Recent Advances in Controlled Synthesis of Two-Dimensional Transition Metal Dichalcogenides via Vapour Deposition Techniques

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Recent Advances in Controlled Synthesis of Two-Dimensional Transition Metal Dichalcogenides via Vapour Deposition Techniques

Yumeng Shi, a Henan Li, b and Lain-Jong Li, a*

Recent years there have been many breakthroughs in two-dimensional (2D) nanomaterials, among which the transition metal dichalcogenides (TMDs) attract significant attention owing to their unusual properties associated with their strictly defined dimensionalities. TMD materials with a generalized formula of MX₂, where M is a transition metal and X is a chalcogen, represent a diverse and largely untapped source of 2D systems. Semiconducting TMD monolayers such as MoS₂, MoSe₂, WSe₂, and WS₂ have been demonstrated to be feasible for future electronics and optoelectronics. The exotic electronic properties and high specific surface areas of 2D TMDs offer unlimited potential in various fields including sensing, catalysis, and energy storage applications. Very recently, the chemical vapour deposition technique (CVD) has shown great promise to generate high-quality TMD layers with scalable size, controllable thickness and excellent electronic properties. Wafer-scale deposition of mono to few layer TMD films have been obtained. Despite the initial success in the CVD synthesis of TMDs, substantial research works on extending the methodology open up a new way for substitution doping, formation of monolayer alloys and producing TMD stacking structures or superlattices. In this tutorial review, we will introduce the latest development of monolayer TMDs synthesis by CVD approaches.

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDs) have received much attention recently since they exhibit a wide range of unique electrical, 1,2 optical, 3-5 thermal 6 and mechanical properties 7 that do not exist in their bulk counter parts. Monolayer molybdenum disulfide (MoS₂), one of the most frequently studied member of TMDs, exhibits not only good chemical stability and mechanical flexibility but also excellent optical and electrical properties. 8,9 The semiconducting nature of MoS₂ ensures its high on/off current ratio and the presence of band gap emissions, while still sharing many of graphene’s advantages for electronic and optoelectronic application. 10 The essential findings for these 2D materials enlighten researchers with innovations to develop future nanoelectronic devices that better serve the urgent needs in compact, light-weight and high-performance integrated electronic systems. 8 The promising performance of the electronic and optoelectronic components made from TMD layers, such as field-effect transistors, 1,10,11 sensors 12,13 and photodetectors 2,14,15 proves them to be potential substitutes of Si in conventional electronics and of organic semiconductors in wearable and flexible systems. 16-19

One major and very important research field of TMDs is the reliable production of atomically thin 2D layers and the manipulation of the electronic properties via scalable approaches. To date, two major strategies have been employed to obtain monolayer TMDs: one is the chemical 20-22 or mechanical exfoliation 23 from bulk crystals; the other is the bottom-up growth method. The top-down approaches allow to produce high-quality and micrometre-sized monolayers. It is generally believed, the mechanical exfoliated TMD monolayers possess higher quality and are clean on surfaces, suitable for fundamental research and proof-of-concept device fabrication. However, mechanical cleavage is not suitable for large scale production due to the absence of layer number control ability. On the other hand, chemical exfoliation of monolayer TMDs relies on the liquid-phase preparation method, which materials are promising for solution-based or printable electronics. Yet, the wet chemical method may unavoidably alter the lattice structure of thin TMD...
layers or introduce extrinsic defects during the exfoliation process and thus require a post treatment to reconstruct the structure of monolayer TMDs.

2. Bottom-up approaches towards controlled synthesis of TMDs

The synthesis of atomically thin TMDs with layer controllability and large-area uniformity is an essential requirement for practical application in electronic and optical devices. Huge efforts have been devoted to the controlled synthesis of 2D TMDs. The large-area and uniform synthesis of 2D TMDs in a controllable manner has remained as a challenge for a long time. Very recently, the CVD technique shows promise to generate high-quality TMD layers with scalable size, controllable thickness and excellent electronic properties. The obtained TMD monolayers or films can be used as the active components for nanoelectronics and as the building blocks for constructing layered heterostructures. For the time being, the CVD or similar method is likely the only available way for achieving wafer scale TMDs.

2.1 Synthesis of TMDs via Vapor Phase Deposition

(i) Sulfurization (or selenization) of metal (or metal oxide) thin film

There have been attempts to produce MoS$_2$ layers via simple sulfurization of Mo metal. In the report by Zhan et al., Mo film was deposited on SiO$_2$/Si wafer and followed by thermal annealing in sulfur vapours to produce MoS$_2$ film (Fig. 1a-e). The reaction mechanism for synthesizing MoS$_2$ could be simply understood as a direct chemical reaction. Therefore, the size and thickness of the pre-deposited Mo film determines the thickness and size of the obtained MoS$_2$ thin film. The direct sulfurization of Mo metal thin film provides a quick and easy way to access atomically thin MoS$_2$ layers on insolating substrates. However, due to the challenge of forming a uniform metal thin film, both single and few layer MoS$_2$ coexist on the substrates. The obtained MoS$_2$ layers show a metallic transport property with a low on/off current ratio, which could be due to the presence of unreacted metal impurities.

Similarly, Kong et al. reported that the vertically aligned MoS$_2$ and molybdenum diselenide (MoSe$_2$) layers can be produced by a rapid sulfurization/selenization process at 550 °C (Fig. 1f-i). Smooth and uniform TMD edge-terminated films with densely packed, strip-like grains can be produced on various substrates including glassy carbon, quartz and oxidized silicon. It is suggested that the distinction between vertical and in-plane growth of TMDs could be due to different sulfurization/selenization conditions. The formation of the vertically aligned TMD layers is proposed to be driven by a kinetic process, where at a high temperature the transition metal thin film converts to sulfide/selenide much faster than the diffusion of sulfur/selenium. Thus the sulfur/selenium diffusion limits the growth process. On the other hand, the anisotropic structure of TMD layers, makes it much faster for sulfur/selenium diffusion along the van der Waals gaps. Therefore, the TMD layers naturally orient perpendicular to the film, exposing van der Waals gaps for fast reaction. These TMD layers with predominately exposed edges exhibit high surface energy and are thought to be metastable which may serve for diverse catalytic reactions.

shall be discussed. The CVD approaches to synthesize TMD monolayer alloys and heterostructures are also introduced.
An alternative effort has also been devoted to producing wafer-scale semiconducting MoS$_2$ thin layers, where the direct sulfurization approach is adapted but replacing the Mo metal with MoO$_3$ thin layer (Fig. 2 a-b). The MoS$_2$ thin film derived from this method shows a high on/off current ratio rather than the resistor-like behaviour. To produce wafer-scale MoS$_2$ thin film, MoO$_3$ thin layer with a desired thickness was firstly prepared by thermal evaporation on sapphire substrates. During the growth, MoO$_3$-coated sapphire substrate was initially reduced to MoO$_2$ or other reduced Mo forms in a H$_2$/Ar environment at 500 °C. The sample was then annealed in a sulfur-rich environment at 1000 °C, which leads to the formation of wafer scale MoS$_2$ thin layer with semiconductor properties. The as-grown MoS$_2$ thin film can be transferred to arbitrary substrates for electronic device fabrication, thus the target substrate does not need to expose to high temperatures. Similar strategy has also been adopted for the synthesis of large-area WS$_2$ sheets with controllable thickness. Although it is still at its infant stage, this approach paves a practical way to the synthesis of TMD films for large scale integrated electronics and optoelectronics.

The aforementioned TMDs synthesis method by direct sulfurization (or selenization) of transition metal (or metal oxide) thin film has several limitations, for example, it is hard to control the thickness of pre-deposited metal oxide or metal thin film, which limits the wafer-scale uniformity. To obtain a high-quality TMD with desired number of layers, the thickness of metal oxides need to be precisely controlled. Recent attempts have been made to improve the synthetic process by depositing metal oxides layer via atomic layer deposition (ALD). By this method, atomically thin TMD nanosheets with systematic thickness controllability and wafer scale uniformity can be achieved (Fig. 2 c-e). Song et al. demonstrated that the number of tungsten disulfide (WS$_2$) layers can be controlled by tuning the number of cycles of ALD tungsten trioxide (WO$_3$). Because ALD is used for the metal oxide deposition, the obtained TMDs retain the benefits of the ALD process including thickness controllability, reproducibility, wafer scale uniformity and high conformity. Yet the precursor WH$_2$(iPrCp)$_2$ used for the forming of metal oxides is not readily and widely available and the growth could also be limited to certain substrates, for example, the chemically inert and hydrophobic substrates may not be able to efficiently initiate the growth of WO$_3$ by ALD.

In the above mentioned TMD thin layers, formation of TMD thin films are realized by the sulfurization/selenization reaction or thermal decomposition of the pre-deposited precursors such as Mo, and MoO$_3$ on the growth substrates. Obviously, the growth of 2D TMD layers can be simplified as deposition of the precursors and large-area thin film can be produced subsequently. However the TMD layers are mostly polycrystalline with a small crystal grain size and uncontrollable layer number. To address this issue, Wang et al. reported a method capable of producing highly crystalline MoS$_2$ flakes with controlled number of layers by using MoO$_2$ microcrystals as templates (Fig. 3). In this method, MoO$_2$ rhomboidal microplates were firstly synthesized by thermal evaporation of MoO$_3$ powder in sulfur environment at 650-850 °C. The surface of MoO$_2$ microplates was further sulfurized to MoS$_2$ at a higher temperature (850 – 950 °C) at a later stage. The resulting MoS$_2$ thin layers can be peeled off from MoO$_2$ microcrystals using polymethylmethacrylate (PMMA) mediated transfer printing method. The surface sulfurization of crystalline MoO$_2$ microplates produces a top MoS$_2$ layer with a high crystallinity. The efficiency of sulfurization was limited by the diffusion rate of sulfur atoms through the existing MoS$_2$ outer layer. Thus the layer-by-layer sulfurization is possible by adjusting the sulfurization conditions. However, the MoS$_2$ growth is still determined by the crystal size of MoO$_2$ flakes, where the MoS$_2$ single crystal obtained are randomly distributed as isolated islands. Also, the peeling and transfer process...
could generally lead to the damage of the MoS$_2$ surfaces and degradation of its electronic properties.

(ii) Thermal decomposition of thiosalts

In order to produce large-area, uniform and high-quality TMD sheets with good electrical performance, efforts have been devoted to the thermolysis of the precursor containing Mo and S atoms. In 2011, Li’s group reported a two-step thermolysis process of ammonium thiomolybdate able to produce highly crystalline and large-area MoS$_2$ thin sheets on a variety of insulating substrates (Fig. 4 a).$^{30}$ For the first time, the field-effect transistors (FETs) devices based on the CVD derived MoS$_2$ films exhibit high on/off current ratio and excellent carrier mobility values that are comparable with those obtained from the micromechanical exfoliated MoS$_2$ thin sheets.$^1$ The thermolysis of the single precursor ammonium thiomolybdate (NH$_4$)$_2$MoS$_4$, dissociated it to MoS$_2$, NH$_3$ and S vapors at above 800 °C. The transformation process of (NH$_4$)$_2$MoS$_4$ to MoS$_2$ involves many steps and the presence of oxygen may significantly affect the reaction. Nevertheless, ammonium thiomolybdate needs to be dissolved in polar organic solvents, the carbon contaminations from the residual solvent molecules could also cause the sulfur deficit in the final composition. Therefore, a two-step annealing process is developed to produce high-quality MoS$_2$ thin film. The (NH$_4$)$_2$MoS$_4$ thin film was firstly prepared by dip-coating method and carried in to a quartz tube chamber with the Ar/H$_2$ flow. Temperature was elevated to 500 °C to efficiently remove the residual solvents, NH$_3$ molecules and other by-products dissociated from the precursors. For the second step, temperature was raised to 1000 °C and the sulfur vapours were introduced. It was suggested that the conversion of (NH$_4$)$_2$MoS$_4$ to MoS$_2$ completed at ~425 °C. However, the addition of sulfur during the second annealing process removes the oxygen-containing defects and improves the crystallinity of MoS$_2$ thin film. The transistor devices fabricated with MoS$_2$ thin layers in a bottom gate geometry exhibit n-type behaviours with a significantly improved on/off current ratio which is $\sim$10$^5$ and the field-effect electron mobility is up to 6 cm$^2$/V s).

Based on this film, MoS$_2$ electric double-layer transistors (EDLTs) formed with an ionic liquid were developed. (Fig. 4 b-g)$^{31}$ These thin-film MoS$_2$ transistors exhibit remarkably high mechanical flexibility, where the electrical characteristics do not significantly change with bending. Most importantly, these MoS$_2$ based field effect transistors show excellent band transport with a low threshold voltage ($<$1 V) and high mobility (12.5 cm$^2$/V s$)$. Although the thermolysis of ammonium thiomolybdate produces high quality of MoS$_2$ thin film, synthesis of large area TMDs by this method is still challenging due to the technical limitation of uniform and ultra-thin ammonium thiomolybdate film preparation. Meanwhile, the as-synthesized films are polycrystalline.

(iii) Vapour phase reaction of transition metal oxides with chalcogen precursors

A very early strategy for growing large-area MoS$_2$ atomic layers reported by Li’s group is based on the direct chemical vapour phase reaction of MoO$_3$ and S powders.$^{32,33}$ During the MoS$_2$ growth, MoO$_3$ in vapour phase undergoes a two-step reaction, where MoO$_3$ is likely formed during the reaction as an intermediate phase and these suboxide compounds diffuse to the substrate and further react with sulfur vapours to grow MoS$_2$ layers. This method allows the growth of single-crystalline MoS$_2$ flakes directly on arbitrary substrates depending on the control of nucleation density. Hence this method has been widely used for producing synthetic TMD monolayers.

The growth of MoS$_2$ is very sensitive to the substrate treatment prior to the growth.$^{32}$ The facilitated nucleus by seeding the substrate with graphene-like species has been explored (Fig. 5).$^{33,34}$ The substrate treatment using aromatic molecules, such as reduced graphene oxide (r-GO), perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), promotes the lateral growth of MoS$_2$. These graphene-like molecules act as the seeds for growing MoS$_2$ thin layers. In their growth, the seed concentration is essential for the growth of large-area, continuous and high-quality MoS$_2$ monolayer. Very recently, the role of various seeding promoters in MoS$_2$ growth was further studied in details.$^{34}$ Aromatic molecules, such as copper(II) 2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine (F$_{16}$CuPc), copper
phthalocyanine (CuPc) and dibenzo[f,f′]-4,4′,7,7′-tetrphenyl-diindenopheryl[1,2,3-cd:1′,2′,3′-lm]perylene (DBP) can facilitate the growth of large-area, high-quality and continuous monolayer MoS$_2$. However, when inorganic seeding promoters including aluminum oxide (Al$_2$O$_3$), hafnium oxide (HfO$_2$) and SiO$_2$ are used, no monolayer MoS$_2$ can be found on the substrates after the growth.

It is anticipated that the presence of aromatic molecules provides a better wetting of the growth surface and lowers the free energy for the nucleation. Among the organic promoters, PTAS as a seeding promoter works exceedingly well for promoting MoS$_2$ growth on hydrophilic substrates, while F$_{16}$CuPc is found to be a promising seeding promoter for the growth of MoS$_2$ uniformly on hydrophobic substrates. F$_{16}$CuPc can significantly promote the heterogeneous nucleation process and allowing the fabrication of hybrid structures between MoS$_2$ monolayers, h-BN and graphene (graphite).

Najmaei et al. used MoO$_3$ nanoribbons and sulfur as the reactants for MoS$_2$ growth. It is found that the MoS$_2$ triangular crystals are commonly nucleated and formed on the step edges (Fig. 6 a-c). By patterning the substrates using conventional lithography processes, the nucleation of MoS$_2$ layers can be controlled (Fig. 6 a). The edge-dominated catalytic process is due to a significant reduction in the nucleation energy barrier of MoS$_2$ at step edges as compared with the flat surface (Fig. 6 b). Further experiments reveal that small triangular MoS$_2$ domains are preferentially nucleated at the step edges (Fig. 6 c) and then continue to grow and form boundaries with other domains. The coalescence finally results in a continuous MoS$_2$ film (Fig. 6 d).

Van der Zande et al. reported a refined route for ultra-large MoS$_2$ single crystal growth with solid MoO$_3$ and S precursors. The highly crystalline islands of monolayer MoS$_2$ can be up to 120 µm in lateral size (Fig. 6 e). Neither seeding molecules nor step-edge were used to promote the nucleation of MoS$_2$. Large MoS$_2$ crystalline islands with average size between 20 and 100 µm were obtained by using ultraclean substrates and fresh precursors. The yield can be significantly decreased if dirty substrates or old precursors are used according to the report.

The direct sulfurization/selenation of various metal oxides or metal chlorides have been widely applied in many research groups to produce TMD layers such as MoS$_2$, WS$_2$, MoSe$_2$ and WSe$_2$. Among the numerous reports on the synthesis of sulfides and selenides, one should notice that for selenides synthesis H$_2$ gas is commonly introduced as an additional reducing agent along with Se to further reduce the metal oxides and assist the selenization reaction. Furthermore, Zhang et al. revealed that minor H$_2$ carrier gas can also tailor the shape of monolayer WS$_2$ from jagged to straight edge triangles under low pressure chemical vapour deposition.

(iv) Vapour phase transport and recrystallization from TMD powders

The chemical vapour phase reaction of metal oxides and sulfur/selenium yields monolayers of TMDs which are suitable for FETs fabrication. Yet both tilt and mirror twin boundaries are commonly found in the CVD TMD layers. It has been proved that intervalley scattering enhanced by defects and impurities can reduce or destroy the valley polarization. Thus a method for producing high optical quality monolayer TMDs is required for investigating valley-related physics.
Wu et al. have developed a vapour-solid (VS) growth method for synthesizing high optical quality MoS\textsubscript{2} monolayer.\textsuperscript{44} MoS\textsubscript{2} monolayer flakes can be produced on insulating substrates (such as Si wafer and sapphire) by simple physical vapour transport of MoS\textsubscript{2} powder in an inert environment. MoS\textsubscript{2} powder was evaporated at \sim 900 °C under a low pressure of 20 torr. The collecting substrates were put in a heating zone at 650 °C (Fig. 7 a). It has been reported that the intervalley scattering increases with temperature due to the enhanced phonon populations, resulting in the decrease of valley polarization. The photoluminescence (PL) polarization obtained from the MoS\textsubscript{2} prepared by VS growth is substantial with a maximum of 35% at \sim 1.92 eV, even at room temperature. The result suggests the VS grown MoS\textsubscript{2} has a superb optical quality and high crystallinity (Fig. 7 b-c). However, for the VS growth the nucleation of MoS\textsubscript{2} crystals appears to be random and thicker layers of MoS\textsubscript{2} can also be frequently found, which is due to the limitation of VS growth technique.

2.2 Synthesis of band gap tuneable monolayer alloys

Bandgap engineering of 2D materials is critical to their applications in nanoelectronics and optoelectronics. Tuning band energies of TMDs can be achieved through strain engineering, the reported tunability of the band gap is within 100 meV per 1% strain.\textsuperscript{45-47} However, the strain engineering remains difficult to be utilized for real electronic devices fabrication. Alternatively, the metallic or semiconducting properties of TMDs can be determined by the choice of transition metals and the substitution doping of chalcogenides also gives the freedom of tuning the electronic properties.\textsuperscript{48} In other words, the intrinsic band gap of TMDs can be engineered by stoichiometry. Fortunately, the isomorphism of the transition metal dichalcogenide families (MX\textsubscript{2}; M=Mo, W; X=S, Se, Te) also makes them promising candidates to form ternary van der Waals alloys without phase separation.\textsuperscript{49-53}

In early studies, the TMD solid solutions both in the metal (e.g., Mo\textsubscript{x}W\textsubscript{1-x}S\textsubscript{2}) and chalcogen (e.g., MoS\textsubscript{2-x}Se\textsubscript{x}) sublattice forms have been realized by the direct vapour transport growth, where the stoichiometric amounts of desired powder elements were introduced into a quartz ampoule for crystal growth.\textsuperscript{49-52} Very recently, the transition-metal dichalcogenide monolayer alloys (Mo\textsubscript{x}W\textsubscript{1-x}S\textsubscript{2}) have been obtained by mechanical cleaving from their bulk crystals,\textsuperscript{51} where a tuneable band gap emission ranging from 1.82 eV to 1.99 eV was obtained. The theoretical calculations show that the mono layers of ternary van der Waals alloys, such as MoS\textsubscript{2-x}Se\textsubscript{x}(1-x) are thermodynamically stable at room temperature.\textsuperscript{48} Therefore, it is possible to directly produce single layer ternary TMD alloys via the...
bottom up technique. By adapting the VS growth approach, Feng et al. reported the growth of 2D MoS$_{2}$Se$_{2}$ (0 ≤ x ≤ 0.40) semiconductor alloys.\textsuperscript{54} MoS$_{2}$ and MoSe$_{2}$ powders are used as the growth precursors and simultaneously evaporated to form the TMD alloys under a pressure of ~8 Pa.\textsuperscript{54} By tuning the evaporation temperature of MoS$_{2}$ and MoSe$_{2}$, the composition of as-synthesized MoS$_{2(1-x)}$Se$_{2x}$ monolayers can be controlled. Furthermore, the bandgap photoluminescence is tunable from 1.86 eV (i.e., 665 nm, reached with x = 0) to 1.73 eV (i.e., 716 nm, reached with x = 0.40).\textsuperscript{54}

Gong et al. utilized the same technique developed for MoS$_{2}$ and WS$_{2}$ synthesis to produce ternary van der Waals alloys where selenium and sulfur were mixed with a certain weight percentage to react with MoO$_{3}$ (Fig. 8 a-d).\textsuperscript{53} It was found the doping of Se in MoS$_{2}$ layer is random and homogeneous at the nanoscale. PL measurement shows that the optical band gap of MoS$_{2}$Se$_{1-x}$ can be continuously tuned between 1.85 eV and 1.60 eV by changing the Se doping level. However, large variations in atomic composition from flakes to flakes are expected owing to the difficulty to precisely control the S and Se vapour diffusion in a small CVD furnace. A scalable method to synthesize monolayer TMD alloys is still urgently needed for practical applications.

Su et al. systematically compared the two approaches of forming MoS$_{2}$Se$_{1-x}$ monolayer alloys: selenization of CVD MoS$_{2}$ and sulfurization of CVD MoSe$_{2}$ (Fig. 8 e-h).\textsuperscript{55} The optical energy gap of as-grown MoS$_{2}$ can be continuously modulated from 1.86 eV to 1.57 eV depending on the reaction temperature. Spectroscopic and TEM evidences show that the Mo-S bonds can be replaced by the Mo-Se bonds in a random manner. In contrast, the replacement of Mo-Se by Mo-S preferentially occurs along certain directions depending on the crystalline orientation of MoSe$_{2}$ and thus the MoSe$_{2}$/MoS$_{2}$ biphases can be observed in the alloys, which makes the optical band gap of these alloys distinctly different. The study suggests that the reaction is kinetically controlled and the temperature is a straightforward control parameter for the composition of monolayer alloys.

2.3 Heterostructural stacking based on MoS$_{2}$ and other 2D monolayers

With various 2D building blocks in hand, it is possible to create novel atomically thin crystals via stacking various materials such as graphene, h-BN and TMDs with proper procedures. Combining the electronic properties of different 2D layered materials in hybrid heterostructures offers the possibility to create devices with new functionalities. Therefore, it is of huge interest in the construction of these hetero-layered materials, e.g. alternating individual layers of different 2D films (Graphene, boron nitride, Mica, MoS$_{2}$, WS$_{2}$, WSe$_{2}$ and MoSe$_{2}$) with particular stacking patterns. Depending on the interlayer coupling strength, the luminescence spectrum of TMDs can be tailored.\textsuperscript{57} These TMD tandem structures provide unlimited opportunities to develop unique properties for both fundamental study as well as electronic and photovoltaic applications.

Many novel devices are based on heterostructures formed between MoS$_{2}$ and graphene. Electronic logic and memory devices have already been constructed from graphene–MoS$_{2}$ hybrids.\textsuperscript{58} The graphene/MoS$_{2}$ heterostructures have also been adopted to demonstrate an extremely high photo gain\textsuperscript{4} and the ultrasensitive detection of DNA hybridization.\textsuperscript{63} Therefore, efforts have also been made in the growth of hybrid graphene/MoS$_{2}$ structures. Lin et al. reported the direct synthesis of TMDs on epitaxial graphene, these large-area van der Waals heterostructures show a significant improvement in photoresponse compared to the TMD layer along.\textsuperscript{60} Shi et al. reported the self-assembly of MoS$_{2}$ flakes on the graphene surface via thermal decomposition of ammonium thiomyobdate (Fig. 9 a).\textsuperscript{52} Notice that the lattice spacing for MoS$_{2}$ is 28% larger than that for graphene, it is likely that the crystal orientation can be incommensurate due to the large strains between layers. However,
for the MoS$_2$/graphene van der Waals stacking layers, all the remaining strain is expected to get accommodated in the van der Waals (vdW) gap. Therefore, even though there is a large lattice mismatch between the MoS$_2$ and graphene structure, it was found that graphene can serve as an epitaxial substrate for MoS$_2$ (Fig. 9a). The heterostructures of graphene/MoS$_2$ hybrids show great potential in the hydrogen evolution reaction (HER).\textsuperscript{63, 64}

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| Table 1 Summary of vapour phase sulfurization/ selenization method |

| Thermolysis of Pre-deposited Thiolsalt | MoS$_2$ | Sulfur powder | 1 to 500 Torr, 500-1000 °C | Bilayer and trilayer thin film | Bottom gate FET: ON/OFF ratio: 1.6 x 10$^6$
Mobility: 6 cm$^2$/V$^s$-1 | Ref. 30 |
|--------------------------------------|--------|---------------|---------------------------|-----------------------------|---------------------------------|-----------|
| MoS$_2$/Graphene | (NH$_4$)$_2$MoS$_4$ | Sulfur powder | 1 to 500 Torr, 500-1000 °C | Bilayer and trilayer thin film | Electric double-layer FET: Low threshold voltage <1 V
High Mobility: 33.5 cm$^2$/V$^s$-1 | Ref. 11, 31 |
| MoS$_2$/Graphene | (NH$_4$)$_2$MoS$_4$ | Sulfur powder | 10 mTorr to Atmosphere, 400 °C | Few layer TMDs on graphene | Ref. 62 |
| Sulfurization/Selenization of Pre-deposited TMD Layers | MoS$_2$(Cu$_2$,MoS$_2$)(0 ≤ x ≤ 0.40) | Sulfur powder (heating at 270°C) | Atmosphere, 600 to 900°C | MoS$_2$Se$_{0.5}$ monolayer alloys | Optical band gap tunable from 1.57 (790 nm) to 1.86 eV (667 nm) | Ref. 55 |
| MoS$_2$(Cu$_2$,MoS$_2$)(0 ≤ x ≤ 0.40) | CVD synthesized MoS$_2$/Cu$_2$Se$_2$ layers, Sulfur powder (heating at 160°C), Sulfur powder (heating at 270°C) | Atmosphere, 600 to 900°C | MoS$_2$Se$_{0.5}$ monolayer alloys | Band gap photoluminescence is tunable from 1.57 eV (790 nm) to 2.0 eV (620 nm) | Ref. 56 |
| Sulfurization/Selenization of Pre-deposited Metal thin film/Metal Oxide | ~1-5 nm Mo film, Sulfur powder (heating at 113°C) | Atmosphere at 500-750 °C | Continues thin film with monolayer and few layer TMDs coexist | Field-effect transistor (FET): Mobility: 0.004 to 0.04 cm$^2$/V$^s$-1
Resistivity: 1.46 x 10$^6$ to 2.84 x 10$^7$Ω cm | Ref. 24 |
| ~0.8 to 3.6 nm MoO$_3$ thin layer, Sulfur powder (heating together with precursor at 1000°C) | 1 to 600 Torr, 500 to 1000 °C | 2 to 3 layers isolated domains, 3 layers continuous film | FET: ON/OFF ratio: 10$^6$
Mobility: 0.8 cm$^2$/V$^s$-1 | Capable for water scale synthesis of TMDs | Ref. 26 |
| MoO$_3$ microcrystals (MoO$_3$ reduced by Sulfur at 650 to 850 °C, Sulfur powder (heating at 145°C) | Atmosphere, 850 to 950 °C | Rhomboidal shape TMD layers | FET: ON/OFF ratio: 10$^6$ to 10$^7$
Mobility: 0.1 to 0.7 cm$^2$/V$^s$-1 | Layer by layer sulfurization of Metal oxides | Ref. 29 |
| MoS$_2$, MoSe$_2$ | 5 nm Mo film, Sulfur powder (heating at 230°C), Sulfur powder (heating at 200°C) | Low pressure, 550 °C | MoS$_2$ and MoSe$_2$ films with vertically aligned layers | Catalyst for hydrogen evolution reaction:
Exchange current density (A/cm$^2$): MoS$_2$: 2.0 x 10$^{-6}$
MoSe$_2$: 2.0 x 10$^{-6}$ | Ref. 25 |
| WSe$_2$ | 5 nm WO$_3$, Sulfur powder (heating at 500°C) | Atmosphere, 800 °C | WSe$_2$, Grown on Graphene/SiC | The edge-terminated films are metastable structures TMDs | Ref. 60 |
| WSe$_2$ thin by atomic layer deposition (ALD), H$_2$S gas | Atmosphere, 470 to 1000 °C | Mono-1, bi-, and tetralayers, WSe$_2$ nanotubes | FET: Using high-k dielectric as gate insulator (50 nm MoO$_3$)
Mobility: 3.90 cm$^2$/V$^s$-1 | Ref. 28 |
| WS$_2$ | ~1 to 2.8 nm WO$_3$ thin film, Sulfur powder (heating at 200°C) | 450 mTorr, 750 to 900 °C | Mono-1, bi-, trilayer WS$_2$ synthesis | WS$_2$, MoO$_3$, can also be produced by MoO$_3$ and WO$_3$ coated substrates | Ref. 27 |
### Vapor Phase Reaction

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<td>Atmosphere, 650 °C</td>
<td>Monolayer</td>
<td>FET: On/Off ratio: ~10⁸ Mobility: 0.02 cm²/V·s⁻¹</td>
<td>Ref. 32: Graphene-like molecules were used for substrate treatment</td>
</tr>
<tr>
<td></td>
<td>MoO₃ Sulfur Powder</td>
<td>Atmosphere, 650 °C</td>
<td>Monolayer</td>
<td>FET: On/Off ratio: ~6 x 10⁷ Mobility: ~4.3 cm²/V·s⁻¹</td>
<td>Ref. 34: Various of aromatic molecules can be used as seeding promoters</td>
</tr>
<tr>
<td></td>
<td>MoO₃ nanoribbons Sulfur Powder</td>
<td>Atmosphere, 650 °C</td>
<td>Monolayer</td>
<td>FET: On/Off ratio: ~1 x 10¹ to 1 x 10⁷ Mobility: ~3 to 4 cm²/V·s⁻¹</td>
<td>Ref. 35: Patterned substrates were used to control the nucleation</td>
</tr>
<tr>
<td></td>
<td>MoO₃ Sulfur Powder</td>
<td>Atmosphere, 700 °C</td>
<td>Monolayer</td>
<td>FET: On/Off ratio: ~1 x 10⁸ Mobility: 0.03 cm²/V·s⁻¹</td>
<td>Ref. 36: Large single domain (&gt; 100 μm) can be synthesized by using ultraclean substrates</td>
</tr>
<tr>
<td></td>
<td>MoO₃ Sulfur Powder (heating at 300 °C)</td>
<td>2 Torr, 850 °C</td>
<td>Monolayer and fewlayer</td>
<td>FET: Mobility: ~0.003 to 0.03 cm²/V·s⁻¹</td>
<td>Ref. 37</td>
</tr>
<tr>
<td></td>
<td>MoO₃ Sulfur Powder (heating at 100 °C)</td>
<td>~225 mTorr, 380 °C</td>
<td>Monolayer on Mica</td>
<td>Perfect valley-related optical properties</td>
<td>Ref. 65</td>
</tr>
<tr>
<td></td>
<td>MoO₃ Sulfur Powder (heating at 130 °C)</td>
<td>5 Torr, 670 °C</td>
<td>Monolayer on Graphene/SiC</td>
<td>10⁴ improvement in photoresponse compared to MoS₂ along</td>
<td>Ref. 60</td>
</tr>
<tr>
<td></td>
<td>WO₃ Sulfur Powder</td>
<td>550 to 750 °C</td>
<td>Monolayer</td>
<td>FET: On/Off ratio: ~1 x 10⁸ Mobility: 0.46 and 0.28 cm²/V·s⁻¹ for electron and hole, respectively</td>
<td>Ref. 6</td>
</tr>
<tr>
<td>W₅S₃</td>
<td>WO₃ Sulfur Powder (heating at 100 °C)</td>
<td>~225 mTorr, 900 °C</td>
<td>Monolayer and fewlayer</td>
<td>FET: On/Off ratio: ~1 x 10⁸ Mobility: 0.46 and 0.28 cm²/V·s⁻¹ for electron and hole, respectively</td>
<td>Ref. 39: Ionic liquid used as the gating dielectric</td>
</tr>
<tr>
<td></td>
<td>W₅S₃, MoS₂</td>
<td>MoO₃, WO₃ Sulfur Powder</td>
<td>Monolayer</td>
<td>MoS₂ FET: On/Off ratio: &gt;10⁸ Mobility: 2.4 cm²/V·s⁻¹</td>
<td>Ref. 33: Small molecules were used as seeding for growth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atmosphere, 650 °C</td>
<td>Monolayer</td>
<td>W₅S₃ FET: On/Off ratio: &gt;10⁸ Mobility: 0.01 cm²/V·s⁻¹</td>
<td>Low mobiltiy of W₅S₃ could be due to the non-optimised metal electrodes</td>
</tr>
<tr>
<td>MoSe₂</td>
<td>MoO₃ powder, Selenium powder (heating at ~300 °C)</td>
<td>Atmosphere, 750 °C</td>
<td>Monolayer and fewlayer</td>
<td>Electric double-layer FET: p channel: On/Off ratio: ~10⁸ Mobility: 90 cm²/V·s⁻¹</td>
<td>Ref. 41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n channel: On/Off ratio: ~10⁸ Mobility: 5 cm²/V·s⁻¹</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td>WSe₂ based invert exhibits a high gain of ~13</td>
<td></td>
</tr>
<tr>
<td>WSe₂</td>
<td>WO₃ powder (heating at 925 °C), Selenium powder (heating at ~270 °C)</td>
<td>Atmosphere, 750 to 850 °C</td>
<td>Monolayer</td>
<td>Optical band gap can be fine tuned between 1.85 and 1.60 eV</td>
<td>Ref. 42</td>
</tr>
<tr>
<td>MoS₁₁₋₃Se₂₄</td>
<td>MoO₃ Sulfur and Selenium Powder</td>
<td>Atmosphere, ~800 °C</td>
<td>Monolayer</td>
<td></td>
<td>Ref. 53</td>
</tr>
</tbody>
</table>

Table 2: Summary of vapor phase reaction method
Besides graphene, fluorophlogopite mica (KMg$_3$AlSi$_3$O$_{10}$F$_2$) is also considered to be a good vdW epitaxy substrate for TMD growth due to their atomic flat and chemically inert surface with a hexagonally arranged in-plane lattice. Ji et al. reported centimetre-scale uniform monolayer MoS$_2$ can be synthesized on mica through low-pressure CVD (LPCVD) process (Fig 9. b-e). It was concluded that the MoS$_2$ growth on mica follows an analogous layer-plus-island (or Stranski-Krastanov) growth mode. The Stranski-Krastanov mode follows a two-step process: initially, monolayer MoS$_2$ domains gather and interconnect with each other till the full coverage of monolayer is nearly completed. Beyond the critical layer number (1 for MoS$_2$ on mica), the growth of MoS$_2$ continues through the nucleation and coalescence of MoS$_2$ nanoparticles or few layers islands. Meanwhile, the epitaxial monolayer MoS$_2$ grown on mica is intrinsically strained due to a small adlayer-substrate lattice mismatch. Room-temperature PL helicity can also be observed when MoS$_2$ layers are transferred to SiO$_2$/Si substrate where the intrinsic strain gets released. The results are similar to the optical quality MoS$_2$ obtained by vapour-solid method, suggesting the high crystal quality of the MoS$_2$ synthesized by combining vdW epitaxy with LPCVD.

Conclusions

This review provides a largely collection of literatures for the preparation of various TMD materials. Table 1, 2 and 3 list the common methods for TMDs synthesis. The reported synthesis conditions and the key properties, such as morphology, number of layers, mobilities, optical band gap have been summarized. Typical experimental setup has also been schematically illustrated. The semiconducting TMD materials with a tuneable doping level make them complementary to graphene. Vapour deposition methods have been developed for the synthesis of monolayer and few-layer TMD nanosheets such as MoS$_2$, WS$_2$, WSe$_2$ and MoSe$_2$. The CVD approaches, suitable for wafer scale fabrication, provide high-quality TMD films useful for electronic and optoelectronic devices. In addition, the electro dispersive property and the semiconducting nature of 2D TMDs can be tailored by bandgap engineering. The stacking of different types of 2D nanomaterials also attracts attention for integrated circuits. Novel properties and new phenomena could arise from the 2D heterostructural stacking or alloys. To realize the practical applications, more efforts are needed to attack many issues related to the growth, including layer number control, size control, area selective growth and the direct growth of heterostructures.

Acknowledgements

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Notes and references