Temperature-dependent morphology of chemical vapor grown molybdenum disulfide

Wang, Yantao; Zhou, Jiadong; Liu, Zheng; Yang, Xiaoyin

2017

Yang, X., Wang, Y., Zhou, J., & Liu, Z. (2017). Temperature-dependent morphology of chemical vapor grown molybdenum disulfide. *Journal of Physics D: Applied Physics*, 50(16), 164002-.

<https://hdl.handle.net/10356/86340>

<https://doi.org/10.1088/1361-6463/aa6220>

© 2017 IOP Publishing Ltd. This is the author created version of a work that has been peer reviewed and accepted for publication by *Journal of Physics D: Applied Physics*, IOP Publishing Ltd. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at:
[<http://dx.doi.org/10.1088/1361-6463/aa6220>].

Downloaded on 26 Apr 2023 20:25:05 SGT

Temperature dependent morphology of chemical vapor grown molybdenum disulfide

Xiaoyin Yang^{1,2}, Yantao Wang^{1,2}, Jiadong Zhou² and Zheng Liu¹

¹ Center of Programable Materials, School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798, Singapore

² School of Physics, Nankai University, Tianjin 300071, PR China

Email: z.liu@ntu.edu.sg

Abstract:

Monolayered molybdenum disulfide (MoS₂) is a promising two-dimensional direct band gap semiconductor with potential applications. In this work, we observed the temperature dependency of the morphologies of MoS₂ monolayers from chemical vapor deposition. At low growing temperature below 850 °C, MoS₂ flakes tend to be in triangle shapes. At 850-950°C, hexagonal MoS₂ flakes can be observed. While at a temperature over 950°C, MoS₂ flakes can form rectangle shapes. Complementary characterizations have been done on these samples. We also proposed a mechanism for such temperature-dependent shape evolution based on thermodynamic simulation.

Key words:

Molybdenum disulfide, morphology, chemical vapor deposition, growing mechanism

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have great potentials in optoelectronics, mechanics, and electronics due to its unique electronic structure. 2D TMDs have been realized by various synthetic methods, including chemical vapor deposition (CVD), wet-chemical synthesis, and liquid exfoliations, etc. Among them, CVD method has been extensively explored due to their potentials for high scalability and morphological controlled [1].

Among TMDs, molybdenum disulfide (MoS₂) have attracted a lot of attentions because of the transition from indirect band gap to direct band gap when it thins down to monolayer. This recently has triggered great interests in the valleytronics, light emitters and ultra-low-power consuming devices, etc [2-4]. A MoS₂ monolayer consists of two sulfur atom layers sandwiching a molybdenum atom layer with strong covalent bonds. Bulk MoS₂ is an indirect semiconductor with a bandgap of 1.3 eV, while MoS₂ monolayer, due to the quantum confinement effect, possesses a direct bandgap

of 1.8~1.9 eV [5], which has been widely testified with photoluminescence (PL) and absorption spectra.

Although a lot of work have been done on the CVD grown MoS₂ in the past decade, the growing mechanism remains unclear. For example, a large variety of shapes can be observed from CVD grown MoS₂, including regular triangle, hexagon, rectangle and many other anomalies. As an analogue of graphene, MoS₂ also exhibits a wide diversity of microstructures characterized by domain sizes, shapes, crystal orientation and lattice defects. Thus, the investigation of shape evolution of MoS₂ is highly demanding.

In this paper, we identified the temperature dependent morphologies of MoS₂. We characterized the samples of different shapes with several tools including scanning electron microscopy (SEM), Raman spectroscopy, photoluminescence (PL). We then applied the first principle Kinetic Monte Carlo method to simulate different shapes of MoS₂ flakes grown at different temperature.

2. Methods

As shown in Fig.1 (a), the MoS₂ flakes were synthesized by CVD method with molybdenum trioxide (MoO₃) and sulfur (S) powder as precursors in a tube furnace equipped with a temperate controller. We put alumina boat with MoO₃ (~ 10mg) inside downstream in the middle of the tube (high temperature zone), and put a plastic boat with sufficient S powder (~ 3g) inside at the low temperature zone. A piece of Si wafer with 280nm SiO₂ was placed face down to MoO₃ powder on the top of the boat. Ar was used as a carrier gas (60 sccm). It took around 15 mins to heat up to certain temperature and remained for another 15 mins.

According to the reference, at deposition temperatures, S vapor reduced MoO₃ powder to volatile suboxide MoO_{3-x}. It will diffuse on the substrate and react with S to form monolayered MoS₂. The possible reactions could be simplified by the the Eqs. (1) and (2). [6]

3. Results and Discussion

Figure 1. CVD growth and optical images of MoS₂. (a) Experimental setup for CVD growth of MoS₂; (b) Schematic of MoS₂ structure; (c) Typical optical images of triangular MoS₂ flakes under low growth temperature (below 850 °C); (d) Optical images of hexagonal MoS₂ flakes grown under 850-950 °C; (e) Optical images of rectangular MoS₂ flakes grown over 950 °C.

Figure 1 shows the optical images of MoS₂ flakes obtained on the SiO₂/Si substrate under different growing temperature. When it grows in a relatively low temperature (750°C), the MoS₂ flakes tend to be in triangle shapes. Increasing the temperature to 850-950 °C makes a high chance for hexagonal flakes. Over 950 °C, rectangular MoS₂ can be observed.

Figure 2. Raman and photoluminescence (PL) characterizations of three kinds of MoS₂ flakes. (a) Raman spectra of MoS₂, (b) PL spectra of the same samples; (c) (e) and (g) Raman mapping of triangular, hexagonal and rectangular MoS₂ flakes; (d) (f) and (h) PL mapping of the same MoS₂ flakes.

We characterized the samples using Raman spectroscopy and photoluminescence (PL) (Figure 2). Two characteristic Raman vibration modes can be seen in the spectra in Figure 2a, where the E_{2g}^1 mode represents the in-plane vibration of molybdenum and sulfur atoms and the A_{1g} mode related to the out-of-plane vibration of sulfur atoms [7]. The frequency difference between these two modes depends on the number of layers of MoS₂. Here, experimental results show that these two modes are located at 383.9 and 403 cm⁻¹, respectively, giving a frequency difference Δk of 20.0 cm⁻¹. This matches well with the frequency difference of CVD-grown monolayer MoS₂ in previous work [8-10]. We also performed intensity mapping on three kinds of MoS₂ domain at A_{1g} mode. We have examined many locations and found that, for most of them, $\Delta k < 20.5$ cm⁻¹, confirming these CVD grown MoS₂ monolayers are homogeneous.

Photoluminescence (PL) spectra were collected from the same samples, as shown in Figure 2b. All three flakes show a similar spectral profile in terms of peak position and FWHM (full width at half maximum).

A strong PL signal is located at 675 nm, which can be correlated to the A1 excitation of MoS₂ [11]. 2D PL mapping for different domain shapes was also performed by stepping a focused excitation laser (532nm) across the sample and integrating the PL signal from each point. Figure 2d, 2f and 2h show corresponding PL intensity maps for triangular, hexagonal and rectangular MoS₂ flakes, respectively, suggesting the high crystallinity and uniformity of the MoS₂ monolayer.

Figure 3. SEM images of three kinds of MoS₂ monolayers. (a) Triangular MoS₂; (b) Hexagonal MoS₂ (c) Rectangular MoS₂.

Figure 3 shows SEM images of three kinds of MoS₂ monolayers. Some of these samples have rough edges. As circled in Fig.3, a few small MoS₂ domains can be observed on the MoS₂ due to the second nucleation and growth. It is well known that, though CVD method can produce large-area MoS₂ films, it can also form grain boundaries (GBs) and point defects on monolayered MoS₂. [12] Those structural defects may server as a nucleation sites for the growth of the second layer MoS₂.

3.1 Grow mechanism

Here, we employed a thermodynamic model to explain the variation in the morphologies of MoS₂ along with the change of temperature. The main contribution to the shape difference phenomenon is the variation of the growth speed of the Mo and S atom along the Si substrate of the surface. [13]

Considering the principle of crystal growth, the shape of crystal is determined by the potential of each face in time [14] The faces with greater potential grow faster and therefore turn out to be sharper facets after deposition. The faces with less potential, on the contrary, grow slower, becoming ultimately larger and flatter. In 2D crystals, due to its two-dimensional geometry, the growing rate of crystal face depends on the free energy of the edges. Naturally, the crystal edge with the low free energy grows slow. As to monolayer MoS₂, its geometry is determined by the growing rate of the edge terminal, and the growing rate mainly relies upon the growing temperature. A few shapes that with Mo zigzag (Mo-zz) terminations and S zigzag (S-zz) terminations have been identified, which are the two states with the lowest energy. [15] Other shapes may also possibly exist due to the different rate of sublimation and combination. Based on this, we propose an assumption that all shapes of domains origin in several hexagonal nuclei that three sides terminated with Mo-zz and the other three sides terminated with S-zz, and then the temperature effect are considered. The simulation is based on first principle kinetic Monte Carlo (KMC) method,

where the simulations focus on the final state of molecular dynamics instead of the process of movement of atoms. [16] As it is well known, the core of KMC simulation is to solve Markovian master equation:

$$\frac{d\varphi_j(t)}{dt} = \sum_i k_{i,j}\varphi_i(t) - \sum_i k_{j,i}\varphi_j(t) \quad (3)$$

Where $\varphi_j(t)$ and $\varphi_i(t)$ are the specific states in matrix form at time t in the state j and i , containing atoms types and its location coordinates. $k_{i,j}$ and $k_{j,i}$ are the probability of the system evolving from state i to state j and from state j to state i . [17-19]

We dismiss the interaction between MoS₂ and Si substrate. If a sulfur (S) atom was added to MoS₂ monolayer the change of energy can written as:

$$\Delta E_{i,j} = -[2n_1\Delta H_{Mo-S} + n_2\Delta H_{S-S}] \quad (4)$$

The energy change of adding a Mo atom can also be written as followed:

$$\Delta E_{i,j} = -[2n_1\Delta H_{Mo-S} + n_2\Delta H_{Mo-Mo}] \quad (5)$$

Where n_1 is the number of the nearest atoms of the position for the follow-up atom, n_2 is the number of the next-nearest neighbors of the position for the follow-up atom. [20] The band energy of MoS₂ in database shows that $\Delta H_{Mo-S} = -1.325eV$, $\Delta H_{Mo-Mo} = -0.882eV$ and $\Delta H_{S-S} = -0.288eV$ [21], the probability of system evolution in equation (1) can be written as:

$$k_{i,j} = \frac{k_B T}{h} \exp\left(\frac{-\Delta E_{i,j}}{k_B T}\right) \quad (6)$$

Figure 4. (a) Flow chart for Bortz-Kalos-Lebwitz (BKL) algorithm. (b) Process for evolution from initial state to final state.

The temperature-dependent shape evolution can be well predicted by KMC simulation. As shown in Fig 4, we use the BKL algorithm to simulate the shape evolution of MoS₂. As shown in Fig 4 a, we start by setting the time $t = 0$ and the simulate time t_{max} . Then, we choose an initial state and determine every possible final state. The probability k_i for evolution obeys Poisson distribution and it is shown in Equation (4),(5) and (6). We also compute the total rate $R = \sum_i k_i$. Afterwards, we set two random numbers ρ_1 and $\rho_2 \in (0,1]$ and randomly choose process “j” by $\sum_{i=1}^{j-1} k_i < \rho_1 R \leq \sum_{i=1}^j k_i$. Finally, we execute the process, update the time $t = t - \frac{\ln(1-\rho_2)}{R}$ and return to the second step. The simulation results are shown in Fig.5. As shown below, the rectangular, hexagonal and triangular MoS₂ can be formed at 1337K, 1137K and 977K, respectively.

Figure 5 shows the process of shape evaluation of MoS₂ flakes. Fig 5 shows the process of shape evaluation of MoS₂ from initial state to the final state with the shape at different time nodes including 0s, 374s, 756s, 1183s and 2400s.

Figure 5. Simulation processes of MoS₂ growth under (a) 977K (704°C), (b) 1137K (864°C) and (c) 1337 K (1064°C)

The termination of the MoS₂ domains depends on the growth speed of the potential energy edge. With the assumption that MoS₂ grows from several hexagonal nuclei and take the band energy into consideration, we can draw the conclusion that S-zz terminations with the higher edge free energy grow faster than the Mo-zz terminations when the temperature is lower than 1000K. Under this circumstance, the shape of MoS₂ domains will turn out distorted hexagon or triangle. When the ratio is beneath 2, S-zz terminations with the lower edge free energy grow slower than the Mo-zz terminations. It will also be in distorted

hexagon or triangle shape, but mostly terminated with S-zz. When the temperature is 1100K, the shape will be hexagonal.

According to our result above, the length of Mo-zz or S-zz terminated edges of triangular and hexagonal MoS₂ flakes are the same. So, the ratio of the length of Mo-zz termination and S-zz termination can be used to describe the shape of MoS₂ in this case. Based on the unit cell parameter $a = 3.12 \text{ \AA}$ [22] and the result above, we get a more specific result for the phenomenon. The length of the terminated edges can be expressed with the energy. S-zz terminations with lower potential energy tend to become much longer than Mo-zz at the temperature of 977K, based on formula (4)(5) and (6), thus the shape of MoS₂ favor triangular. Similarly, this is the reason MoS₂ flakes become hexagon in the temperature of 1137K. Formula (6) shows that the higher the temperature the smaller difference between growing speed of Mo-zz and S-zz termination. Therefore, the shape evolves into hexagon. When the temperature is above 1137 K, the MoS₂ domains show quite different properties. The difference between Mo-zz and S-zz termination becomes indiscernible in this temperature. Rectangular MoS₂ flakes can be found at such temperature. As shown in Fig. 5 (b), one facet does have a probability to grow slower than other facets, which means it will be flatter than the other facets. Formula (4) and (5) shows that its nearest facets have higher potential energy, and tends to become sharper. Apparently, the last facet become another flat facet. Therefore, MoS₂ tends to form a rectangle shape.

4. Conclusion

In this work, we observed the temperature-dependent morphologies of MoS₂ monolayers grown by CVD method. At low temperature, MoS₂ flakes tend to be in triangle shape; with the increasing temperature of up to 850-950°C, hexagonal MoS₂ flakes can be observed; when the growth temperature reaches over 950°C, MoS₂ flakes can be in rectangle shape. According to the simulation process based on the first principle kinetic Monte Carlo method, similar shapes simulated at corresponding temperatures are observed, which can preferably explain the MoS₂ grow mechanism at different temperature.

5. Acknowledgement

6. Reference

- [1] Bhimanapati, Ganesh R. et al. ACS Nano 9.12 (2015): 11509–11539.
- [2] J. Chen, N. Kuriyama, H. Yuan, H.T. Takeshita, T. Sakai, J. Am. Chem. Soc. 123 (2001) 11813–11814.
- [3] M. Chhowalla, G.A.J. Amaratunga, Nature 407 (2000) 164–167
- [4] J. Zhang, J.M. Soon, K.P. Loh, J.H. Yin, J. Ding, M.B. Sullivan, P.Wu, Nano Lett. 7 (2007) 2370–2376
- [5] Yan, Aiming et al. Nano Lett. 15.10 (2015): 6324–6331.
- [6] Perkgoz NK, Bay M. Nano-Micro Letters. 10.5 (2015):70–9.
- [7] Tonndorf, P.; Schmidt, R.; Böttger, P.; Zhang, X.; Börner, J.; Liebig, A.; Albrecht, M.; Kloc, C.; Gordan, O.; Zahn, D. R. T. Opt. Express 2013, 21, 4908–4916.

- [8] Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B. I.; Idrobo, J.-C.; Ajayan, P. M.; Lou, J. *Nat. Mater.* 2013, 12, 754–759
- [9] Yu, Y.; Li, C.; Liu, Y.; Su, L.; Zhang, Y.; Cao, L. *Sci. Rep.* 2013, 3, 1866
- [10] Ling, X.; Lee, Y.; Lin, Y.; Fang, W.; Yu, L.; Dresselhaus, M. S.; Kong, J. *Nano Lett.* 2014, 14, 464–472.
- [11] Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. *Nano Lett.* 2010, 10, 1271–1275.
- [12] Lee, Y., Park, S., Kim, H., Han, G. H., Lee, Y. H., & Kim, J. *Nanoscale* 2015, 7(28), 11909–11914.
- [13] A.F. Voter, Introduction to the Kinetic Monte Carlo Method, in *Radiation Effects in Solids*, K.E. Sickafus, E.A. Kotomin and B.P. Uberuaga (Eds.), Springer, Berlin (2007).
- [14] De Yoreo, J. J.; Vekilov, P. G. In *Biomineralization: Review in Mineralogy and Geochemistry*; Dove, P. M., De Yoreo, J. J., Weiner, S., Eds.; Mineralogical Society of America Geochemical Society: Chantilly, VA, 2003; Vol. 4, pp 81–82.
- [15] Wang, S.; Rong, Y.; Fan, Y.; Pacios, M.; Bhaskaran, H.; He, K.; Warner, J. H. Shape Evolution of Monolayer MoS₂ Crystals Grown by Chemical Vapor Deposition. *Chem. Mater.* 2014, 26, 6371–6379.
- [16] E.A. Carter, *Science* 321, 800 (2008)
- [17] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland Publishing, Amsterdam (1980).
- [18] C.J. Kramer, *Essentials of Computational Chemistry: Theories and Models*, 2nd edn., Wiley, Chichester (2004).
- [19] R.M. Martin, *Electronic-Structure: Basic Theory and Practical Methods*, Cambridge University Press, Cambridge (2004).
- [20] J.N. Brønsted, K.J. Pedersen, *Z. Phys. Chem.* 108 (1924) 185.
- [21] N. Dinter, M. Rusanen, P. Raybaud, S. Kasztelan, P. da Silva, H. Toulhoat, *J. Catal.* 267 (2009) 67.
- [22] Cao, T. *et al. Nat. Commun.* 3:887 doi: 10.1038/ncomms1882 (2012).