Influence of Oxalic Acid Concentrations on The Growth of Molybdenum Disulfide via Spin Coating Technique

A L Tan1,a, S S Ng2,b and H Abu Hassan1,c

1 School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.
2 Institute of Nano Optoelectronics Research and Technology (INOR), Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.

aelwinharrisontan92@gmail.com, bshashiong@usm.my, chaslan@usm.my

Abstract. In this context, the molybdenum disulfide (MoS2) films were grown by spin coating technique and thermal vapour sulfurization (TVS) under the condition of different oxalic acid concentrations. Atomic force microscopy (AFM) surface topography shows the improved homogeneity and higher compactness of films with the increasing acid concentration. However, high concentration favoured the formation of larger grains and poor continuity of films. These observations were further proven by the particle size distribution profile. Apart from that, two distinct Raman phonon modes of the MoS2 can be detected in all the deposited films. In addition, molybdenum dioxide (MoO2) was detected at higher acid concentration due to the slower rate of diffusion of sulfur atoms during the surface sulfurization. From the direct analysis of frequency difference between in-plane (\(E_{2g1}\)) and out-of-plane (\(A_{1g}\)) phonon modes, it proves that multilayers of MoS2 films were synthesized. Ultraviolet-visible (UV-Vis) specular reflectance results also reveal that crystallite MoS2 films with the absorption peaks of 612 nm and 660 nm were detected.

1. Introduction

Research advances in two dimensional (2-D) graphene have triggered the research interest in other 2-D materials, such as boron nitride [1], black phosphorus [2], silicene [3], and semiconducting 2-D transition metal dichalcogenides (TMDs) [4]. There is a wide range of semiconducting 2-D TMDs where molybdenum disulfide (MoS2) certainly becomes the rising star among the family. The layered structure of MoS2 consists of an atomic plane of molybdenum (Mo) sandwiched between two planes of sulfur (S) atoms. With the analogous layered structure to graphene, the weakly bonded interlayer enable to be isolated into single or multi-layers of MoS2. In such the way, the energy bandgap experiences transition from indirect (bulk, \(~1.2\) eV) to direct (monolayer, \(~1.8\) eV) [4]. Hence, the semiconducting behaviour of MoS2 has significant advantages over the zero bandgap graphene which is potentially to be applied in optoelectronic and electronic switching devices.

Major reports in the early research on the production of mono or multilayers of MoS2 were based mainly on exfoliations, either by mechanical or chemical technique [5, 6]. This approach was also extended with the implementation of electrochemical and surfactant-based solution [7, 8]. However, the resulting exfoliated MoS2 was structurally and electronically different from the bulk MoS2. Thus, the MoS2 experienced the conversion of the Mo atom molecular geometry from trigonal prismatic to octahedral, and change of electronic structure from semiconducting to metallic [9]. Besides, this method...
also resulted in poor uniformity and lower yield of MoS\textsubscript{2} flakes amount. In contrast, the growth of MoS\textsubscript{2} by chemical vapour deposition (CVD) of MoS\textsubscript{2} was rather a better approach in wafer-scale fabrication [10-13]. In this work, thermal vapour sulfurization (TVS) method and performed spin coating technique was applied as the pre-deposition of MoS\textsubscript{2}-based compound films, followed by sulfurization of the deposited films as surface treatment process. Moreover, we suggest different acid concentrations have significant effect on the growth of molybdenum disulfide. Up to now, there have no reported works for the growth of MoS\textsubscript{2} with different acid concentrations.

Herein, we demonstrate the growth and characterizations of MoS\textsubscript{2} thin films with the variation of oxalic acid concentrations. Through this study, a better understanding of the growth MoS\textsubscript{2} under different acid concentration conditions. The research findings in this work, therefore, it significantly contributes to the research in the growth of 2-D semiconducting TMDs.

2. Methodology and characterizations

In this work, 4 inches of silicon, Si (111) substrate was cleaved into squared shaped with the dimension of 1 cm x 1 cm. Prior to the spin coating process, the cleaved Si (111) substrates were cleaned with acetone and diluted hydrofluoric acid (HF) solution. Next, the cleaned substrates were subjected to the oxygen plasma treatment as to improve the wettability of prepared precursors. The precursor was first prepared by mixing the powders, which contained ammonium molybdate tetrahydrate [(NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}•4H\textsubscript{2}O, QReC\textsuperscript{TM} 99.5\%], thiourea [(NH\textsubscript{2})\textsubscript{2}S, UNILAB 99.0\%] and oxalic acid (OA) [C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}, Brendosen 99.5\%] with a drop of distilled water (DW) in ultra sonic agitation. After that, ethylenediamine [C\textsubscript{2}H\textsubscript{8}N\textsubscript{2}, Merck 99.0\%] solvent was then added into the precursor after the dark-blue colloid was observed.

To investigate the effects of acid concentrations on the growth of MoS\textsubscript{2} films, the precursor solutions with different oxalic acid concentrations (M, molar) of 2 M, 6 M and 10 M were prepared. A series of precursor solution with colour contrast are shown in Figure 1. The prepared precursors were dropped and spin for 25 s at the speed of 4000 rpm. To transform the deposited films into crystalline MoS\textsubscript{2} thin films, they were first annealed at 500°C, next, the system was slowly ramped up to 750°C for the sulfurization process in sulfur-rich environment. The experimental parameters were chosen based on the references [12] and [13]. This process was conducted by continuous bubbling carbon disulfide, CS\textsubscript{2} vapour with nitrogen gas into the quartz tube. At the end of the process, the furnace system was purged to remove excessive CS\textsubscript{2} and sulfur, S vapour and cooled passively before removed the samples.

To access the material properties, tapping mode atomic force microscopy (AFM, Bruker Dimension Edge) was used to study the changes of surface topography of the grown MoS\textsubscript{2} thin films. The dimension of 10 µm x 10 µm was obtained with 256 lines/scan. Next, the optical phonon modes of MoS\textsubscript{2} were determined by Raman spectroscopy (Horiba Jobin Yvon HR800UV), argon (Ar) ion laser with excitation wavelength of 514.5 nm and excitation power of 20 mW was used. Finally, the absorption measurements were performed by using ultraviolet-visible-near infrared (UV-Vis-NIR) spectrometer (Agilent Cary 5000 UV-Vis-NIR spectrometer) to determine the optical absorbance of MoS\textsubscript{2} films.
3. Results and discussion

Through the investigation of AFM imaging, different aggregation processes and growth of MoS$_2$ grains were observed with the variation of OA concentrations. Particle-like MoS$_2$ grains are formed and well dispersed on the surface of substrate for all acid concentrations. At 2 M acid concentration, fine and homogenous MoS$_2$ grains were observed as shown in Figure 2(a). By referring to Figure 2(b), the smaller grains start to aggregate and form highly compact MoS$_2$ films. This observation leads to the lower formation of pinholes density when the OA concentration increases from 2 M to 6 M. However, at 10 M acid concentration, the aggregation of MoS$_2$ grains, which in turns causes the decomposition of MoS$_2$ films. As can be seen in Figure 2(c), films decomposition results in the formation of isolated larger grains with poor continuity of MoS$_2$ films. With increasing acid concentration, the root-mean square surface roughness of the films increases from 11.6 nm [Figure 2(g)] to 20.6 nm [Figure 2(i)].

Apart from that, the particle size also increases with increasing OA concentration, as evidenced from the particle size distribution profiles. For the 2 M OA concentration, the statistical analysis reveals that the distribution of particle sizes was narrow and centred at about 80 nm [Figure 2(d)]. As the OA concentration increases to 6 M, wide distribution of particle sizes with the highest maximum at around 75 nm and a shoulder position at 100 nm was observed [Figure 2(e)]. At 10 M concentration, the particle size increases to around 140 nm and a sharp maximum corresponds to about 170 nm [Figure 2(f)].
The changes in the growth of MoS$_2$ grains and surface topography can be realized by hydrolysis and polycondensation process in the intermediate steps of the solution preparation process. Through this study, it was found that the more acidic condition enables the growth of larger MoS$_2$ grains. The dissociation of OA in water which results in the partially formation of oxalate, C$_2$O$_4^{2-}$ ions and hydrogen, H$^+$ ions [14] as proposed by the equations (1) and (2) below.

$$C_2O_4H_2 \rightleftharpoons HC_2O_4^- + H^+ \quad (1)$$
$$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+ \quad (2)$$

From these equations, higher acid concentration produces higher effective density of H$^+$ ions in the colloid. Therefore, in these conditions, it facilitates the higher rate of hydrolysis and condensation process [15], which leads to larger aggregates of MoS$_2$ grains.

Figures 3(a) to (c) show the typical Raman spectra for the MoS$_2$ thin films prepared using different oxalic acid concentrations. Two significant peaks correspond to the in-plane (E$_{2g}^1$) and out-of-plane phonon modes (A$_{1g}$) of MoS$_2$ located at ~384 cm$^{-1}$ and ~409 cm$^{-1}$, respectively were detected. These values were in good agreement with that reported by Chakraborty et al [16]. Further increase of OA
concentration, vibrational phonon mode originated from the molybdenum dioxide, MoO₂ was detected at around ~365 cm⁻¹ [17]. This probably due to the higher acid concentration will favour the polycondensation process of Mo-O-S compounds at the primary stage, and hence, the larger Mo-O-S based compounds were formed. This observation was in line with the AFM imaging results as discussed previously.

![Raman spectra for MoS₂ thin films prepared using different oxalic acid concentrations, (a) 2 M, (b) 6 M, and (c) 10 M. The variation of the FWHM and intensity of Raman peaks as a function of the OA concentration was summarized in (d). The * represents MoS₂, while # indicates MoO₂.](image)

Figure 3: Raman spectra for MoS₂ thin films prepared using different oxalic acid concentrations, (a) 2 M, (b) 6 M, and (c) 10 M. The variation of the FWHM and intensity of Raman peaks as a function of the OA concentration was summarized in (d). The * represents MoS₂, while # indicates MoO₂.

The formation mechanism of the MoS₂ films can be briefly explained as below. Firstly, the decomposition of CS₂ vapour occurred at elevated temperature and the suggested chemical reaction is as shown in equation (3) [18]. The decomposed radicals species and sulfur gases cause the partial reduction of Mo-O-S based compounds and convert into MoS₂ crystalline.

\[
CS₂ \rightarrow CS + S \tag{3}
\]

During the sulfurization process, the oxygen, O atoms in the Mo-O-S compounds are slowly replaced by the S atoms by diffusion. The layers on the surface of Mo-O-S compounds were sulfurized quickly in the beginning of the sulfurization process. Increasing formation of MoS₂ outer surface layers limited further diffusion of S atoms into the Mo-O-S compounds thus MoO₂ exists below the MoS₂ layers. As a result, the significantly larger Mo-O-S based compounds slowing down the rate of diffusion which leads to incomplete conversion into MoS₂ crystalline state [17]. The above explanations are summarized in the schematic drawing in Figure 4.
Fig. 4 The schematic drawing of the formation of the MoO\textsubscript{2} below the MoS\textsubscript{2} layers.

It is known that the direct analysis of the frequency difference (\(\Delta k\)) between the two phonon modes (\(\Delta k = A1g - E2g\)) can estimate the thickness of the MoS\textsubscript{2} films. According to Ye et al. [19], \(\Delta k \approx 20\ \text{cm}^{-1}\) corresponded to the monolayer of MoS\textsubscript{2}, while \(\Delta k \approx 25\ \text{cm}^{-1}\) indicated the multi-layers or bulk MoS\textsubscript{2} was obtained. From the calculation, the value of \(\Delta k = \sim 25\ \text{cm}^{-1}\) are obtained which represents the grown samples for all acid concentrations are multi-layers of MoS\textsubscript{2} films.

Further analyses on the full width at half maximum (FWHM) and the intensity of the Raman peaks of the MoS\textsubscript{2} were carried out in which the Raman spectrum was fitted using Lorentz function. The obtained results were summarized in Fig. 3(d). It was found that the FWHMs for both phonon modes are insensitive to the changes of acid concentrations. Yet, the intensity of the Raman signal increases for the 6 M of OA concentrations. One can explain that higher compactness of MoS\textsubscript{2} films which results in higher volume to surface ratio. Thus, more MoS\textsubscript{2} phonon will be exited by the incident laser beam. Under the higher acidic conditions (i.e., >6 M), the intensity of MoS\textsubscript{2} Raman signal shows significant reduction. This is mainly attributed to the incomplete conversion of MoS\textsubscript{2} crystalline as discussed previously.
Figure 5: The UV-Vis absorption spectra of MoS$_2$ thin films prepared at different oxalic acid concentrations (a) 2 M, (b) 6 M, and (c) 10 M. A and B represent the absorption peaks of MoS$_2$.

Figure 5 shows the absorption spectra of MoS$_2$ thin films. Two weak features located at around 612 nm and 660 nm which originated from the exciton absorption peaks of the MoS$_2$ can be observed for samples prepared with 2 M and 6 M acid concentrations. While no absorption feature was observed for sample prepared with 10 M acid concentration. This is likely due to the lower formation MoS$_2$ at 10 M OA concentration, which leads to weak and untraceable absorption.

4. Conclusion

In summary, the MoS$_2$ films prepared using different OA concentrations were successfully grown by TVS and spin coating as pre-deposition technique. Due to changes in acid concentration, the surface topography and the grain size of the MoS$_2$ films were greatly influenced where the grain size and the root-mean-square surface roughness of MoS$_2$ films increased with the OA concentration. The optical properties were accessed by Raman analysis, which revealed the in-plane (E$_{2g}^{1}$) and out-of-plane phonon modes (A$_{1g}$) of MoS$_2$ crystalline. Two significant MoS$_2$ Raman peaks were detected for all the samples. At higher acid concentration, MoO$_2$ was detected due to the larger aggregate of MoS$_2$ grains, which resulted in slower rate of diffusion of sulfur atoms during the sulfurization process. Apart from that, multi-layers of MoS$_2$ films were obtained via the direct analysis of the frequency different ($\Delta k \approx 25$ cm$^{-1}$). Finally, the two exciton energies of MoS$_2$ was detected, however it is undetectable for higher acid concentration due to the lower formation of MoS$_2$.

Acknowledgement

The authors gratefully acknowledge the financial support from Ministry of Higher Education (MOHE) Malaysia for granting the Fundamental Research Grant Scheme (FRGS) (account no. : 203.PFIZIK.6711561). The corresponding author would like to offer gratitude to the MOHE for offering the MyMaster scholarship to pursue his Master’s degree.
References

[1] Kim K K, Hsu A, Jia X, Kim S M, Shi Y, Hofmann M, Nezich D, Rodriguez-Nieva J F, Dresselhaus M and Palacios T 2011 *Nano Lett.* 12(1) pp 161-166.
[2] Smith J B, Hagaman D and Ji H F 2016 *Nanotech.* 27(21) 215602.
[3] Tao L, Cinquanta E, Chiappe D, Grazianetti C, Fanciulli M, Dubey M, Molle A and Akinwande D 2015 Nat. *Nanotech.* 10(3) pp 227-231.
[4] Duan X, Wang C, Pan A, Yu R and Duan X 2015 *Chem. Soc. Rev.* 44(24) pp 8859-8876.
[5] Eda G, Yamaguchi H, Voiry D, Fujita T, Chen M and Chhowalla M 2011 *Nano Lett* 11(12) pp 5111-5116.
[6] Li H, Wu J, Yin Z and Zhang H 2014 *Acc. Chem. Res.* 47(4) 1067-1075.
[7] Zeng Z, Yin Z, Huang X, Li H, He Q, Lu G, Boey F and Zhang H 2011 *Angew. Chem. Int. Ed.* 50(47) pp 11093-11097.
[8] Smith R J, King P J, Lotya M, Wirtz C, Khan U, De S, O'Neill A, Duesberg G S, Grunlan J C and Moriarty G 2011 *Adv. Mater.* 23(34) pp 3944-3948.
[9] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 *Nat. Nanotechnol.* 7(11) pp 699-712.
[10] Lee Y H, Zhang X Q, Zhang W, Chang M T, Lin C T, Chang K D, Yu Y C, Wang J T W, Chang C S and Li L J 2012 *Adv. Mater.* 24(17), pp 2320-2325.
[11] 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 *Nat. Mater.*, 12(6), pp 554-561.
[12] Liu K K, Zhang W, Lee Y H, Lin Y C, Chang M T, Su C Y, Chang C S, Li H, Shi Y, Zhang H, Lai C and Li L J 2012 *Nano lett.* 12 1538.
[13] Yang J, Gu Y, Lee E, Lee H, Park S H, Cho M H, Kim Y H, Kim Y H and Kim H 2015 *Nanoscale* 7 9311
[14] Kettler R M, Palmer D A and Wesolowski D J 1991 *J. Solution. Chem.* 20(9) pp 905-927.
[15] Houng B, Huang C L and Tsai S Y 2007 *J. Cryst. Growth.* 307(2) pp 328-333.
[16] Chakraborty B, Matte H, Sood A and Rao C 2013 *J. Raman Spectrosc.* 44(1) pp 92-96.
[17] Wang X, Feng H, Wu Y and Jiao L 2013 *J. Am. Chem. Soc.* 135(14) pp 5304-5307.
[18] Bamford C H 1972 *Decomposition of Inorganic and Organometallic Compounds* vol 4, ed Bamford C H, and Tipper C F H (Elsevier Publishing Company) chapter 2 pp 58
[19] Ye M, Winslow D, Zhang D, Pandey R and Yap Y K 2015 *Photonics.* 2 pp 288-307.