes in the range of 90–100 μm. On the other hand, the yellow bounding box domain of sample 1 contains a high density of uniformly distributed MoS2 films. The observed color difference between the two regions on sample 1 is due to a difference in the areal coverage of the substrate by MoS2. The lack of a color contrast in sample 2 that was at the downstream end of the flowing gas indicates that the entire surface is covered by a high density of continuous MoS2 film. The entire sample 2 is therefore shown...
bound by the yellow box in figure 1(b). These results indicate that the location of the growth region with respect to the carrier gas flow as well as the concentration of the precursors in the vicinity of the growth substrate affects the areal density of the growing films. At this stage, the role played by NaCl in the overall growth process was still not evident.

To elucidate the role of NaCl in the growth process, several samples were prepared with 0.25, 0.5, 1, 2, 4, and 5 mg·ml⁻¹ of NaCl/NH₃H₂O spin coated onto 4.0 cm² SiO₂/Si substrates. A pilot substrate with no NaCl pre-treatment was used as the control substrate. The optical images of figure 2 shows that the areal coverage of MoS₂ on the growth
substrates increased from 5% to 100% as the NaCl concentration varied from 0 to 2 mg·mL⁻¹. The pilot substrate that received no pre-treatment with NaCl was found to contain very few, randomly distributed small domains of MoS2 monolayers (figure 2(a)). At the lowest NaCl concentration of 0.25 mg·mL⁻¹ (figure 2(b)), isolated and homogeneously distributed MoS2 triangles were produced. However, at a NaCl concentration of 0.5 mg·mL⁻¹ (figure 2(c)), the triangular flakes merged, resulting in a continuous film with randomly distributed epilayers. As the NaCl concentration was further increased to 1 and 2 mg·mL⁻¹, the epilayers coalesced in some regions resulting in the formation of multi-layered MoS2 films (figures 2(d), (e)). An increase in the NaCl concentration to 4 and 5 mg·mL⁻¹ resulted in a drastic reduction in the areal coverage of substrate by monolayers and multi-layers, causing more of the bare substrate to be exposed. Star-shaped dendrites of mono- and multi-layers were observed on substrate surface for 4 mg·mL⁻¹ NaCl pre-treatment (Figure 2(f)), while circular pads of multi-layers were observed at 5 mg·mL⁻¹ NaCl pre-treatment (figure 2(g)). The experiment is reproducible with predictable growth pattern results.

To compare the areal coverage of the substrate with mono- and multi-layers, the images in figure 2 were processed using a Color Threshold module by Photoshop CC software. This technique of image analysis that uses pixels of colors to detect objects of consistent color values enables a clear determination of the MoS2 film coverage. The optical contrast between monolayers, bi-layer, and tri-layers as well as the bare substrate is obvious and has been reported before [18].

Figure 3 correlates the NaCl concentration during the pre-growth phase to the MoS2 film coverage profile. As seen in the plot, MoS2 monolayer coverage peaks at an NaCl concentration of 0.5 mg·mL⁻¹. At NaCl concentrations exceeding this value, there were multi-layer formations, for which the coverage peaked at 2 mg·mL⁻¹ concentration. These results show that the domain size, film thickness as well as the coverage of the substrate with monolayer and epilayer domains can be controlled by varying the NaCl concentration during the substrate pre-treatment phase. This growth recipe is promising because at low NaCl concentrations, it becomes possible to obtain isolated and homogeneously distributed MoS2 monolayers with controllable dimensions, while for higher concentrations both mono-layered and multi-layered MoS2 domains are formed.

The physical characteristics of the MoS2 films on the same substrate were further examined using AFM. The AFM images (figure 4) depicts a height profile around a single isolated triangular domain and around a star-like flake. In figure 4(a), the triangular domain is a monolayer with a few multi-layers in the center. A second morphology observed on the same substrate is shown in figure 4(b), where the monolayer extends out spanning the region around the star-like flake in figure 4(b). The black line that crosses the flakes, corresponding to monolayer height profiles of 0.63 and 0.64 nm, respectively, indicates the AFM sampling region [31]. The growth substrate that was pre-treated with 0.5 mg·mL⁻¹ NaCl/NH₃H₂O had maximum coverage of monolayers and so was subjected to more qualitative and quantitative analysis.

The Raman spectrum obtained from the 0.5 mg·mL⁻¹ NaCl/NH₃H₂O pre-treated sample (figure 5(a)) exhibits the characteristic Raman peaks of MoS2 and the band-edge related emission peak at 4000 cm⁻¹ (corresponding to an emission wavelength of 676 nm). The double peak with the E₂g mode at 382 cm⁻¹ and the A₁g mode at 403 cm⁻¹ corresponds to a frequency difference of 21 cm⁻¹, characteristic of the monolayer quality of MoS2 [5, 18]. Figure 5(b) shows the PL spectra of the same MoS2 monolayer samples that were previously characterized by Raman spectroscopy. The spectrum shows an intense PL peak at around 1.83 eV with a full width at half maximum (FWHM) of about 68.6 meV. These values are consistent with the emission peak at 4000 cm⁻¹ measured in the Raman spectrum and also with the direct band gap nature of MoS2 monolayers. Moreover, the strong PL intensity and a narrow FWHM is indicative of high crystalline quality of the film [5].

To evaluate the electronic quality of the MoS2 monolayers, back-gated FETs were fabricated by isolating a single MoS2 monolayer and patterning four electrodes on it. The transfer characteristics of the FETs obtained at drain voltages (V_d) ranging from 0.5 to 1.5 V with a 500-mV step exhibited typical n-type behavior (figure 6(a)). Inset shows the semi-log plots of the transfer characteristics. The output curve of figure 6(b) shows that MoS2 monolayers contacted by Au electrodes exhibits linear ohmic contact behavior in the gate range from −5 to +20 V.

At V_g = 1.0 V, the FET had a threshold voltage (V_th) of ≈ 11.0 V. Due to the relatively large band gap of MoS2 monolayer and its atomically thin channel, a relatively high I_on/I_off of 10⁷ was achieved. Considering that the gate oxide used in this work was 285 nm thick, there is room for further improvement of the I_on/I_off ratio. The field-effect mobility of MoS2 was determined to be 6.45 cm²V⁻¹s⁻¹ which was
obtained using the equation: $\mu_{\text{FE}} = \frac{L}{WCV_{ds}} \left( \frac{dI_{ds}}{dV_{gs}} \right)$, where $\frac{dI_{ds}}{dV_{gs}}$ is the transconductance extracted from the slope of the black dashed line in figure 6(a) at $V_{ds} = 1$ V. The channel length ($L$) and width ($W$) are 4.0 $\mu$m and 6.0 $\mu$m respectively. $C_{ox}$ is the back-gate capacitance per unit area estimated to be $1.23 \times 10^{-4}$ Fm$^{-2}$ for the 285 nm thick SiO$_2$. The carrier concentration was estimated to be $6.9 \times 10^{11}$ cm$^{-2}$, obtained using the equation: $n_{2D} = C_{bg} (V_{bg} - V_{th})$, where $C_{bg}$, $V_{bg}$, and $V_{th}$ are $1.23 \times 10^{-4}$ Fm$^{-2}$, 20.0 V and 11.0 V, respectively.

Considering the low value of $I_{ds}$ at zero gate bias, a four probe measurement [32, 33] was performed on the device.
Figure 6. Evaluation of the electrical quality of the MoS$_2$-FET. (a) Gate characteristics of the device at drain source voltages of 0.5, 1 and 1.5 V. Inset is the semi-log plot of the gate characteristics. (b) $I-V$ characteristics of the device at gate bias ranging from $-5$ to $+20$ V.

Figure 7. Device description and results of 4-terminal measurements on MoS$_2$ monolayer. (a) Optical image of the fabricated device showing a monolayer MoS$_2$ contacted by four Au electrodes. (b) Schematic of the four-probe measurement setup. Measurements of voltages and currents $V_{23}$, $I_{14}$, $I_T$, and $V_T$ are denoted in the respective circuits. The Au pads are numbered to indicate the pads between which measurements are made. (c) Current–voltage plot for determination of monolayer and contact resistance.

(optical image shown in figure 7(a)) to determine the contact resistance.

A schematic of the measurement platform is shown in figure 7(b). The film resistance was determined using the equation: $R_m = V_{23}/I_{14}$, estimated to be $\approx 150$ M$\Omega$. The contact resistance is subsequently obtained from the equation $V_T = I_T R_c + I_T R_m$ and is estimated to be $\approx 10$ G$\Omega$. It is therefore evident that the contact resistance dominates the total resistance and is the most likely reason for the reduced value of field effect mobility and drain-source current at zero gate bias. Challenges related to contacts will be addressed in a future work where experiments with improved metal-film contacts are being designed.

3.2. Discussion

Pre-treatment of the growth substrate with NaCl and achievement of precise control over precursor (Mo-source) feed in a sulfur-rich ambient were major factors favoring the growth of uniform monolayer MoS$_2$ films with very large
domain sizes (2 cm). This technique is easily scalable to enable large areal coverage on 4 inch wafers; a feat that can be achieved by increasing the size of the growth chamber. The role of NaCl in the growth process is elucidated in greater detail in the following paragraph. The texture and quality of the substrate surface following spin coating with NaCl/NH$_3$H$_2$O during the substrate pre-treatment stage is a key factor influencing MoS$_2$ film growth. During the spin-coating process, the NaCl salt crystals react with ambient moisture in the air and re-crystallizes, the process occurring in millisecond time scale [34, 35]. It is these re-crystallized salt crystals that determine the texture and quality of the pre-treated substrates. An SEM image characterizing the sample surface after NaCl spin coating is shown in figure 8. It is worth noting that since the spin-coating was done in ambient air and since the measurements take time to perform, the texture of the sample surface evolves with time during characterization and sample transportation.

Figure 8. Distribution of monolayer MoS$_2$ on growth substrate following pre-treatment with 0.25 and 0.5 mg·ml$^{-1}$ of NaCl. (a) Left: SEM image of SiO$_2$/Si substrate treated with 0.5 mg·ml$^{-1}$ NaCl/NH$_3$H$_2$O. Right: optical image of substrate, post-growth, showing dense coverage by MoS$_2$. (b) Left: SEM image of SiO$_2$/Si substrate treated with 0.25 mg·ml$^{-1}$ NaCl/NH$_3$H$_2$O. Right: optical image of substrate, post-growth, showing sparse coverage by MoS$_2$.

Figure 9. SEM image and EDX spectra of the MoS$_2$ films grown using 0.5 mg·ml$^{-1}$ NaCl. (a) SEM image of dendrites of MoS$_2$. Inset image is a magnified view of the MoS$_2$ film. (b1) and (b2) are the EDX spectra collected from regions indicated by the green and yellow circle in the inset of figure (a).
In Figure 8, the surface quality of two SiO₂/Si substrates pre-treated with 0.25 mg·ml⁻¹ and 0.5 mg·ml⁻¹ NaCl solution were examined using SEM. The images confirm that there is an obvious and expected difference in the areal coverage of NaCl on the substrates. The corresponding growth results are shown to the right side of the SEM images in Figure 8. As expected, a lower level of complexity in the NaCl texture results in low areal coverage of the substrate by the MoS₂ film. On the other hand, at a NaCl concentration of 0.5 mg·ml⁻¹, the substrate surface texture is complex and MoS₂ films cover a high percentage of the substrate.

Figure 9 (a) is a SEM image of highly dense MoS₂ monolayer grown using the 0.5 mg·ml⁻¹ NaCl pre-treatment. An enlarged view of a select area is shown as an inset in the right corner, with the two circles indicating the area used for composition analysis.

An EDX analysis, performed to confirm the chemical composition of the MoS₂ crystals, indicate concentrations of Mo and S, in 9.1 wt% and 6.0 wt%, respectively. This corresponds to Mo:S ratio of 0.506, representing a MoS₂ composition close to stoichiometry. The higher Mo concentration indicates presence of sulfur vacancies which has been
Table 1. Distribution range of MoS2 film sizes as a function of NaCl concentration.

| NaCl concentration (mg·ml⁻¹) | Fractal sizes (μm) | Median (μm) |
|-----------------------------|-------------------|-------------|
| 0                           | 2.5–25 monolayer  | 10          |
| 0.25                        | 2.5–75 monolayer  | 50          |
| 0.5                         | 2.5–20k mostly monolayer | 20 k |
| 1–4                         | 2.5–20k mostly multilayer | 20 k |
| 5                           | 5–30 multilayer   | 25          |

diagnosed as the major defect in CVD grown MoS2 samples [16, 20–22, 36, 37, 38]. No signal corresponding to Na or Cl was detected. As seen in figure 9(b1), the bare substrates show signal from the SiO2 surface.

To quantify the various MoS2 morphologies that were observed when using different NaCl pre-treatment, the fractal dimensions of these films were calculated using a conventional box-counting method. The monolayer and multi-layer contrast images in figure 10 are extracted from their corresponding images in figure 2, corresponding to different NaCl concentrations. Figures 10 (a1) and (a2) correspond to the color contrast image of figure 2 (a) grown from a NaCl concentration of 0 mg·ml⁻¹. Similarly, figures 10 (b1) and (b2) are extracted from figure 2(b) and correspond to an NaCl concentration of 0.25 mg·ml⁻¹. It should be noted that the image (a1), (b1), (c1), (d1), (e1) to (f1) in figure 10 is a depiction of monolayer contrast imaging where only the monolayers are shown in white against a black background. Similarly, images shown in figures 10 (a2), (b2), (c2), (d2), (e2), (f2) and (g) represent multi-layer contrast imaging with the multi-layers shown in white color against a black background. The fractal dimensions of these black and white images were then computed by Fractalyse software using the box counting method. In this method, the images were broken into smaller box-shaped pieces and each box was then analyzed to calculate the number of boxes (N) that enclosed the prescribed patterns [13]. A plot of $\log(N)$ versus $\log(1/s)$ allows for determination of fractal dimension ($D$) based on the equation: $\log(N) = D \cdot \log(1/s)$. An example of the determination on fractal dimension is shown in figure 11 for an NaCl concentration of 0.5 mg·ml⁻¹.

table 1 shows the distribution of fractal sizes in terms of NaCl concentration. The control group with 0 mg·ml⁻¹ NaCl concentration has fractal sizes in range of 2.5–25 μm. For 0.25 and 5 mg·ml⁻¹ NaCl concentrations, the fractal sizes are in the range of 2.5–75 μm and 5–30 μm, respectively. NaCl concentrations of 1, 2 and 4 mg·ml⁻¹ produce a wide range of fractal sizes in 2.5 μm–2 cm. This analysis is illustrated in table 1 as well as estimated median.

To determine a trend in the fractal dimension variation with NaCl concentration, a plot describing the variation of $D$ with NaCl concentration is shown in figure 12. As the concentration of NaCl in the pre-treatment stage is increased, the fractal dimension of the monolayer initially decreases and subsequently increases above a critical NaCl concentration. On the other hand, there is no noticeable trend in the fractal dimension of multi-layers, which appears to hold a relatively stable value. The significance of fractal dimension is that its value denotes the complexity of a pattern, a fact that is used in this work to describe the nucleation and growth mechanism of MoS2 monolayers and multi-layers [39]. It is evident that the complexity of monolayer and multi-layer patterns over a mm scale (the size of images in figure 2) relates to the areal coverage of the pattern. Although single crystal domains for different NaCl concentrations may have different shapes and possess a different $D$ value, the cm scale of the pattern consists of cross-linked domains that influences the domain edges in the overall MoS2 film pattern. Correlating the areal coverage statistics to the fractal dimension value ($D$), an inverse relationship is experimentally validated (figures 3 and 12) between $D$ and the areal coverage of the substrates by monolayers and multi-layers. This result is useful for future analysis as it can be exploited to provide insight into the growth modes of NaCl-assisted 2D MoS2 films.

The FactSage software was used to determine the partial pressures of Mo- and S-based compounds in gaseous phase at 800 °C. Based on the principle of Gibbs energy minimization during equilibrium reaction, the software determines the various chemical phases present in the growth chamber as a function of time. The concentration of these phases is critically dependent on experimental parameters like the amount of S, MoO3 and NaCl used in the experiment as well as the growth temperature, duration, and carrier gas flux. Figures 13(a), (b) describes this environment in terms of the partial pressures of various precursor components during the
10 min growth time with an Ar gas flow of 70 sccm. Figure 13(a) represents the condition when the substrates were not pre-treated with NaCl. As seen in this plot, sulfur-based gaseous components dominate the environment after the first couple of minutes. The higher and lower oxidation states of Mo have a significantly lower partial pressure. There is a clear difference in the growth chamber environment when NaCl is introduced into the analysis. As seen in the plot (figure 13(b)), after the first couple of mins, there is a high concentration of MoO$_2$Cl$_2$ which dominates other oxidation states of Mo by about two orders of magnitude. Hence, based on the thermodynamics of the growth process, there is an obvious difference between the two growth cases (one without and one with NaCl). In the presence of NaCl, in addition to the Mo-oxides there are several chloride-based Mo compounds like MoO$_2$Cl$_2$, MoOCl$_3$, and MoOCl$_2$. These compounds are known to be catalysts for forming various oxidation states of Mo, effectively increasing the concentration of Mo ions [40]. Theoretical calculations have shown that NaCl performs the role of a molecular seeding promoter,
where it lowers the potential barrier for MoS$_2$ nucleation, thereby facilitating growth. It also facilitates layered growth by increasing the surface adhesion energy. A recent theoretical work has proposed a mechanism explaining the evolution of various MoS$_2$ morphologies as a function of incident flux, temperature and precursor ratio [28]. Here, we highlight the significance of the chalcogen to metal (X/M) ratio and relate it to the formation of various experimentally observed morphologies. According to the principles of crystal growth, there are two major competing mechanisms: (i) diffusion of atoms along the domain boundary and (ii) attachment of atoms to the domain edges. The competition between these two mechanisms result in different morphologies such as compact triangles, star-shapes, dendrites, and non-symmetrical fractals. The X/M ratio is one of the factors that governs the rate of diffusion and attachment. During the growth phase, substrates with a high concentration of NaCl on its surface suffer a decrease in the X/M ratio, due to an increase in the concentration of metal ions (Mo-containing components in vapor phase, figure 13(b))- promoted by the reaction between NaCl and MoO$_3$ source. For stoichiometric MoS$_2$ growth, the ideal X/M ratio is 2. When this ratio decreases from the ideal value, the rate of attachment dominates over the rate of diffusion. This leads to fractal growth. In the extreme case, for high concentrations of NaCl (concentration greater than 4 and 5 mg·ml$^{-1}$), the X/M ratio decreases even further and results in a condition close to diffusion limited aggregation [28, 41]. The rate of attachment in this case is much higher than the rate of diffusion and as shown in figures 2, 3 and 10, the substrate has a high areal coverage of multi-layers as well as a high density of dendrites visible in multi-layer contrast images. At very low NaCl concentration, the phenomenon of diffusion dominates over that of attachment and MoS$_2$ film growth is inhibited. This is validated in figure 3, where at a NaCl concentration of 0.25 mg·ml$^{-1}$, the areal coverage of monolayers and multi-layers is low at 19.4% and 0.4% respectively. A moderate increase in the NaCl concentration to 0.5 mg·ml$^{-1}$ increased the areal coverage of the substrate with MoS$_2$ monolayers to the extent of 81.2%. In this regime, the mechanisms of diffusion and attachment both contribute to film growth.

4. Conclusion

The work presented here highlights the effect of substrate pre-treatment (using NaCl and Mo-precursors) on film growth of MoS$_2$ monolayers and multi-layers. An optimization of the concentration of NaCl enabled a significant increase in the domain size of the film. At an NaCl concentration of 0.5 mg·ml$^{-1}$, approximately 81% of the substrate was covered by high-crystal quality monolayers. The film complexity as quantified by fractal dimension calculations reveal a relationship between the NaCl concentration and fractal dimensions. Using FactSage software, theoretical estimates of the partial pressure of Mo and S gaseous components were computed and used to explain the growth kinematics. The chalcogen/metal (X/M) ratios determine various crystal morphologies based on two competing mechanisms that favor diffusion or attachment of atoms along the domain boundary. At low NaCl concentrations, the ratio of X/M is high, causing diffusion to dominate over attachment, resulting in low areal coverage growth of MoS$_2$ films. On the other hand, at high NaCl concentrations, the ratio X/M is low, and attachment dominates over diffusion, resulting in fractal growth. At an optimum NaCl concentration, the effects of diffusion and attachment contribute equally towards large areal growth of MoS$_2$ layers. This work therefore analyzes the growth kinematics and provides a reproducible recipe for tuning the fractal dimension of 2D MoS$_2$ films to the order of several cms.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID IDs

Yan Jiang @ https://orcid.org/0000-0003-0054-5193
Usha Philipose @ https://orcid.org/0000-0001-9065-0274

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[2] Ma R and Sasaki T 2010 Nanosheets of oxides and hydroxides: ultimate 2D charge-bearing functional crystallitles Adv. Mater. 22 5082–104
[3] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699–712
[4] Chow P K, Jacobs-Gedrim R B, Gao J, Lu T-M, Yu B, Terrones H and Koratkar N 2015 Defect-induced photoluminescence in monolayer semiconducting transition metal dichalcogenides ACS Nano 9 1520–7
[5] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C-Y, Galli G and Wang F 2010 Emerging photoluminescence in monolayer MoS$_2$ Nano Lett. 10 1271–5
[6] Mak K F and Shan J 2016 Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides Nat. Photon. 10 216–20
[7] Lin Z et al 2018 Research update: recent progress on 2D materials beyond graphene: from ripples, defects, intercalation, and valley dynamics to straintronics and power dissipation APL Mater. 6 080701
[8] Huang X, Zeng Z and Zhang H 2013 Metal dichalcogenide nanosheets: preparation, properties and applications Chem. Soc. Rev. 42 1934–46
[9] Liu L et al 2018 Phase-selective synthesis of 1T’ MoS$_2$ monolayers and heterophase bilayers Nat. Mater. 17 1108–14
[10] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Single-layer MoS$_2$ Transistors Nat. Nanotechnol. 6 147–50
[11] Smyth C M, Addou R, McDonnell S, Hinkle C L and Wallace R M 2016 Contact Metal-MoS2 interfacial reactions and potential implications on MoS2-based device performance J. Phys. Chem. C 120 14719–29
[12] Li X et al 2009 Large-area synthesis of high-quality and uniform graphene films on copper foils Science 324 1312–4
[13] Shao G et al 2019 Shape-engineered synthesis of atomically Thin 1T-SnSe2 catalyzed by potassium halides ACS Nano 13 8265–74
[14] George A S, Mutlu Z, Ionescu R, Wu R J, Jeong J S, Bay H H, Chai Y, Mkhoyan K A, Ozkan M and Ozkan C S 2014 Wafer scale synthesis and high resolution structural characterization of atomically thin MoS2 layers Adv. Funct. Mater. 24 7461–6
[15] Artyukhov V I, Hu Z, Zhang Z and Yakobson B I 2016 Topochemistry of bowtie-and star-shaped metal dichalcogenide nanosiland formation Nano Lett. 16 3696–702
[16] Van Der Zande A M, Huang P Y, Chenet D A, Berkelbach T C, You Y, Lee G-H, Heinz T F, Reichman D R, Muller D A and Hone J C 2013 Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide Nat. Mater. 12 554–61
[17] Wang J et al 2018 Twin defect derived growth of atomically thin MoS2Dendrites ACS Nano 12 635–43
[18] Jiang Y, Lin Y, Cui J and Philipose U 2018 Effects of strategically placed water droplets on monolayer growth of molybdenum disulphide J. Nanomater. 2018 6192532
[19] Wang S, Rong Y, Fan Y, Pacios M, Bhaskaran H, He K and Warner J H 2014 Shape evolution of monolayer MoS2 crystals grown by chemical vapor deposition Chem. Mater. 26 6371–9
[20] Chen W et al 2015 Oxygen-assisted chemical vapor deposition growth of large single-crystal and high-quality monolayer MoS2 J. Am. Ceram. Soc. 137 15632–5
[21] Li H, Li Y, Aljarrah A, Shi Y and Li L-J 2017 Epitaxial growth of two-dimensional layered transition-metal dichalcogenides: growth mechanism, controllability, and scalability Chem. Rev. 118 6134–50
[22] Yu H et al 2017 Wafer-scale growth and transfer of highly-oriented monolayer MoS2 continuous films ACS Nano 11 12001–7
[23] Almeida K et al 2018 High-vacuum particulate-free deposition of wafer-scale mono-, Bi-, and trilayer molybdenum disulphide with superior transport properties ACS Appl. Mater. Interfaces 10 33457–63
[24] Kim H, Ovchinnikov D, Deiana D, Unucheck D and Kis A 2017 Suppressing nucleation in metal-organic chemical vapor deposition of MoS2 monolayers by alkali metal halides Nano Lett. 17 5056–63
[25] Lee D K, Kim S, Oh S, Choi J-Y, Lee J-L and Yu H K 2017 Water-soluble epitaxial NaCl thin film for fabrication of flexible devices Sci. Rep. 7 8716
[26] Wang Z et al 2017 NaCl-assisted One-step Growth of MoS2-WS2 In-plane Heterostructures Nanotechnology 28 325602
[27] Zhang K et al 2018 Considerations for utilizing sodium chloride in epitaxial molybdenum disulphide ACS Appl. Mater. Interfaces 10 40831–7
[28] Nie Y, Liang C, Zhang K, Zhao R, Eichfeld S M, Cha P-R, Colombo L, Robinson J A, Wallace R M and Cho K 2016 First principles kinetic monte carlo study on the growth patterns of WSe2 monolayer 2D Mater. 3 025029
[29] Li H, Wu J, Huang X, Yin Z, Liu J and Zhang H 2014 A universal, rapid method for clean transfer of nanostructures onto various substrates ACS Nano 8 6563–70
[30] Shi Y, Yang P, Jiang S, Zhang Z, Huan Y, Xie C, Hong M, Shi J and Zhang Y 2018 Na-assisted fast growth of large single-crystal MoS2 on sapphire Nanotechnology 30 034002
[31] Mak K F, Lee C, Hone J and Heinz T F 2010 Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805
[32] Wisniewski D, Byrne K, de Souza C F, Fernandes C and Ruda H E 2018 Enhancement of transport properties in single ZnSe nanowire field-effect transitors Nanotechnology 30 054007
[33] Salj J, Philipose U, De Sousa C, Aouba S and Ruda H 2006 Electrical properties of ohmic contacts to zno nanowires and their application to nanowire-based photodetection Appl. Phys. Lett. 89 261112
[34] Lee D K, Kim T S, Choi J-Y and Yu H K 2018 Recrystallized NaCl from thin film to nano-/micrometersis sacrificial metal for metal nanostructures Cryst. Growth Des. 18 5295–300
[35] Oliva-Ramirez M, Macias-Montero M, Borras A and Gonzalez-Elipe A R 2016 Ripening and recrystallization of NaCl nanocrystals in humid conditions RSC Adv. 6 3778–82
[36] Hong J et al 2015 Exploring atomic defects in molybdenum disulphide monolayers Nat. Commun. 6 1–8
[37] McDonnell S, Addou R, Buie C, Wallace R M and Hinkle C L 2014 Defect-dominated doping and contact resistance in MoS2 ACS Nano 8 2880–8
[38] Najmaei S, Liu Z, Zhou W, Zou X, Shi G, Lei S, Yakobson B I, Idrobo J-C, Ajayan P M and Lou J 2013 Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers Nat. Mater. 12 754–9
[39] Dhanaraj G, Byrappa K, Prasad V and Dudley M 2010 Springer Handbook of Crystal Growth (London New York: Springer Science & Business Media) (https://doi.org/10.1007/978-3-540-74761-1)
[40] Rempel K, Williams-Jones A and Migdisov A 2008 The solubility of molybdenum dioxide and trioxide in HCl-bearing Water Vapour at 350 °C and Pressures up to 160 Bars Geochim. Cosmochim. Acta 72 3074–83
[41] Jung J-S and Hwang N-m 2016 Non-classical crystallization of thin films and nanostructures in CVD process Chemical Vapor Deposition: Recent Advances and Applications in Optical, Solar Cells and Solid State Devices (Croatia: InTech): p 23