INTRODUCTION

Transition metal dichalcogenides (TMDCs) are layered materials with strong in-plane covalent bonding and weak out-of-plane van der Waals bonding which is similar with graphene (Novoselov et al., 2005; Ramakrishna Matte et al., 2010). In particular, semiconducting two-dimensional (2D) TMDCs such as MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, have been demonstrated to be feasible for various advanced electronic and optical applications. In these regards, process to synthesize high quality 2D TMDCs layers with high reliability, wafer-scale uniformity, controllable layer number and excellent electronic properties is essential in order to use 2D TMDCs in practical applications. Vapor deposition techniques, such as physical vapor deposition, chemical vapor deposition and atomic layer deposition, could be promising processes to produce high quality 2D TMDCs due to high purity, thickness controllability and thickness uniformity. In this article, we briefly review recent research trend on vapor deposition techniques to synthesize 2D TMDCs.

Key Words: Molybdenum disulfide, Transition metal dichalcogenides, Two-dimensional materials, Chemical vapor deposition, Atomic layer deposition
Radisavljevic et al., 2011; Li et al., 2012; Nicolosi et al., 2013). The exfoliated 2D TMDCs are suitable for basic research and demonstration of concept application since they have high crystallinity and inherent properties. However, the exfoliated 2D TMDCs have shown several limitations such as isolation, small size (usually less than a few μm), and low productivity, which make it difficult to be used 2D TMDCs in practical devices. Thus, significant efforts have been devoted to synthesize high quality and large area 2D TMDCs. Recently several studies have shown synthesis of 2D TMDCs using various methods based on the vapor deposition techniques: sulfurization of metal and metal oxide thin films (Lin et al., 2012; Zhan et al., 2012; Elias et al., 2013; Liu et al., 2014b), chemical vapor deposition (CVD) (Lee et al., 2012; Huang et al., 2013; Najmaei et al., 2013; van der Zande et al., 2013; Cong et al., 2014; Ji et al., 2014; Ling et al., 2014; Shaw et al., 2014; Dumcenco et al., 2015; Kang et al., 2015) and atomic layer deposition (ALD) (Song et al., 2013; Jin et al., 2014; Tan et al., 2014; Song et al., 2015). In this review, synthetic methods for 2D TMDCs, mainly focused on the MoS$_2$ and WS$_2$ which are the most studied 2D TMDCs, will be presented.

**CHALCOGENIZATION OF METAL AND METAL OXIDE THIN FILM**

Initial studies on the synthesis of 2D MoS$_2$ were focused on the sulfurization of Mo and MoO$_x$ thin films, which were deposited by physical vapor deposition (PVD) at high temperature. Zhan et al. (2012) reported that the synthesis of MoS$_2$ film by thermal annealing (at 750°C) of PVD Mo thin film on SiO$_2$/Si substrate as shown in Fig. 1A-D. Similarly, Lin et al. (2012) reported wafer-scale (2 inch) MoS$_2$ thin layers synthesis by sulfurization of MoO$_3$ thin film at 1,000°C (Fig. 1E-G). Although these
sulfurization methods are simple and easy to produce 2D MoS$_2$, several limitations exist such as difficulty in precise thickness control and in wafer-scale thickness uniformity of PVD Mo and MoO$_x$. Thus, precise control on the thickness of metal oxide film is essential to obtain layer number controlled, wafer-scale uniform 2D TMDCs. Recently, Song et al. (2013) demonstrated the synthesis of high quality WS$_2$ by the sulfurization of WO$_3$ thin film deposited by ALD. Since ALD has inherently excellent ability to control the film thickness over wafer scale, the synthesized WS$_2$ layer has retained the inherent benefits of the ALD process as well as high mobility of approximately 4 cm$^2$/Vs (Fig. 1H-L). Further, latest report by Song et al. (2015) has shown that the composition controllable synthesis of Mo$_{1-x}$W$_x$S$_2$ alloy using sulfurization of super-cycle ALD Mo$_{1-x}$W$_x$O$_y$. Based on this, they synthesized a vertically composition-controlled Mo$_{1-x}$W$_x$S$_2$ multilayer that has broadband light absorption. Since the various transition metal oxides can be easily deposited by ALD, sulfurization (or selenization) of ALD metal oxide could be extended to synthesis of various 2D TMDCs.

**CHEMICAL VAPOR DEPOSITION**

The synthesis of 2D TMDCs using CVD with metal oxide

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*Fig. 2.* (A) Schematic illustration of chemical vapor deposition (CVD) MoS$_2$. (B) The optical microscopy (OM) images of CVD MoS$_2$ on the SiO$_2$ substrate treated with reduced graphene oxide solution. (C) OM image of CVD MoS$_2$ on a SiO$_2$ substrate, and OM image of a monolayer CVD MoS$_2$ triangle with size up to 120 μm in lateral (inset). (D) High-resolution transmission electron microscopy image of the grain boundary of CVD MoS$_2$ with a period line of 8-4-4 ring defects. (E) An atomic model of the experimental structure shown in Fig. 2D. (F) Large-area (1×7 cm$^2$) mono-, bi-, and trilayered CVD WS$_2$ on SiO$_2$ substrates. (G) Schematic illustration of metal-organic CVD MoS$_2$ and WS$_2$. (H) Batch-fabricated 8×100 MoS$_2$ field effect transistor arrays on a 4-inch SiO$_2$ wafer. Top inset: enlarged image of one square containing 100 devices. Middle and bottom insets: corresponding color maps of $\sigma$ at gate bias $V_{BG}$=50 V and −50 V, respectively. Fig. 2A and B reproduced from the article of Lee et al. (2012) (*Advanced Materials* 24, 2320-2325) with original copyright holder’s permission. Fig. 2C-E reproduced from the article of van der Zande et al. (2013) (*Nature Materials* 12, 554-561) with original copyright holder’s permission. Fig. 2F reproduced from the article of Park et al. (2015) (*Nanoscale* 7, 1308-1313) with original copyright holder’s permission. Fig. 2G and H reproduced from the article of Kang et al. (2015) (*Nature* 520, 656-660) with original copyright holder’s permission.
(MO$_3$, M=Mo and W) and chalcogen (X=S and Se) powders at 600°C~700°C has been extensively studied (Lee et al., 2012; Najmaei et al., 2013; van der Zande et al., 2013; Ling et al., 2014). In this process scheme, MO$_{3-x}$ is formed by the reduction of MO$_3$ vapor. Subsequently, MO$_{3-x}$ vapor diffuses to the substrate and reacts with X vapor. Lee et al. (2012) reported the promotion of 2D MoS$_2$ synthesis using substrate treatment by graphene like species, such as reduced graphene oxide, perylene-3,4,9,10-tetracarboxylic acidtetrapotassium salt and perylene-3,4,9,10-tetracarboxylicdianhydride. Here, the species used for surface treatment promote act as seeds for 2D MoS$_2$ formation and enhance the lateral growth of MoS$_2$, as shown in Fig. 2A and B (Lee et al., 2012). Meanwhile, van der Zande et al. (2013) reported the synthesis of large MoS$_2$ single crystal grains (at 700°C) up to 120 µm without seeding. In this report, they used ultraclean substrates and fresh precursors to promote grain size (Fig. 2C). Further, they have observed that formation of periodic line of 8-4-4 ring defects at grain boundary of CVD MoS$_2$ as represented in Fig. 2D and E. Recent studies on the CVD with MO$_3$ and X powder have been focused on the synthesis of MoS$_2$ and WS$_2$ on single crystal substrate for enhancing grain size. In particular, orientation aligned growth of CVD MoS$_2$ on c-plane sapphire has been reported by Ji et al. (2014) and Dumcenco et al. (2015). They have shown that the same hexagonal lattice symmetry induces van der Waals epitaxy of MoS$_2$ on c-plane sapphire, which suggests possibility of wafer-scale growth of single-crystal MoS$_2$ similar with graphene on hydrogen-terminated germanium (Lee et al., 2014b).

However, the CVD process based on MO$_3$ and X powder is critically depending on process conditions such as amount of MO$_3$ and X powder, non-homogeneous diffusion of vaporized molecules, and outgoing flow of vapors from the chamber. Since these process conditions cannot be easily controlled, uniform and high quality synthesis is hardly achievable (Najmaei et al., 2013; van der Zande et al., 2013;}

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Fig. 3. (A) Schematic illustration of one growth cycle of atomic layer deposition (ALD) MoS$_2$. (B) High-resolution transmission electron microscopy (HRTEM) image of mono- and multilayer ALD MoS$_2$. (C) Optical absorption. (D) Photoluminescence spectra for ALD-deposited, as-grown or annealed MoS$_2$. (E) Cross-sectional HRTEM image of the ALD MoS$_2$ after annealed at 900°C for 5 minutes. Fig. 3A-D reproduced from the article of Tan et al. (2014) (Nanoscale 6, 10584-10588) with original copyright holder’s permission. Fig. 3E reproduced from the article of Jin et al. (2014) (Nanoscale 6, 14453-14458) with original copyright holder’s permission.
Park et al., 2015). Thus, CVD of 2D TMDCs based on gas precursor and reactant is more promising. As shown in Fig. 2F, Park et al. (2015) reported layer number controllable and wafer-scale uniform growth of WS₂ using WCl₆ and H₂S at 700°C. More recently, Kang et al. (2015) reported high quality WS₂ synthesis based on metal-organic CVD (MOCVD) using Mo(CO)₆, W(CO)₆, and (C₂H₅)₂S at 700°C (Fig. 2G). The synthesized MOCVD 2D TMDCs exhibited homogeneous electrical properties with high electron mobility of 30 cm²/Vs and 99% devices yield (Fig. 2H). However, the growth rate was reported to be very low, which requires 26 hours to grow monolayer 2D TMDCs.

### ATOMIC LAYER DEPOSITION

Due to benefits of ALD in terms of thickness controllability of thin film in nanometer scale, ALD is considered to be a promising candidate to synthesis technique for 2D TMDCs. In fact, various ALD processes of chalcogenides thin films such as ZnS, GaS, CdS, etc, have been reported for photovoltaic and energy storage materials (Dasgupta et al., 2015). Recently, a few reports on ALD MoS₂ are available as shown in Fig. 3. Tan et al. (2014) reported growth of ALD MoS₂ film using MoCl₅ and H₂S at 300°C (Fig. 3A-D). In addition, low temperature (at 100°C) ALD MoS₂ process using Mo(CO)₆ and (CH₃)₂S is available.

### Table 1. Summary of the vapor deposition techniques for synthesis of two-dimensional TMDCs

| TMDCs          | Process                                      | Process temperature (°C) | Layer number             | Electrical properties (cm²/V·s⁻¹) | Reference               |
|----------------|----------------------------------------------|--------------------------|--------------------------|-----------------------------------|-------------------------|
| MoS₂           | Sulfurization (S powder) of PVD Mo (1–5 nm)  | 750                      | Mono- and few-layer mixing | Back gate FET Mobility: 0.004 to 0.04 | Zhan et al. (2012)      |
|                | Sulfurization (S powder) of PVD MoO₃         | 1,000                    | Bi- and few-layer        | Back gate FET Mobility: 0.8       | Lin et al. (2012)       |
|                | Sulfurization (H₂S) of ALD MoO₃              | Annealing: 1st, 600; 2nd, 1,000 | Mono-, bi-, and tri-layer | -                                 | Song et al. (2015)      |
| WS₂            | Sulfurization (S powder) of PVD WO₃          | 800                      | Mono-, bi-, and tri-layer | Top gate FET Mobility: 3.9        | Song et al. (2013)      |
|                | Sulfurization (H₂S) of ALD WO₃              | 1,000                    | Mono-, bi-, and tetra-layer | -                                 |                        |

| Chemical vapor deposition                                      |
| MoS₂           | MoO₃ and S powder with seeding                | 650                      | Monolayer                | Back gate FET Mobility: 0.02      | Lee et al. (2012); Ling et al. (2014) |
| MoO₃ and S powder  |                                             | 700                      | Monolayer                | Back gate FET Mobility: 3 to 4    | van der Zande et al. (2013) |
| MoO₃ nanoribbons and S powder                                 |                                             | 850                      | Monolayer                | Back gate FET Mobility: 4.3       | Najmaei et al. (2013) |
| MoO₃ and S powder  |                                             | 850                      | Monolayer on sapphire    | Back gate FET Mobility: 0.1 to 1  | Ji et al. (2014) |
| MoO₃ and S powder  |                                             | 700                      | Monolayer on sapphire    | Back gate FET Mobility: 25        | Dumcenco et al. (2015) |
| WS₂            | WO₃ and S powder                             | 750                      | Monolayer                | Back gate FET Mobility: 25        | Cong et al. (2014)       |
| WCl₆ and H₂S gas    |                                             | 700                      | Mono-, bi-, and tetra-layer | -                                 | Park et al. (2015)      |
| MoS₂, MoO₃, W(CO)₆, and diethyl sulfide                      |                                             | 550                      | Monolayer                | Top gate FET Mobility: 30        | Kang et al. (2015)      |
| MoSe₂          | MoO₃ and Se powder                           | 750                      | Mono- and few-layer      | Electric double-layer FET Mobility: 90 | Shaw et al. (2014)       |
| WSe₂           | WO₃ and Se powder                            | 750                      | Monolayer                | -                                   | Huang et al. (2013)      |
| Atomic layer deposition                                      |
| MoS₂           | Mo(CO)₆ and dimethyl disulfide               | 100                      | Amorphous                | -                                   | Lin et al. (2014)        |
|                | MoCl₆ and H₂S gas                            | 300                      | Amorphous                | -                                   | Tan et al. (2014)        |

TMDCs, transition metal dichalcogenides; PVD, physical vapor deposition; FET, field effect transistor; ALD, atomic layer deposition.
reported by Jin et al. (2014). However, the reported ALD MoS₂ films show low optical property attributed to amorphous phase as shown in Fig. 3E, which limits there use for the electrical and optical applications. The basic problem of ALD processes for TMDCs are the difficulty in the formation of layered structure. The deposition of high quality TMDCs by direct ALD process is yet to come.

CONCLUSIONS

This review provides a brief collection of literatures on the synthesis of 2D TMDCs materials as summarized in Table 1. Vapor deposition techniques, which are suitable for wafer-scale and high-quality synthesis of 2D TMDCs such as MoS₂, WS₂, WSe₂ and MoSe₂ for electronic and optoelectronic devices have been developed. To realize the advanced applications using 2D TMDCs, more efforts are needed to resolve many issues related to the growth, including high reliability, layer number controllability, wafer-scale uniformity and high crystallinity. Furthermore, synthesis of high quality 2D TMDCs will boost the study on the stacking of different types of 2D materials which could exhibit novel properties and new phenomena.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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