Influence of initial sulfur content in precursor solution for the growth of molybdenum disulfide

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Abstract. This work investigated the influence of initial sulfur content in the precursor solution for the growth of molybdenum disulfide (MoS2) films by thermal vapour sulfurization (TVS) with sol-gel spin coating as pre-deposition technique. The early introduction of sulfur shows the presence of grains are uniformly distributed and homogeneous on the surface of the film. MoS2 (002) planes are detected for both films with and without initial sulfur conditions, however, the presence of initial sulfur contents gives slightly higher intensity of diffraction peak. Two phonon modes for MoS2, namely the E2g1 (in-plane) and the A1g (out-of plane), are well detected from which the frequency difference of Raman peaks between E2g1 and A1g suggest the grown MoS2 consisted of multi-layers. There is a slight shift of E2g1 which is caused by the carbon impurities but no shift for A1g. Besides, MoS2 film with the presence of initial sulfur content shows better crystal as indicated by its narrower Raman peaks linewidth. Two broad absorption peaks of MoS2 are detected at 614nm and 665nm. Hence, the early introduction of sulfur content in prepared precursor solution is one way of optimizing the growth of MoS2 films.

1. Introduction
The discovery of graphene by two physicists in 2004 has intensively re-ignited the research on 2-dimensional (2-D) materials [1]. The atomic thickness of sp hybridization bonded carbon has excellent mechanical, optical, and electronic properties that can be utilized in a wide range of applications [2]. However, the zero bandgap of graphene has limited its applications in optoelectronics and electronic switching devices. Transition metal dichalcogenides (TMDs) becoming the alternative as they have analogous layer structure to graphene. Besides, TMDs have diverse properties such as semiconducting and metallic [3]. Basically, the TMDs indicate a wide family of metal disulfide layered structure compounds with formula of MX2, where M is d-block transition metals while X is group VI elements namely chalcogens. These materials have relatively strong in-plane covalent bonding however weak in inter-planar Van der Waals forces [4]. Example of TMDs are molybdenum disulfide (MoS2), tungsten disulfide (WS2), tantalum disulfide (TaS2), and Niobium disulfide (NbS2) [5,6]. MoS2 is one of the TMDs which has attracted significantly attention recently. Renewed interests in MoS2 are on its unique optical properties where the reduced dimensionality resulting in the transition from indirect (~1.2eV, bulk) to direct (~1.8eV, monolayer) bandgap, which is due to the quantum confinement effect [7].

Exfoliation method is the typical top-down method that is implied to cleave bulk MoS2 into monolayer or multi-layers of flakes [7]. The exfoliated MoS2 gives the good quality of free standing flakes, however, the inconsistency and non-uniform flakes size production has limited its application
in large area devices. Due to these circumstances, researchers are begun to search for alternative solutions to overcome the limitations. Vapour phase growth namely chemical vapour deposition (CVD) is the well-known fabrication technique for thin film technology. A wafer scale graphene has successfully been grown by using this approach with the comparable quality to the exfoliated graphene [8]. This has lead the possibilities to the other 2-D materials. Based on the literature review on the CVD MoS	extsubscript{2}, this approach is categorized into two cases, i.e. thermal vapour deposition (TVD) and thermal vapour sulfurization (TVS) [9]. TVD process requires the dual precursors, for example molybdenum oxide (MoO	extsubscript{3}) and molybdenum chloride (MoCl	extsubscript{3}) as Mo source while sulfur powder and hydrogen sulphide (H	extsubscript{2}S) gases as S sources. The precursors will eventually evaporate in the reaction chambers and carried by inert gases to the targeted substrate. On the other hand, TVS process involve the pre-deposition of Mo films and subsequently sulfurization process in sulfur-rich ambient. Several techniques can be applied to deposit Mo films, for example, sputtering, thermal evaporation, dip coating, spin coating and etc [10-13]. Yet, TVD is relatively more complexities to TVS as the controlling of gases flow-rate and partial pressure in the reaction chamber are crucial, so, the reactive species can be absorbed onto the targeted substrate rather than remain as by-product in the exhaust.

In this work, the TVS growth of MoS	extsubscript{2} used sol-gel spin coating as the pre-deposition method instead of dip coating method that was reported by Liu et al [12]. However, poor surface coverage due to accumulation of unevaporated solution at certain areas when the substrates are totally pulled out from the solution. In contrast, spin coating is capable of depositing a large area and uniform MoS	extsubscript{2} films on the substrates. Up to now, there are no reported works that discussed the effect of initial sulfur precursor content in the prepared solution for the growth of MoS	extsubscript{2}. This may be due to most reported works use single source precursor (SSP), i.e. ammonium tetrathiomolybdate [(NH	extsubscript{4})	extsubscript{2}MoS	extsubscript{4}], for the process. This material has the required contents for the synthesis and growth of MoS	extsubscript{2}. However, due to the improper stoichiometry ratio of the SSP, a higher temperature is required for the re-crystallization process. In addition, a new sulfur source, carbon disulfide (CS	extsubscript{2}), is implied for the sulfurization process. Hence, it is worth noting that the novel solution and sulfurization process in this work will introduce a new approach in the investigation of the growth of MoS	extsubscript{2}.

2. Methodology and characterizations
Ammonium molybdate, AM (QReC, 99.5%), thiourea (UNILAB, 99.0%), oxalic acid, OA (Brendosen, 99.5%), ethylenediamine, EDA (Merck, 99.0%), diethanolamine, DEA and distilled water, DW were used as the starting materials for the solution preparation. All materials were used without further treatment. For the preparation of solution with initial sulfur content, a drop of DW was added to the powder mixture of AM, OA and thiourea. The mixture was gently stirred by using a cleaned spatula until the colloidal state. Next, EDA was added and left for ultrasonication until a clear and homogeneous solution was observed. After that, DEA was added into the solution and left for ultrasonication until completely dissolved. The preparation of precursor solution without initial sulfur content was similar except that thiourea was excluded. Prior to the spin coating process, the Si(111) substrates were cleaned by using the acetone and diluted HF solution. The cleaned substrates were removed and rinsed several times with DW. Then, the substrates were nitrogen blow dried and subjected to oxygen plasma treatment. During the spin coating process, the prepared solutions were dropped onto the substrates and spun at 4000rpm for 25s. Subsequently, the coated substrates were subjected to annealing in a tube furnace at 500°C. The tube furnace was then slowly ramped up to 700°C and the CS	extsubscript{2} solution was bubbled by the nitrogen (N	extsubscript{2}) gas and its vapour was carried into the reaction chamber for sulfurization process. Finally, the tube furnace was flushed with nitrogen gas to remove excess sulfur fume and cooled passively before removing the sample. The chosen experimental parameters was based on the reference [12] and [13]. The working principle of the pre-deposition and sulfurization process are illustrated in Figure 1.

Spin coating technique can deposit a flat and homogeneous film as illustrated in Figure 1(a). As shown in the figure, a fixed amount of prepared precursor solutions was dispensed and spun to be deposited on the Si(111) substrates in order to drive away and evaporate the excessive liquid. The coated films are then annealed at 500°C in N	extsubscript{2} ambient.
Figure 1. Schematic illustration of (a) spin coating process on Si(111) substrates and through TVS, (b) tube furnace setup with samples mounted on alumina boat in quartz chamber for sulfurization process. Red ellipse shaped represents the heating coils.

Figure 1(b) illustrates the tube furnace setup showing the working principle of the sulfurization process. The annealed films were then sulfurized at 700°C by continuous flowing of N₂ carrying CS₂ vapour into the reaction chamber. The thermal energy decomposes the vapour compounds into S and other radicals by-product through the chemical equation (1) [14],

$$CS_2 \rightarrow CS + S$$  \hspace{1cm} (1)

In the reaction chamber, the Mo compounds in pre-deposited films are partially reduced by the decomposed gases. Thus, the reactive species are absorbed onto the targeted substrate and substitution of oxygen in the films occurs, the by-product gases are released and exhausted.

The deposited films were investigated by using several characterization tools. To examine the surface texture, tapping mode atomic force microscopy (AFM, Dimension Edge) was applied. The silicon tip-width of <10nm was used then programmed with 1.0Hz frequency and 256 lines/sample scan. The glancing incidence angle x-ray diffraction (GIA-XRD, PANalytical X’Pert Pro MRD) with incident angle of 3° and wavelength of 1.5406 Å was used to investigate the crystal orientation and quality of the deposited MoS₂ films. Furthermore, the Raman-active optical phonon modes of MoS₂ were determined by Raman spectroscopy (Horiba Jobin Yvon HR800UV). An argon ion laser with wavelength of 514.5nm and excitation power of 20mW were applied. Ultra-violet-near infrared (UV-Vis-NIR) spectrophotometer (Cary 5000 UV-Vis-NIR spectrometer) was used to study the optical absorption of MoS₂.
3. Results and discussions

Figure 2. The AFM texture topography of MoS$_2$ (a) with initial sulfur contents and (b) without initial sulfur content. The scanning area is 10x10µm.

Figure 2 shows the AFM surface texture of the MoS$_2$ films after the sulfurization process. The dark shadows in figure 2(b) are the distortions caused by the abnormal large plate-like structures on the surface. Figure 2(a) shows small grains which are uniformly distributed and homogeneous, in contrast, large grains with no consistent grain size are scattered all over the surface for figure 2(b). On close inspection it can be observed that the large plate-like structures consisted of highly compact smaller grains below the large scattered grains. Hence, the initial sulfur content in prepared precursors have a strong influence on the growth of MoS$_2$ grains. This is most probably due to the introduction of initial sulfur content in the beginning of the process gives rise to the early formations of Mo-S compound nuclei. So, high temperature sulfurization favors the grain boundary migrations and recrystallizations of MoS$_2$ films. Hence, the further supply of sulfur causes the nuclei to grow rapidly and orderly over a large area as in figure 2(a) with low density of void formations and columnar texture surface. These observations are based on the reported works by Katagiri et al [15].

Figure 3. The GIA-XRD of MoS$_2$ films with initial sulfur content (Red, S1) and without initial sulfur contents (Black, S2). The blue colour diffractogram shows the standard data of MoS$_2$. (JCPDS ref code: 00-037-1492)
Figure 3 displays the XRD patterns of the MoS$_2$ films with and without the initial sulfur content. It can be seen that both MoS$_2$ samples have diffraction peak of (002) plane at $2\theta=13.9^\circ$ (S1) and $2\theta=14.1^\circ$ (S2) and no other plane orientations are detected (hexagonal P6$_3$/mmc, JCPDS ref. code:00-037-1492). Plane (002) is usually detected for MoS$_2$ with a hexagonal structure. The S2 diffraction peak tends to shift to a larger 20 angle indicating that the absence of initial sulfur content causes the crystal growth experiences compressive stress. Apart from that, the presence of initial sulfur contents in the film (S1) results in better crystal growth orientation which is designated by higher (002) diffraction peak signal as compared to that of the S2.

Raman spectroscopy is a powerful tool that can be applied to study 2-D materials. Figure 4 displays the Raman spectra of MoS$_2$ films for S1 and S2. MoS$_2$ has two significant phonon modes which is represented by $E_{2g}$ (in-plane vibration) and $A_{1g}$ (out-of-plane vibration) as indicated by the schematic drawing of atomic vibrations in figure 4. The $E_{2g}$ mode obtained is located at 385.6 cm$^{-1}$ and 384.5 cm$^{-1}$ for S1 and S2, respectively. While the $A_{1g}$ mode is detected at 411.4 cm$^{-1}$ for both S1 and S2. The Raman results matched with previous reported works [16]. The frequency differences ($\Delta k$) between the Raman peaks of $E_{2g}$ and $A_{1g}$ peaks are around $\Delta k = 25.8$ cm$^{-1}$ (S1) and $\Delta k = 26.9$ cm$^{-1}$ (S2). According to Ye et al., the values of frequency differences can be the direct measure of the thickness of MoS$_2$ films. A monolayer MoS$_2$ has a value of around $\Delta k = 20.7$ cm$^{-1}$ and for values of more than $\Delta k = 24.3$ cm$^{-1}$, the MoS$_2$ film can be considered as having more than 4 (or multi-) layers and classified as bulk [16]. By comparing the reported and experimental obtained values, it implies that the grown MoS$_2$ could have multilayers of MoS$_2$. Furthermore, it seems that the early introduction of sulfur content in the films has some influence on the $E_{2g}$ but insensitive to $A_{1g}$ mode. However, need to be cautious on this matter since the shifting of a Raman line can be triggered by many other factors. The source for sulfur originated from thiourea (CH$_3$N$_2$S) which consists of other elements that can be introduced as impurities into the coated films, especially the carbon residues, creating interstitials carbon into the lattice site which changes the Mo-S crystal lattice, thus shifting the raman peak. However, the concentrations of carbon related centers are low which cannot be detected in the Raman scattering. Lorentz function fitting for both Raman spectra (which is not shown here), indicated that S1 has a slightly better crystal quality as compared to S2 by studying the full width at half maximum (FWHM) of their peaks. The FWHMs of $E_{2g}$ and $A_{1g}$ for S1 are 6.85 and 6.18 cm$^{-1}$, while for S2 are 7.38 and 6.43 cm$^{-1}$ respectively. Besides, the intensity of S1 peaks are higher than those of S2. One can explain that the lateral grain size increases which in turn increases the volume to surface ratio of the films, and hence, more MoS$_2$ compounds are being excited by the incident laser beam. As a result, the Raman peaks intensity increasae.

![Figure 4. The Raman spectra of MoS$_2$ with initial sulfur content (Red, S1) and without initial sulfur content (Black, S2).](image-url)
The optical absorption measurements are done by using transparent substrates. So, the grown MoS$_2$ films are transferred to glass substrates by the assistance of Poly(methyl methacrylate) (PMMA)-capped MoS$_2$ with potassium hydroxide (KOH) solution as buffered oxide etchant (BOE). A uncoated glass substrate is then used as the reference for the measurements. From figure 5, two broad absorption peaks are detected at 614nm and 665nm represented by A and B respectively. These are in good agreement with the works of Eda et al on 2-D MoS$_2$ grown by chemical exfoliation [7].

![Figure 5. The absorption spectra of MoS$_2$ with the initial sulfur contents (Red, S1) and without the initial sulfur contents (Black, S2). A and B indicate the absorption peaks of MoS$_2$.](image)

4. Conclusions
In conclusion, MoS$_2$ films have been grown successfully by TVS with sol-gel spin coating as the pre-deposition method. Mo source powder and S source powder have been used as the starting materials due to the controllable stoichiometry ratio of S/Mo. From the AFM results, the addition of sulfur content in the precursor solution resulted in a uniform and consistent grains growth for sample S1 as compared to large grains scattered on the compacted smaller grains surface for sample S2. Formations of Mo-S compound nuclei provided better growth conditions for S1 when further subjected to sulfurization process. XRD patterns showed that the grown MoS$_2$ films have (002) plane orientation for both sample. The intensity of (002) peak for S1 was slightly higher than the S2. Raman E$_{2g}^\text{1}$ modes of the MoS$_2$ occurred at 385.6 cm$^{-1}$ (S1) and 384.5 cm$^{-1}$ (S2), while the A$_{1g}$ modes located at 411.4 cm$^{-1}$ for both samples. The direct comparison of Raman shift differences between E$_{2g}^\text{1}$ and A$_{1g}$ modes indicated the number of layers of MoS$_2$ to be more than 4 or multi-layers. The early introduction of sulfur content into the precursor gave rise to better crystal quality and larger lateral grain size which is indicated by the intensity of the peaks. Two broad absorption peaks of MoS$_2$ films were detected at 614nm and 665nm. Through the studies, the addition of initial sulfur content in the precursor solution can be the optimum growth condition compared to the absence of initial sulfur content.

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