A General Two-Step Chemical Vapor Deposition Procedure to Synthesis Highly Crystalline Transition Metal Dichalcogenides: A Case Study of MoS₂

Reza Shidpour^{a,*1}, Manouchehr Vosoughi^c, Hadi Maghsoudi^b, Abdolreza Simchi^{a,*}

^a *Material Science & Engineering Department, Sharif University of Technology, Tehran, Iran*

^b *Material Science and Engineering, University of California, Riverside, United States.*

^c *Chemical & Oil Engineering Department, Sharif University of Technology, Tehran, Iran*

Abstract:

A green and simple synthesis method based on a two-step chemical vapour deposition approach has been developed to synthesis transition metal dichalcogenides flakes. With non-toxic precursor such as transition metal oxides and elemental sulphur, large-area, strong photoluminescent, and uniform MoS₂ nanoflakes was produced at a relatively low growth temperature (650 °C). Controlling layer number and morphology was achieved only by precursor concentration without any oxide impurity revealed by SEM, PL and Raman spectroscopy. This method can be used to make wide range of metal chalcogenides such as ZnS, SnS₂, PtS₂ and PdS₂.

Keywords: Electronic Materials; Vapor Deposition; Raman Spectroscopy; Chalcogenides; Electron Microscopy

¹ Corresponding author Address: Material Science & Engineering Department, Sharif University of Technology, Tehran, Iran, Tel.: +98 966165262; fax: +98 6616-5261. E-mail address , rezashidpour@gmail.com, reza.shidpour@ucr.edu (R. Shidpour) and simchi@sharif.edu (A. Simchi)

1) Introduction

One of the most promising TMD's, MoS₂, presents a wide range of applications such as selective gas sensors^{1,2}, catalysis³⁻⁵, lithium ion battery anodes⁶ and field-effect transistors (FETs) with high mobility and current On/Off ratios^{7,8}. Several growth methods have been developed to prepare thin-layer MoS₂, including micromechanical exfoliation⁸⁻¹⁰, electrochemical synthesis¹¹ and chemical vapour deposition¹²⁻¹⁵. Generally, these methods have benefits and some disadvantages. For example, atomically thin flakes of MoS₂ exfoliated by mechanical cleavage show the highest quality, but the size of the flakes was small, and their thickness and shape were not controllable¹⁶ or solution-phase production of MoS₂ by exfoliation or hydrothermal synthesis holds promise for large-scale production, but application of these materials in electronics is restricted by the low quality of thus MoS₂ made¹³. Chemical vapor deposition (CVD) has been one of the most practical methods to synthesize large-area graphene^{8,17} and insulator 2D materials such as boron nitride¹⁸. MoS₂ can be made by the CVD method without any catalyst and with various solid, liquid and gas precursors. Some of these methods involve hazardous materials such as hydrogen sulphide (H₂S) and carbon disulfide (CS₂) conducted over a long period of time yield them unfavourable for applications in electronic and optical device fabrication industries. Other problem is that the growth of MoS₂ is very sensitive to the substrate treatment prior to the growth^{19, 20}. In a practical growth strategy, direct growth of MoS₂ films on SiO₂ surfaces is done by using sulphur powder and a molybdenum oxide precursor at elevated temperature in N₂ atmosphere²¹⁻²³. Although, this growth method has apparent advantages such as simplicity of experimental setup and not exhausting hazardous gasses but there are some flaws included 1) producing inhomogeneous thin film because of inability to precisely control the layer number of MoS₂ films. 2) Existence of undesired MoO₃ and MoO₂ impurities. As the properties of MoS₂ materials strongly depend on the layer number and purity, this unsatisfactory uniformity and controllability poses a formidable challenge for the improvement of device performance. One of the main reasons leading to abovementioned problems is that large transfer rate of MoO₃ precursor leading to inhomogeneous deposited thinfilm. In this paper, a simple growth method was presented to overcome most problems. Using weak solvent of oxide precursors very thin MoS₂ flakes was made by annealing at moderate temperature. This method can be used to fabricate monolayer or multilayer of other hexagonal close packed oxides and metal chalcogenides such as TMD's, ZnO, ZnS, PtS₂, PdS₂ and SnS₂.

Experimental method

Our strategic method to pass over obstacle is selecting a weak solvent for MoO₃ to make a low concentration MoO₃ solution and using it instead to powder MoO₃. Partial dissolving causes to very low mass transfer of MoO_x onto substrate to grow very thin MoS₂ nanocluster. Water is a weak solvent for MoO₃ that dissolution of MoO₃ proceeds via this reaction²⁵: $MoO_3 + yH_2O \leftrightarrow MoO_3(H_2O)_y$ where the hydration number (y) increased with increasing water fugacity.

To synthesize, 0.1 g MoO₃ powder was partially dissolved in a 100 ml beaker at temperature that solution is boiling. Our growth procedure includes a pre-treatment before a two-stage annealing. So that experimental steps are: 1) transferring and drying of solution on substrate: an amount of up-section hot solution transferred on a 1.5

cm $\times$ 1.5 cm SiO₂ /Si substrate (it relates to sample size but it was 0.1 ml in our work) and a same size SiO₂ /Si substrate was faced down on main substrate to trap the solution on substrate. After rapid doing above step, the two substrates were cooled suddenly to 25°C and were dried at this temperature. 2) Annealing in air atmosphere: these samples were annealed at 600 °C for 20 min in a cubic furnace with static air atmosphere. If the annealing time increases more than 40 min, there will not remain good results. 3) Sulfurizing in nitrogen atmosphere: Two molybdenum oxide coated substrates were put on a ceramic crucible and 1.2 g of sulphur powder was placed in a crucible 15 cm away from the center of a quartz tube. During the synthesis of MoS₂ sheets, the reaction chamber was heated to 650 °C with a heating rate of 15 °C / min in N₂ flow (1 sccm). The scheme of work stages has been shown in Figure 1.

<Figure 1>

The chamber was kept at 650 °C for 15 min before cooling down. The MoO_x species convert to MoS₂ species with increasing temperature. X-ray diffraction (XRD) was used to determine the chemical composition and crystallinity of the products. Generally, there exists two phases of layered 2H- MoS₂ and 3R-MoS₂²⁶.

2) Results and discussion

This growth method has three stages. 1) Elementary stage: drying in air 2) intermediate stage: annealing in air 3) final stage: annealing in N₂. The most important stage to make uniform coverage of single-layer MoS₂ clusters on SiO₂/Si is intermediate stage that the MoO₃ convert to MoO_x species. To explore the crystal structure and chemical composition of intermediate products, the XRD and Raman spectroscopy were utilized. Figure 2.A shows XRD patterns of our MoS₂ samples. Based on XRD pattern, it has been indexed to the hexagonal structure of MoS₂ with lattice constants: a=3.160, c=12.29 Å (PDF 37-1492).

<Figure 2>

The diffraction peaks at 32.48 and 61.18 degree are attributed to the (100) and (110) crystal planes respectively. A shift in the (110) peak position of MoS₂, is usually regarded as a key mechanism for the strain relief of the folded structure¹³ and our XRD pattern is consistent with other reports^{5,13,27,22,28}. From Figure 2.A, it was estimated that the (110) peak of MoS₂ was shifted by about 0.4 % values. The layer consists mainly of 2H-MoS₂ but some 3R-MoS₂ cannot be excluded²⁸. The (110) orientation has the highest reflection intensity, and therefore, a part of the crystals must have an orientation of the basal planes unparallel to the substrate surface.

XRD pattern (Figure 2.A) shows that the intermediate thin-film annealed at air after 15 min has an amorphous structure without any distinct XRD peaks. This conclusion was confirmed by Raman spectra of intermediate thin-film (Fig. 3.A) compared with molybdenum oxide hydrate, Mo₃O_{8.n} (H₂O) (Figure 3.B), MoO₂ (Figure 3.C), MoO₃ (Figure 3.D).

<Figure 3>

From the scanning electron microscopy (SEM) image shown in Fig. 4.A, it is found that there are triangular MoS₂ clusters in area about 1cm × 1cm . The typical side length of the triangles is about 3μm, which is also confirmed by a close up SEM image, see Fig. 4.B. Based on Fig. 4.A we estimated that the total area of the triangular clusters covered 70% of the sample. Today, there is a well-defined and standard characterization method by photoluminescence and Raman spectroscopy to demonstrate single-layer and multilayer MoS₂.

<Figure 4>

In this method that has completely been confirmed by TEM and AFM measurements^{1,5,9,13,19,22,26}, two characteristics of Raman spectroscopy can be used to determine the number of layers of MoS₂ samples. First, the position of E_{2g} and A_{1g} peaks and second, the frequency difference between the E_{2g} and A_{1g} that the former can be shifted a little depended to growth conditions but the later is strongly related to layer number. The E_{2g} mode corresponds to in-plane vibrations (two S atoms are displaced in one direction and the Mo atom is displaced in the opposite direction). The A_{1g} mode corresponds to perpendicular vibrations (two S atoms are displaced in opposite directions while the Mo atom does not move).

For single-layer MoS₂, the peak position of E_{2g} is between 404 and 406 cm⁻¹ and A_{1g} is between 383 and 386 cm⁻¹^{5,13,18,19,26}. In addition, the difference between the E_{2g} and A_{1g} Raman modes which is widely used to identify the layer number²⁹ is about 20 cm⁻¹ for monolayer MoS₂, ~ 22 cm⁻¹ for bilayer, ~ 23 cm⁻¹ for trilayer and about 25 cm⁻¹ for bulk MoS₂^{5, 30, 31}.

<Figure 5>

As shown in Fig. 5.A, sample 1 exhibits two Raman characteristic bands for the E_{2g} mode at 384.85 cm⁻¹ and A_{1g} mode at 404.08 cm⁻¹ attributing to the single layer component. The frequency difference for the single layer is 19.23cm⁻¹, which is identical to the exfoliated monolayer, 19.4 cm⁻¹ unlike other CVD synthesized monolayer with previous results around 20.4 cm⁻¹^{29,31}. This could be related with certain crystalline imperfection, for example, smaller crystalline grains in the synthesized thin film. The full-width-half-maximum (FWHM) of peak can be used to determine the crystalline quality of the sample. In general, the smaller the width, the higher the crystalline quality of the sample²⁹. The FWHM values related to the E_{2g} is 4.4, close to that of the exfoliated monolayer, 3.7 cm⁻¹. This suggests a good crystalline quality in the synthesized film.

There is a direct 1.8-1.9 eV band gap equalled with 652-689 nm for single layer MoS₂³²⁻³⁵ that leads to strong photoluminescence (PL). This strong PL intensity depends to layer number and it only is considerable in monolayer and bilayer MoS₂ so it can be used as an good indicator for mono layer/bilayer. In Fig. 5.B, the PL

spectrum shows pronounced emission peak at 660 nm equalled to 1.88 eV with a superior photoluminescence (~50000). Recently, strong photoluminescence enhancement of MoS₂ through defect engineering and oxygen boning was reported³⁶ but we proceed to higher photoluminescence only by using MoO₃ solution.

3) conclusion

In conclusion, producing the high quality growth of MoS₂ and other TMD's with CVD method solid powder MoO₃ and sulphur precursor as the most safe and simple method is so challenging because often it leads to impure MoS₂ thin-film mixed with molybdenum oxide residue and inhomogeneity in layer number. To find a safe growth method but with more qualify thin-film characteristics, *utilizing dilute aqueous MoO₃ solution as a Mo precursor* instead to solid power MoO₃ may be worthwhile synthesis method. Raman & PL spectroscopy, SEM and XRD have demonstrated the CVD growth of single layer clusters of MoS₂ on a SiO₂/Si substrate by above mentioned precursors yields homogenous coverage of triangular MoS₂ nanoclusters without any molybdenum oxide impurity in a centimetre area. Other main advantage is that there is superior strong photoluminescence at 660 nm applying in optoelectronics. With this growth method, single layer MoS₂ nanoclusters may be synthesized on powder supports such as ZnO and SiO₂ to apply in catalysis and photocatalysis. Also, with further modification, monolayer & bilayer form of transition metal dichalcogenides such as WS₂, WSe₂ and transition metal chalcogenides such as ZnS and hexagonal close packing oxides such as ZnO would be simply achieved by using this new precursor and air annealing.

4) References

- 1 H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, and H. Zhang, *Small*, 2012, **8**, 63.
- 2 F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, B. T. Jonker, *Nano Lett.* 2013, **13**, 668.
- 3 T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science*, 2007, **317**,
4 100.
- 5 T. R. Thurston, J. P. Wilcoxon, *J. Phys. Chem. B*, 1999, **103**, 11.
- 6 Y. Yu, S. Y. Huang, Y. Li, S. N. Steinmann, W. Yang, L. Cao, *Nano Lett.* 2014, **14**, 553.
- 7 K. Chang, W. Chen, L. Ma, H. Li, H. Li, F. Huang, Z. Xu, Q. Zhang, Y. Lee, *J. Mater. Chem.*, 2011, **21**, 6251.
- 8 M. Amani, M. L. Chin, A. G. Birdwell, T. P. O'Regan, S. Najmaei, Z. Liu, P. M. Ajayan, J. Lou, M. Dubey, *Appl. Phys. Lett.*, 2013, **102**, 193107.
- 9 B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nature Nanotech.* 2011, **6**, 147.
- 10 S. Balendhran, J. Z. Ou, M. Bhaskaran, S. Sriram, S. Ippolito, Z. Vasic, E. Kats, S. Bhargava, S. Zhuiykovd, K. Kalantar-Zadeh, *Nanoscale*, 2012, **4**, 461.
- 11 K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett* 2010, **105**, 136805.
- 12 Q. Li, J. T. Newberg, E. C. Walter, J. C. Hemminger, and R. M. Penner, *Nano Lett.* 2004, **4**, 277.
- 13 X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science*, 2009, **324**, 1312.
- 14 X. Wang, H. Feng, Y. Wu, L. Jiao, *J. Am. Chem. Soc.* 2013, **135**, 5304.
- 15 I. Endler, A. Leonhardt, U. Ko'nig, H. van den Berg, W. Pitschke, V. Sottke, *Surf. Coat. Technol.*, 1999, **120**, 482.
- 16 X. L. Li, J. P. Ge, Y. D. Li, *Chem. Eur. J.* 2004, **10**, 6163.
- 17 Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* 2012, **7**, 699.
- 18 C. Y. Su, A. Y. Lu, C. Y. Wu, Y. T. Li, K. K. Liu, W. Zhang, S. Y. Lin, Z. Y. Juang, Y. L. Zhong, F. R. Chen, L. J. Li, *Nano Lett.* 2011, **11**, 3612.

- 19 Y. Shi , C. Hamsen , X. Jia , K. K. Kim , A. Reina , M. Hofmann , A. L. Hsu , K. Zhang , H. Li , Z. Y. Juang , M. S. Dresselhaus , L.J. Li, J. Kong , Nano Lett. 2010 , **10** , 4134 .
- 20 Y.H. Lee , X.Q. Zhang ,W. Zhang , M.T. Chang , C.T. Lin, K.D. Chang , Y.C. Yu , J.T. Wang , C.S. Chang , L.J. Li ,T. W. Lin, Adv. Mater. 2012, **24**, 2320.
- 21 X. Ling, Y.H. Lee, Y. Lin, W. Fang, L. Yu, M. S. Dresselhaus, J. Kong, Nano Lett. 2014, **14**, 464.
- 22 A. M. Van der Zande,P.Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.H. Lee, T.F. Heinz, D.R. Reichman, D.A. Muller, J. C. Hone, Nat. Mater. 2013, **12**, 554.
- 23 S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.C. Idrobo, P. M. Ajayan, J. Lou, Nat. Mater. 2013, **12**, 754.
- 24 T. Weber, J. C. Muijsers, J. H. M. C. Van Wolput, C. P. J. Verhagen, J.W. Niemantsverdriet, J. Phys. Chem. 1996, **100**, 14144.
- 25 N. C. Hurtig, A. E. Williams-Jones, Geochimica et Cosmochimica Acta, 2014, **136**, 169.
- 26 Y. Cheng, K. Yao, Y. Yang, L. Li, Y. Yao, Q. Wang, X. Zhang, Y. Hanb, U. Schwingenschlogl, RSC Advances, 2013, **3**, 17287.
- 27 M. R. Laskar, L. Ma, S. Kannappan, P. S. Park, S. Krishnamoorthy, D. N. Nath, W. Lu, Y. Wu, S. Rajan, Appl. Phys. Lett., 2013, **102**, 252108.
- 28 M. N. McCain, B. He, J. Sanati, Q. J. Wang, T. J. Marks, Chem. Mater. 2008, **20**, 5438.
- 29 C. Lee, H. Yan, L. E. Brus, T.F. Heinz, J. Hone, S. Ryu, ACS Nano, 2010, **4**, 2695.
- 30 A. Molina-Sanchez, L. Wirtz, Phys. Rev. B 2011, **84**, 155413.
- 31 J. Aizenberg, A.J. Black, G.M. Whitesides, Nature 1999, **398**, 495.
- 32 Y.F. Yu, C. Li, Y. Liu, L.Q. Su, Y. Zhang, L.Y. Cao, Sci. Rep. 2013, **3**, 1866.
- 33 A. Splendiani , L. Sun , Y. Zhang , T. Li , J. Kim , C. Y. Chim , G. Galli , F. Wang , Nano Lett. 2010 , **10** , 1271.
- 34 Y. C. Cheng, Z. Y. Zhu and U. Schwingenschlo"gl, RSC Adv., 2012, **2**, 7798.
- 35 Z. Zhu, Y. Cheng and U. Schwingenschlo"gl, Phys. Rev. B, 2011, **84**, 153402.
- 36 H. Nan, Z. Wang, W. Wang, Z. Liang, Y. Lu, Q. Chen, D. He, P. Tan, F. Miao, X. Wang, J. Wang, Z. Ni, ACS Nano, 2014, **8**, 5745.
- 37 Raman Database : RRUFF Project website: www.ruff.infor

Figure captions

Figure 1. The scheme of synthesis stages that they are different from conventional synthesis by MoO_3 precursor. These six steps result in crystalline, pure and more homogenous thin film rather than conventional method including Sulfurizing MoO_3 .

Figure 2. X-ray diffraction (XRD) of MoS_2 film on $\text{SiO}_2(300\text{ nm})/\text{Si}$ grown by CVD using MoO_3 solution precursor. Peaks are labeled with the corresponding (hkl) reflections from the hexagonal phase of MoS_2 (PDF 37-1492). B) XRD of MoO_x thinfilm resulted from second stage. The substrate peak has been subtracted.

Figure 3. Raman spectra of A) MoO_x thinfilm resulted from second stage. B) $\text{Mo}_3\text{O}_{8.n}(\text{H}_2\text{O})$. C) MoO_2 . D) MoO_3 . The excitation wavelength is 532.5 nm. The Raman Spectra of this compound and MoO_2 and MoO_3 are extracted from ref. [37].

Figure 4. SEM image of MoS_2 on SiO_2/Si substrate. A) Large area coverage of triangular MoS_2 clusters. B) close-up image of a triangular MoS_2 cluster after a Pd sputtering to reach more clear image.

Figure 5. A) Raman spectra of MoS_2 samples. The peak intensity ratio E_{2g}/A_{1g} is less than 1 for sample 1, confirming growth method leads to improved film quality. B) Spectra of MoS_2 sample 1 The PL intensities are normalized by the intensities of the A_{1g} Raman modes. The excitation wavelength is 532.5 nm.

Figure 1

Figure 2

A **B** **C** **D**

Figure 3

Figure 4