Synthesis of monolayer MoS_2 by CVD approach

Y. Y. WEN, X. B. ZENG*, X. X. CHEN, W. Z. WANG, J. DING , S. E. XU

School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

*Corresponding author: eexbzeng@163.com

Keywords: CVD, monolayer MoS_2, Raman, photoluminescence, bandgap

Abstract: The monolayer MoS_2 thin film was deposited directly on quartz substrate by chemical vapor deposition (CVD) approach using MoO_3 and sulfur powders as reactants. Raman spectroscopic and photoluminescence (PL) spectroscopic analyses were conducted to evaluate the structural and optical property of the grown MoS_2 thin films. The Raman characteristic peaks in 385cm^{-1} (E_{2g}^1) and 405cm^{-1} (A_{1g}) prove the grown film is monolayer MoS_2. In comparision, we also found in some areas of the grown fim is bulk MoS_2 film, the Raman characteristic peaks of which are 384 cm^{-1} (E_{2g}^1) and 409 cm^{-1} (A_{1g}). And two pronounced emission peaks at 620 and 670 nm were observed in photoluminescence spectrum of monolayer MoS_2. The results suggest that we synthesize monolayer MoS_2 with optical bandgap of 1.85eV.

Introduction

Recently, researchers have been focusing on graphene-like 2D materials, aiming at overcoming the shortage of graphene and broadening its range of applications. Monolayer molybdenum disulphide (MoS_2) is a typical example from the layered transition-metal dichalcogenide (TMD) family of materials with a direct bandgap of 1.8eV [1]. Due to its attractive electronic, optoelectronic, and mechanical properties [2-5], great effort has been devoted to the study of MoS_2. Bulk MoS_2 is known to have an indirect bandgap of ~1.2 eV and widely used as lubricants at first, whereas single-layer MoS_2 is a direct gap semiconductor [1, 5, 6] with a bandgap of 1.8 eV. The direct bandgap also results in photoluminescence from monolayer MoS_2, which opens the possibility of many optoelectronic applications [7]. In addition, bulk (or multilayer) MoS_2 exhibits relatively high in-plane carrier mobility comparable to that of crystalline silicon[7] as well as robust mechanical and chemical properties, which makes it an attractive material for making flexible electronic devices with high performance and long lifetime[3,8,9].

The current approaches for fabricating thin layers of MoS_2 are as follows, mechanical and liquid exfoliation [10, 11] of bulk materials, physical vapor deposition [12] and chemical vapor deposition [13, 14]. CVD is a direct bottom-up method for producing large-area uniform poly crystalline thin films. In this article, we describe the approach for preparing monolayer MoS_2 films on quartz by CVD. We used MoO_3 powder and sulfur powder is as reactants. Furthermore, structural, spectral, and morphology of the monolayer MoS_2 films were studied.

Experimental Procedure

The quartz substrate was treated according to the standard Radio Corporation of America (RCA) cleaning procedure. As illustrated in Figure 1, monolayer MoS_2 film was synthesized in a horizontal quartz tube furnace with sulfur and MoO_3 powders as reactants. The MoO_3 (0.1 g, 99.99%) was placed downstream in a ceramic boat and loaded into the central uniform-temperature zone of the furnace. The quartz substrate was faced down and mounted on the top of boat. Another ceramic boat with sulfur powder (0.8g, 99.9%) was placed upstream in a low-temperature zone. The center of the furnace was heated from room temperature to 550°C in 30min at a rate of approximately 20°C per minute. As the temperature approached 550°C, the sulfur slowly evaporated, and then the chamber was heated to 850°C at a slower pace of ~5°C per minute. After the temperature was kept at 850 °C for 10 min, at such a high temperature, MoO_3 powder evaporated and reacts with sulfur vapor to

form volatile suboxide MoO_{3-x}. [13] these suboxide compounds diffused to the substrate and further reacted with sulfur vapor to grow MoS_2 films [15]. Finally, the furnace was cooled down to room temperature naturally. Ultra-high purity N_2 gas was flowed with the flowing rate of 100 sccm during the whole growth process. Optical microscopy (OM) images, Raman spectroscopic and photoluminescence (PL) spectroscopic analyses were conducted to observe the surface morphology of the films, the structural and optical property of the grown MoS_2 thin films.

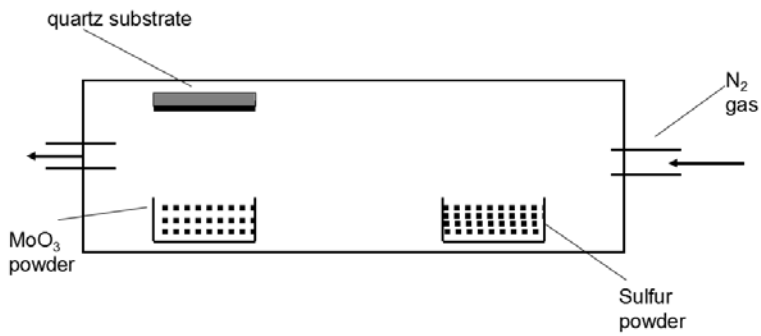

Figure 1 Schematic diagram of the CVD system used for the growth of MoS_2.

It has been reported that MoS_2 formed as the result of the stepwise reaction of substitution and reduction which lead to an intermediate product of MoO_{3-x}.[13,16] Although the growth dynamics of MoO_{3-x} and sulfur are still not fully understood, there are two possible channels for the surface growth that can be expected: (1) MoO_{3-x} species adsorb and diffuse on the substrate, reacting with S to form MoS_2; (2) MoO_{3-x} and sulfur react directly in the gas phase, and the resulting MoS_2 clusters adsorb, nucleate, and grow on the substrate[17].

In our experiment, the reaction process is described as follows. Firstly, a precursor MoO_3 powder and the quartz substrate are placed in downstream location in furnace. When the temperature in the central furnace rise up to 550°C, the MoO_3 powder begins evaporating. Meanwhile, the sulfur powder also evaporates, and is conveyed by N_2 gas to downstream in the furnace. The MoO_3 then react with sulfur vapour to form volatile MoO_{3-x} species, which subsequently deposit on the quartz substrate to form MoO_{3-x} microplates. Finally, the oxygen atoms in the well-ordered packing of MoO_{3-x} are replaced with sulfur atoms to form MoS_2 films on the substrate. Considering the fact that MoO_2, the most common intermediate product, is one of the most stable oxides of molybdenum, we can assum the x=1. A possible stepwise reaction process of MoO_3 and S is given in equations (1) and (2) [13].

$$MoO_3 + \frac{1}{2}S \rightarrow MoO_2 + \frac{1}{2}SO_2 \quad (1)$$

$$MoO_2 + 3S \rightarrow MoS_2 + SO_2 \quad (2)$$

Results and discussion

Optical microscopy images of the MoS_2 layers

Figure 2 shows the OM image of the layered MoS_2 films grown on quartz substrate. It indicates that we fabricated MoS_2 films on the quartz substrate. The largest area of the films is about $20\times20\mu m^2$, indicating uniform MoS_2 film. Furthermore, as the optical image shows, the shape of the MoS_2 is rhombus. This can be explained that the intermediate product MoO_2 films was nucleated on quartz substrates and grew up to rhomboidal microplates, which is in consistent with the work of Xinsheng Wang etc[18]. They thermally evaporated MoO_2 powder on the SiO_2/Si substrate, and it grew up to rhomboidal microplates. D. O. Scanlon etc.[19] theoretically proved that the shape of MoO_2 films to be closely related to rutile, which further confirms our assumption.

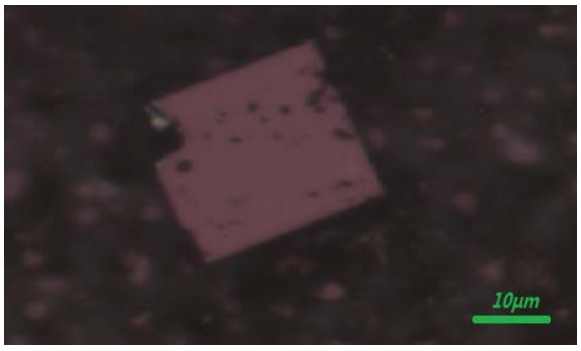

Figure 2 OM images of the layered MoS_2 films grown on quartz substrate.

Raman spectra

Figure 3 shows the Raman spectra of the monolayer MoS_2 and the inset shows the bulk MoS_2 film in other area of the quartz substrate. Both Raman spectras of the monolayer MoS_2 films show two signature peaks, which are in-plane and perpendicular-to-plane Raman active modes respectively. In E_{2g}^1 mode both Mo and S atoms vibrate along the in-plane direction (yet opposite to each other), whereas in the A_{1g} mode the S atoms vibrate in the perpendicular-to-plane direction [20]. Raman spectroscopy could serve as a reliable tool for identifying monolayer MoS_2, and the E_{2g}^1 and A_{1g} peak frequencies can be used to identify the layer number of an ultrathin MoS_2 flake with high accuracy [21]. Figure 3 exhibits two Raman characteristic peaks at 405cm^{-1}(E_{2g}^1) and 386 cm^{-1}(A_{1g}) where the distance between the in-plane E_{2g}^1 mode and out-of-plane A_{1g} mode is 19 cm^{-1}, indicating the formation of monolayer MoS_2, consistent with other reports [21, 22].As a comparison, for the bulk MoS_2 films the Raman shift between the E_{2g}^1 mode and A_{1g} mode is 25 cm^{-1}. In comparison, we also found in some areas of the grown film is bulk MoS_2 film, the Raman characteristic peaks of which are 384 cm^{-1} (E_{2g}^1) and 409 cm^{-1} (A_{1g}).

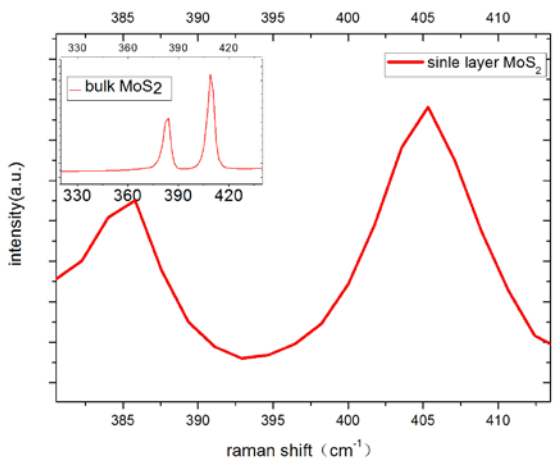

Figure 3 Raman spectra of monolayer MoS_2 inset shows the Raman spectra of bulk MoS_2 film in other area of the quartz substrate.

PL spectrum

The presence of monolayers is then confirmed by performing PL measurements. The PL of monolayer MoS_2 was measured at room temperature using the 532 nm laser (Figure 4). A strong photoluminescence is observed at the direct excitonic transitions energies in a monolayer MoS_2. The PL spectrum of monolayer MoS_2 exhibits two peaks at 670 nm (1.85 eV) and 620 nm (2 eV). They are associated with excitonic transitions at the K point of the Brillouin zone[6], which can be correlated to the A1 excitation and B1 excitation of MoS_2 , respectively. The dominated PL peak at 670 nm arises from the direct intraband recombination of the photogenerated electron-hole pairs in

the monolayer layer MoS_2, and the weak shoulder peak at 620nm is attributed to the energy split of valence band spinorbital coupling of MoS_2[6,23] .The energy difference of 0.15 eV in PL spectrum is in good agreement with the theoretical value of 0.148 eV, calculated for monolayer MoS_2.[23] Such luminescence is absent in the indirect bandgap bulk MoS_2 films. This observation is consistent with the theoretical prediction of indirect to direct bandgap transition with the structure of MoS_2 turning from multilayer to monolayer.

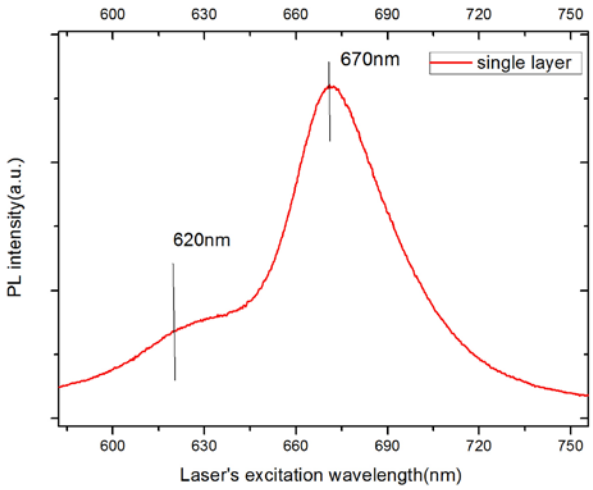

Figure 4 Photoluminescence spectra of monolayer MoS_2 .The laser excitation wavelength is 532 nm.

Conclusions

In summary, we fabricated the monolayer MoS_2 directly on quartz substrate by CVD approach. The OM image shows we fabricated MoS_2 films on the quartz substrate. The largest area of the films is about $20\times20\mu m^2$, indicating uniform MoS_2 film. The Raman spectra and PL spectrum co-prove that we fabricated monolayer MoS_2 film on the quartz substrate. The Raman shift of characteristic peaks of monolayer MoS_2 is 19 cm^{-1}. Whereas in bulk MoS_2 films, the Raman shift of characteristic peaks between the E_{2g}^1 mode and A_{1g} mode is 25 cm^{-1}. In PL spectrum, we find a strong photoluminescence at 670nm in a monolayer MoS_2. This suggests that monolayer MoS_2 is direct bandgap semiconductor, the optical bandgap of which turns to be 1.85eV. Besides, the photoluminescence is absent in the indirect bandgap bulk MoS_2 films.This work opens an avenue to develop single-layer semiconducting materials for future photoelectric device applications in switches, memories, signal-amplifiers, and light-related sensors, photovoltaic etc.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant No.51472096). We also acknowledge the Analytical and Testing Center of Huazhong University of Science and Technology for Raman spectra and PL spectrum measurements.

Reference

[1]R. Ganatra, Q. Zhang:‘Few-layer MoS2: ‘a promising layered semiconductor’’, ACS nano, 2014, 8(5): 4074-4099.

[2]B. Radisavljevic, A. Radenovic, J. Brivio: ‘Single-layer MoS2 transistors’, Nature nanotechnology, 2011, 6(3): 147-150.

[3]J. Pu, Y. Yomogida, K. K. Liu,: ‘Highly flexible MoS2 thin-film transistors with ion gel dielectrics’, Nano letters, 2012, 12(8): 4013-4017.

[4]T. Korn, S. Heydrich , M. Hirmer: ‘Low-temperature photocarrier dynamics in monolayer MoS2’, Applied Physics Letters, 2011, 99(10): 102109.

[5]K. F. Mak, C. Lee, J. Hone: ‘Atomically thin MoS 2: a new direct-gap semiconductor’ Physical Review Letters, 2010, 105(13): 136805.

[6]A. Splendiani, L. Sun, Y. Zhang: ‘Emerging photoluminescence in monolayer MoS2’, Nano letters, 2010, 10(4): 1271-1275.

[7]R. Fivaz, E. Mooser: ‘Mobility of charge carriers in semiconducting layer structures’ Physical Review, 1967, 163(3): 743.

[8]H. Wang, L Yu, Y. H. Lee: ‘Integrated circuits based on bilayer MoS2 transistors’, Nano letters, 2012, 12(9): 4674-4680.

[9]A. Ayari, E. Cobas, O. Ogundadegbe: ‘Realization and electrical characterization of ultrathin crystals of layered transition-metal dichalcogenides’, Journal of applied physics, 2007, 101(1): 14507-14507.

[10]J. N. Coleman, M. Lotya: ‘Two-dimensional nanosheets produced by liquid exfoliation of layered materials’, Science, 2011, 331: 568-571.

[11]P. Joensen, R. F. Frindt, S. R. Morrison: ‘Single-layer MoS2’, Mater Res Bull, 1986, 21: 457-461.

[12]K. Ellmer: ‘Preparation routes based on magnetron sputtering for tungsten disulfide (WS2) films for thin -1760 solar cells’, Physica status sol

[13]X. L. Li, Y. D. Li: ‘Formation of MoS2 inorganic fullerenes (IFs) by the reaction of MoO3 nanobelts and S’, Chemistry-A European Journal, 2003, 9(12): 2726-2731.

[14]S. Balendhran, J. Z. Ou, M. Bhaskaran: ‘Atomically thin layers of MoS 2 via a two step thermal evaporation–exfoliation method’, Nanoscale, 2012, 4(2): 461-466.

[15]Y. H. Lee, X. Q. Zhang, W. Zhang: ‘Synthesis of Large -Area MoS Chemical Vapor Deposition’, Advanced Materials, 2012, 24(17): 2320-2325.

[16]T. Weber, J. C. Muijsers: ‘facial method to prepare MoS2 with nanoflower-like morphology’, Phys. Chem. 1996, 100, 14 144 -14 150

[17]Q. Ji, Y. Zhang: ‘Chemical vapour deposition of group-VIB metal dichalcogenide monolayers: engineered substrates from amorphous to single crystalline’, Chemical Society Reviews, 2015.

[18]X. Wang, H. Feng, Y. Wu: ‘Controlled synthesis of highly crystalline MoS2 flakes by chemical vapor deposition’, Journal of the American Chemical Society, 2013, 135(14): 5304-5307.

[19]D. O. Scanlon, G. W. Watson, D. J. Payne: ‘Theoretical and experimental study of the electronic structures of MoO3 and MoO2’, The Journal of Physical Chemistry C, 2010, 114(10): 4636-4645.

[20]M. Shanmugam, C. A. Durcan, B. Yu: ‘Layered semiconductor molybdenum disulfide nanomembrane based Schottky-barrier solar cells’, Nanoscale, 2012, 4(23): 7399-7405.

[21]H. Li, Q. Zhang, C. C. R. Yap: ‘From bulk to monolayer MoS2: evolution of Raman scattering’, Advanced Functional Materials, 2012, 22(7): 1385-1390.

[22]R. S. Sundaram, M. Engel, A. Lombardo: ‘Electroluminescence in single layer MoS2’ Nano letters, 2013, 13(4): 1416-1421.

[23]Z. Y. Zhu, Y. C. Cheng: ‘Schwingenschlögl U. Giant spin-orbit-induced spin splitting in

two-dimensional transition-metal dichalcogenide semiconductors', Physical Review B, 2011, 84(15): 153402.