IOP Conference Series: Materials Science and Engineering

PAPER • **OPEN ACCESS**

Induced Synthesis of Vertically Oriented Multilayer MoS_2 via CVD Method

To cite this article: Shuang Liu and Changbin Nie 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **563** 022002

View the article online for updates and enhancements.

This content was downloaded from IP address 221.226.175.204 on 15/10/2019 at 22:22

IOP Conf. Series: Materials Science and Engineering **563** (2019) 022002 doi:10.1088/1757-899X/563/2/022002

Induced Synthesis of Vertically Oriented Multilayer MoS_2 via CVD Method

Shuang Liu[1, 2], Changbin Nie[1]

[1]Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, China

[2]University of Chinese Academy of Sciences, Beijing, China

Corresponding author e-mail: liushuang@cigit.ac.cn

Abstract. Fabrication of nanostructured MoS_2 for photodetector applications has become increasingly attractive due to its atomically thin profile and favorable bandgap. In this paper, vertically oriented multilayer MoS_2 (V-MoS_2) are grown directly on a SiO_2 substrate by chemical vapor deposition (CVD) with TiO_2 being adopted as an induced precursor for the first time. The interim morphologies of the synthesized MoS_2 are investigated and the growth mechanism of the MoS_2 film is proposed.

1. Introduction

With the age of two-dimensionally (2D) layered materials approaching, two-dimensional transition metal sulfides (TMDs) have been considered as the promising candidates for photodetectors due to their 2D conjugated structures, large specific surface area, low electrical noise, and broad band response [1-5]. Especially, MoS_2 becomes an alternative material for the photodetection chips of the next generation, on account of its atomically thin profile and favorable bandgap [6]. However, monolayer MoS_2 can only absorb a small portion of incident light due to its ultrathin thickness (0.72 nm), which usually leads to the low quantum efficiency for the MoS_2-based devices [7-8]. To conquer the drawbacks of optical absorption, researchers have devoted significant effects by preparing multilayer [9] and bulk MoS_2 [10], or combining it with other semiconductor materials [11-12]. However, the relevant bandgap becomes indirect, meanwhile the carrier mobility has been greatly reduced. Even for high-quality parallel-oriented multilayer or bulk MoS_2-based heterostructure, the photoelectric response becomes undesirable, as the carrier mobility of interlayer is non-ideal. In contrast, vertically oriented multilayer MoS_2, which has the advantages of both strong light absorption and quick longitudinal in-plane carrier transport, may show significant potential in optoelectronic devices.

To date, high quality MoS_2 have been exploited via many different methods, including mechanical exfoliation, chemical vapor deposition (CVD) and epitaxial growth [13-15]. However, it is extremely difficult to obtain vertically oriented multilayer MoS_2 (V-MoS_2) on the SiO_2 substrate, because the lattice mismatch between MoS_2 and SiO_2 is very high. What's more, most synthesis methods require templates, surfactants or self-assembly [16], which often need multi-step and costly operations. In this paper, a high-quality V-MoS_2 were developed on the TiO_2 coated SiO_2 substrate, by introducing ultrathin TiO_2 into the interlayer of MoS_2 and SiO_2 to induce the growth direction of MoS_2. Spectroscopic and microscopic results reveal that the synthesized V-MoS_2 are highly crystalline. The

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

induced epitaxial growth method herein opens a new avenue to synthetize vertically oriented materials with excellent optoelectronic performances.

2. Experimental Sections

2.1 Growth of V-MoS_2 nanosheets array

The V-MoS_2 was grown on a Si wafers substrate with a SiO_2 layer of 300 nm deposited through a chemical vapor deposition (CVD) method. The MoO_3 powder (2g) was placed in a ceramic boat and the SiO_2/Si substrate covered with a layer of sputtered titanium dioxide layer (10-30 nm) for inducing the growth direction of MoS_2 was faced down and mounted on the top of boat. A separated ceramic boat filled with sulfur powder (20 g) was placed close to the ceramic boat filled with MoO_3 powder, as shown as in figure 1. After the reaction chamber was heated to 800℃ for 40 minutes in an argon environment, the sample was taken out until the furnace down cooled to room temperature.

2.2 Characterization

Surface morphology of the samples was examined with commercial scanning electron microscope (SEM, FEI VS600) and optical microscope (Nikon, 50I POL). Energy Dispersive Spectrometer was used to obtain the distribution of elements (EDS, FEI VS600). Raman spectra was obtained with a confocal microscope system (Bruker, Dimension Fast Scan) with a 100× objective (NA=0.9) under ambient condition. A 532 nm laser with a low laser power (50 μW) was applied to measure photoelectronic performance.

3. Results and Discussion

The V-MoS_2 was successfully grown on a TiO_2 coated SiO_2 substrate by appropriately controlling the preparation parameters. The schematic illustration of the experimental set-up is shown in Figure 1. Moderate-doped N-type Si wafer (resistivity of 0.2~0.4 Ω cm, thickness of 600 μm) with a SiO_2 layer of 300 nm was used as the substrate. The wafer was sputtered with TiO_2 film (30 nm) on the surface. The MoO_3 powder (2 g) was placed in a ceramic boat and the SiO_2/Si substrate covered with a layer of titanium dioxide layer was faced downward and mounted on the top of boat. A separate ceramic boat with sulfur powder (20 g) was placed next to the MoO_3 powder. The inert gas flowed from sulphur source to molybdenum source. At the beginning of the growth process, with the chamber temperature rising to 800 ℃ in an argon environment, MoO_3 powder started to transform into volatile suboxide MoO_{3-x} under the reduction function of sulfur vapor [17]. The suboxide compounds diffused to the substrate, and further reacted with sulfur vapor, leading to the formation of V-MoS_2.

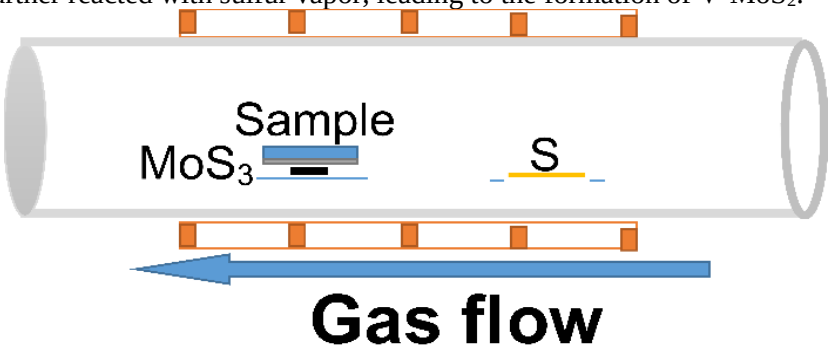


Figure 1. Schematic illustration of the experimental set-up.

An ultra-low magnification scanning electron microscopy (SEM) image of V-MoS_2 is shown in Figure 2a, which clearly exhibits a lot of microspheres. These microspheres were verified to be of V-MoS_2. Figure 2b shows the enlarged SEM image of one microsphere, which clearly demonstrates that the MoS_2 layer is uniformly standing on the TiO_2 film and interconnect with each other. A high magnification image shows the V-MoS_2 structures are composed of layered nanosheets, as shown in

Figure 2c. The MoS_2 nanosheets vertically extend in a random distribution with thickness of several hundred nanometers from the cross-section SEM image of V-MoS_2 in Figure 2d.

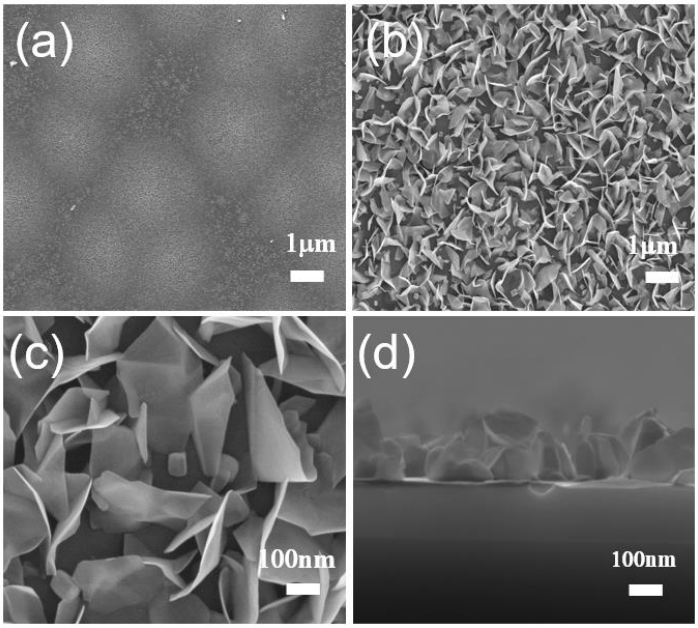


Figure 2. (a) An ultra-low magnification scanning electron microscopy (SEM) image of V-MoS_2; (b) Low-magnification and (c) high-magnification SEM images of V-MoS_2 obtained by CVD method; (d) Side view image of V-MoS_2.

The Raman spectroscopy in Figure 3a clearly shows that the vertically grown MoS_2 sheets in the van der Waals layers have an edge-terminated spectral feature, because the out-of-plane M-X vibration mode (A_{1g}) is over the in-plane M-X vibration mode (E_{2g}). From the Raman spectrum, the V-MoS_2 exhibits two Raman characteristic peaks at 407.30 cm^{-1} and 381.56 cm^{-1}, corresponding to the A_{1g} and E_{2g} modes respectively. The value of Δ (25.34 cm^{-1}) in Fig.3a evidences the existence of MoS_2 [18-20]. The V-MoS_2 was further confirmed by Energy Dispersive Spectrometer (EDS) in Figure 3 (b, c and d). In Figure 3 (b, c and d), distributions of Mo, S and Ti elements are represented respectively, which further proved the existence of MoS_2.

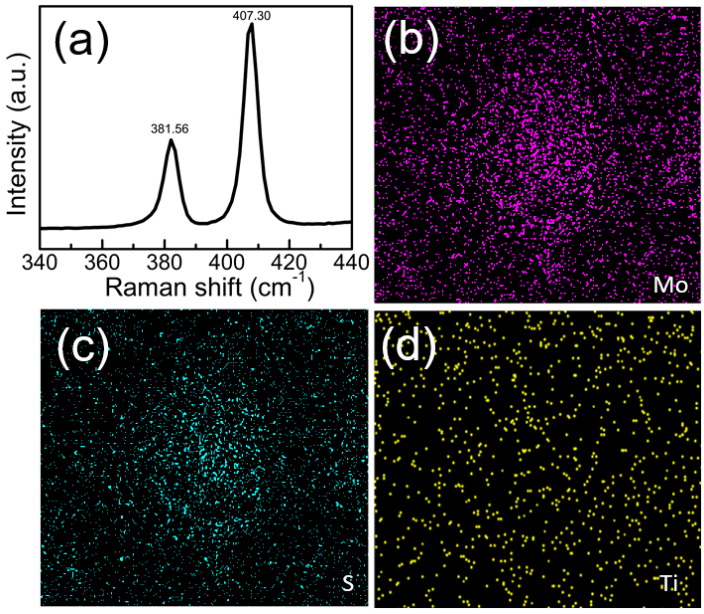


Figure 3. (a)The Raman spectra of the V-MoS_2; The EDS spectra of V-MoS2: (b) Mo; (c) S; (d) Ti.

In order to obtain further evidences about the interaction between TiO_2 and MoS_2, we sputtered half of a piece of the substrate with titanium dioxide, and the other without sputtered titanium dioxide. The experimental result is shown in Figure 4a. As shown in the red line marked in Figure 4a, on the part without sputtering TiO_2 film, MoS_2 of single crystal with horizontal structure was obtained. The green line marked the black rounded area consist of V-MoS_2. It can be seen that the formation of V-MoS_2 is mainly due to the presence of TiO_2 layer. Based on the observation, we could illustrate the formation mechanism of the V-MoS_2. At first, molybdenum source was rapidly sulfurized into granular MoS_2. Meanwhile, TiO_2 layer under high temperature annealed, which made the TiO_2 morphology change and the surface of the substrate becomes rough in Figure 4b, and then MoS_2 nanoparticles were orientated grown with two-dimensional direction on the TiO_2 surface.

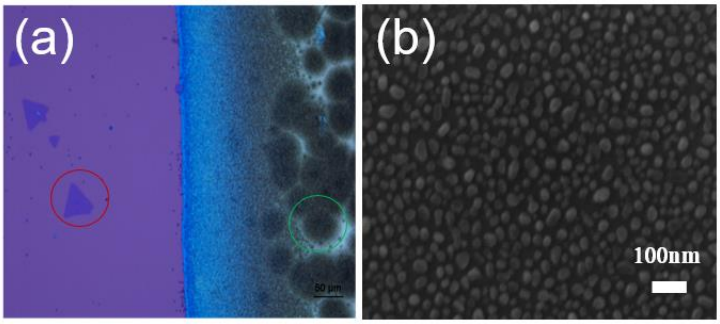


Figure 4. (a) The optical micrograph of the single crystal MoS_2 with horizontal structure and V-MoS_2 on the same substrate; (b) SEM images of annealed TiO_2.

4. Conclusion

In summary, highly dispersive V-MoS_2 with height of about 2 μm was synthesized via a simple CVD approach under TiO_2 induce. The experimental results suggest that the layer of TiO_2 plays an important role in controlling the structures growth direction. Moreover, a possible growth mechanism was proposed to explain the formation of the V-MoS_2. Considering the simple synthetic process, it is believed that these vertically oriented nanostructures can be directly used for the making of nanodevices.

References

[1] Lan F, Lai Z, Xu Y, Cheng H, Wang Z, Qi C, Chen J, and Zhang S 2016 *J. Sci. Rep.* **6** 31980
[2] Zhang Y, Ji Q, Wen J, Li J, Li C, Shi J, Zhou X, Shi K, Chen H, and Li Y 2016 *J. Adv. Funct. Mater.* **26** 3299-3305
[3] Zhang K, Kim H, Lee J, Chang G, Shi X, Kim W, Ma M, Kong K, Choi J, and Song M 2015 *J. ChemSusChem.* **7** 2489-2495
[4] Gao D, Si M, Li J, Zhang J, Zhang Z, Yang Z, and Xue D 2013 *J. Nanoscale Res. Lett.* **8** 129-129
[5] Zhou W, Yin Z, Du Y, Huang X, Zeng Z, Fan Z, Liu H, Wang J and Zhang H 2013 *J. small.* **9** 140-147
[6] Zhang K, Zhang T, Cheng G, Li T, Wang S, Wei W, Zhou X, Yu W, Sun Y, and Wang P 2016 *J. Acs Nano.* **10** 3852
[7] Cong R, Qiao S, Liu J, Mi J, Yu W, Liang B, Fu G, Pan C, and Wang S 2018 *J. Adv. Sci.* **5** 1700502
[8] Qiao S, Zhang B, Feng K, Cong R, Yu W, Fu G, and Wang S 2017 *J. ACS Appl. Mater. Interfaces.* **9** 18377-18387
[9] Das S, Chen H, Penumatcha A V, and Appenzeller J 2013 *J. Nano Lett.* **13** 100-105
[10] Liu K, Zhang W, Lee Y, Lin Y, Chang M, Su C, Chang C, Li H, Shi Y, and Zhang H 2012 *J. Nano Lett.* **12** 1538-1544
[11] Rehman A U, Khan M F, Shehzad M A, Hussain S, Bhopal M, Sang H, Eom J, Seo Y, Jung J, and Lee S 2016 *J. ACS Appl. Mater. Interfaces.* **8** 29383
[12] Hao L, Liu Y, Gao W, Liu Y, Han Z, Yu L, Xue Q and Zhu J 2016 *J. J. Alloys Compd.* **682** 29-34

[13] Li H, Wu J, Yin Z, and Zhang H 2014 *J. Acc. Chem. Res.* **47** 1067-1075
[14] Zhang W, Huang J, Chen C, Chang Y, Cheng Y, and Li L 2013 *J. Adv. Mater.* **25** 3456-3461
[15] Li M, Shi Y, Cheng C, Lu L, Lin Y, Tang H, Tsai M, Chu C, Wei K, and He J 2015 *J. Science.* **349** 524
[16] Chang K and Chen W 2011 *J. Acs Nano.* **5** 4720-4728
[17] Lee Y, Zhang X, Zhang W, Chang M, Lin C, Chang K, Yu Y, Wang J, Chang C, and Li L 2012 *J. Adv. Mater.* **24** 2320-2325
[18] Dai R, Zhang A, Pan Z, Al-Enizi A, Elzatahry A, Hu L, and Zheng G 2016 *J. Small.* **12** 2792-2799
[19] Zhang J, Huang L, Lu Z, Jin Z, Wang X, Xu G, Zhang E, Wang H, Zhe K, and Xi J 2016 *J. J. Alloys Compd.* **688** 840-848
[20] Yu J H, Lee H R, Hong S S, Kong D, Lee H W, Wang H, Xiong F, Wang S, and Cui Y 2015 *J. Nano Lett.* **15** 1031-1035