Methane-Mediated Vapor Transport Growth of Monolayer WSe\(_2\) Crystals

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Abstract: The electrical and optical properties of semiconducting transition metal dichalcogenides (TMDs) can be tuned by controlling their composition and the number of layers they have. Among various TMDs, the monolayer WSe\(_2\) has a direct bandgap of 1.65 eV and exhibits p-type or bipolar behavior, depending on the type of contact metal. Despite these promising properties, a lack of efficient large-area production methods for high-quality, uniform WSe\(_2\) hinders its practical device applications. Various methods have been investigated for the synthesis of large-area monolayer WSe\(_2\), but the difficulty of precisely controlling solid-state TMD precursors (WO\(_3\), MoO\(_3\), Se, and S powders) is a major obstacle to the synthesis of uniform TMD layers. In this work, we outline our success in growing large-area, high-quality, monolayered WSe\(_2\) by utilizing methane (CH\(_4\)) gas with precisely controlled pressure as a promoter. When compared to the catalytic growth of monolayered WSe\(_2\) without a gas-phase promoter, the catalytic growth of the monolayered WSe\(_2\) with a CH\(_4\) promoter reduced the nucleation density to 1/1000 and increased the grain size of monolayer WSe\(_2\) up to 100 \(\mu\)m. The significant improvement in the optical properties of the resulting WSe\(_2\) indicates that CH\(_4\) is a suitable candidate as a promoter for the synthesis of TMD materials, because it allows accurate gas control.

Keywords: TMD; 2D material; WSe\(_2\); monolayer; methane promoter; single-crystal

1. Introduction

The discovery of graphene and its unique properties has triggered the development of various types of layered materials [1]. In particular, transition metal dichalcogenides (TMDs), atomically thin semiconductors of the type MX\(_2\) (M = Mo, W; X = S, Se), have attracted considerable attention as their physical and electrical properties are tunable. Depending on their composition and thickness, two-dimensional (2D) TMDs have a variety of electrical properties ranging from metal, to insulator, to semiconductor, which could lead to a new dimension of atomic thickness for future device applications [2,3]. TMD materials have useful device characteristics, such as a high on/off ratio, a wide range of photoluminescence, and a low subthreshold voltage, making them suitable for spintronics and...
optoelectronics [4]. Among the numerous TMD materials, WSe$_2$ has been extensively studied because its electrical transport properties can be easily adjusted from p-type to bipolar behavior depending on the type of contact metal [5–7]. Bulk WSe$_2$ crystallizes in the “2H” or trigonal prismatic structure (space group $P6_3/mmc$; $a = 0.330$ nm, $c = 1.298$ nm), in which each W atom is surrounded by six Se atoms, defining two triangular prisms. It was also reported that the energy band structure of WSe$_2$ can be altered according to its layer number. WSe$_2$ shows a direct bandgap of 1.65 eV in the monolayer, compared to an indirect bandgap of 1.2 eV in the multilayered bulk [8,9]. Similar to another 2D layered material, TMD is typically prepared using a mechanical exfoliation method. However, this top-down approach is not suitable for practical high-performance device applications, so bottom-up approaches for large-scale and mass-production have been extensively studied. The chemical vapor deposition (CVD) method is one of the bottom-up approaches that allows the synthesis of large-area TMDs. The CVD growth of TMDs has largely been studied using two different approaches. The first approach is to pre-deposit transition metal sources such as MoO$_3$, WO$_3$, etc., on the growth substrate and convert them to TMD by sulfidation (or selenization) [10–18]. The second is a noncatalytic growth method, in which a transition metal source and sulfur (or selenium) are heat-treated in a growth tube and flowed in a gaseous state to synthesize the TMD layer on a target substrate [19,20]. However, these CVD approaches have not been successful in uniform, high-quality TMD synthesis because it is difficult to control the thickness and nucleation density of TMDs [21]. Recently, to overcome such problems, many researchers have studied various types of promoters and methods applied for CVD-based TMD synthesis to control gas-phase transport of precursors and the reaction of TMD on the growth substrate [22–26]. Ling et al. reported the synthesis of highly-crystalline MoS$_2$ at a relatively low growth temperature ($650\, ^\circ\text{C}$) using various aromatic molecules as seeding promoters [13]. In particular, domain size of MoS$_2$ increased up to 60 $\mu$m through vaporized aromatic-molecule catalysts such as perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) and F$_{16}$CuPc. They also reported that uniform monolayer MoS$_2$ can be synthesized on the entire area of the SiO$_2$/Si substrate; however, the use of such an organic catalyst leaves a residue on the growth substrate that acts as a defect of the synthesized TMD. Another limitation of this method is that it is not applicable to the growth of WS$_2$ and WSe$_2$, which require high growth temperatures. In addition, inorganic materials were also reported in assisted WSe$_2$ growth methods [15,27]. Liu et al. demonstrated a Cu-assisted self-limited growth (CASLG) method that allowed the synthesis of a high-quality, uniform WSe$_2$ monolayer while maintaining a balance between high crystallinity and fast growth rates. They explained that Cu atoms, which occupy the hexagonal sites positioned at the center of the six-membered rings of the WSe$_2$ surface, induce self-limited growth of WSe$_2$ and prevent unwanted reactions [15]. However, this approach also had disadvantages, for example, the synthesized WSe$_2$ had small grain sizes with multilayered regions and the vapor pressure of the solid catalyst could not be precisely controlled.

Herein, we report a catalytic growth of the large-area monolayer WSe$_2$ by utilizing CH$_4$ (methane) with precisely controlled pressure as a promoter. Through a systematic investigation, it is confirmed that grain size and the nucleation density of WSe$_2$ can be controlled according to the ratio of carrier gases (Ar/CH$_4$). The gas promoter leads to synthesis of about 100 $\mu$m size domains of WSe$_2$ and significantly reduces nucleation density from $1.6 \times 10^5$ to $1.5 \times 10^2$ mm$^{-2}$. Various analytical tools such as Raman, photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) analysis are used to demonstrate the properties of synthesized monolayer WSe$_2$.

2. Materials and Methods

2.1. Preparation

The WSe$_2$ precursor powders (Alfa Aesar, Ward Hill, MA, U.S., 99.8%; metal basis, 10 microns) were placed on the cleaned alumina boat. Prior to the growth, the SiO$_2$/Si wafer (thermal oxide wafer: 300 nm SiO$_2$ layer on Si (100), MTI Inc., Richmond, CA, U.S.) substrate was washed by acetone, ethyl alcohol, and deionized (DI) water, for 5 min, to remove the organic residue and was then treated with
oxygen plasma (100 sccm, 100 W). High-purity Ar gas (99.999%, JC gas Inc.) and methane gas diluted in Ar (1% CH₄, 99% Ar, JC gas Inc., Suwon-si, Gyeonggi-do, Korea) were used as carrier gases.

2.2. Synthesis of WSe₂

The homemade CVD system was designed to flow gas in both directions with a three-zone furnace and a double-quartz tube (outer: 34 mm diameter, inner: 15 mm diameter tube). The WSe₂ powders were placed in an alumina boat located at the center furnace of the homemade CVD. The SiO₂/Si substrate was cut to 1 cm × 5 cm size and then placed in the left furnace, about 10 cm from the alumina boat. The CVD system was pumped to the base pressure (2 × 10⁻³ torr) by a rotary pump for 10 min and then filled with Ar gas to 760 torr. In the process of increasing the temperature to the WSe₂ growth temperature, the flow direction of the carrier gas (Ar 200 sccm) was reversed to prevent unwanted deposition. After the temperature reached 1050 °C, the flow direction of the carrier gas was reversed again to allow the evaporated precursor to reach the growth substrate. In the synthesis process, the experiment was carried out by flowing a different ratio of Ar and CH₄ (1% diluted at Ar) for 60 min at atmospheric pressure. After the reaction, the furnace was quenched down to room temperature while maintaining the gas flow, and the samples were collected for characterization.

2.3. Characterization of Synthesized WSe₂

The morphology and size of synthesized WSe₂ samples were characterized using optical microscopy (OM, Olympus DX51, Tokyo, Japan) and a SEM (JEOL JSM-7401F, JEOL LTD, Tokyo, Japan) operating at 5 kV and 10 µA. The nucleation density and grain size of WSe₂ were analyzed using the Image J program tool. The thickness and surface potential of the WSe₂ monolayer were confirmed by atomic force microscopy and Kelvin probe force microscopy (KPFM) using Park NX10 (Park system, Suwon-si, Gyeonggi-do, Korea) with a Si cantilever Pt-coated tip. X-ray photoelectron spectroscopy analysis was carried out by ESCA2000 spectrometry (Termo Fisher Scientific, Walthan, Massachusetts, U.S.) using monochromatic Al-Kα radiation (1468.6 eV). Raman and photoluminescence spectra were collected with micro-Raman spectroscopy (WITEC Raman system, Ulm, Germany) using a 532 nm laser.

3. Results and Discussion

As shown in Figure 1a, monolayer WSe₂ was synthesized on the SiO₂/Si substrate by a homemade three-zone furnace CVD using WSe₂ powder as a precursor. Briefly, the CVD system can control the temperature at each zone and adjust the direction of the carrier gas as required. During the ramping process for increasing the temperature of the furnace, the carrier gas flowed from the right to left direction to prevent the evaporated precursor from reaching the growth substrate, and the flow direction of the carrier gas was reversed during the growth process to synthesize the WSe₂ monolayer. A 1 × 5 cm² SiO₂/Si growth substrate was placed 10 cm away from the alumina boat containing the precursor. The growth behavior of WSe₂ was investigated by observing the product at the same location as the growth substrate, because the morphology and density of the WSe₂ crystals depended upon the distance between the precursor and the growth substrate [12,16]. Figure 1b illustrates the catalytic growth of WSe₂ crystals via vapor-solid transport mechanism, when CH₄ gas diluted in Ar (1% CH₄, 99% Ar) was used as both a carrier gas and a promoter. Like other catalysts for the growth of 2D materials, such as the Cu substrate commonly used for graphene growth, CH₄ induces the lateral epitaxy growth of WSe₂, increasing its grain size while suppressing its vertical growth or deposition. During the synthesis of WSe₂, methyl radicals and hydrogen are produced by thermal decomposition of CH₄ at the precursor hot zone (1050 °C) [28]. Methyl radicals can react with oxygen atoms on the SiO₂ surface to form O-CH₃, reducing the nucleation site of WSe₂. In addition, carbon-related radicals can react with the unstable W vapor to form metastable metallo-organic compounds, which may induce growth of low-defect WSe₂ crystals. Hydrogen is also known to induce the growth of low-defect WSe₂ crystals while suppressing vertical growth into bilayers and multilayers by etching defective WSe₂ [29–31]. Figure 1c,d show that while randomly distributed triangular WSe₂ crystals were grown,
the size, density, and thickness uniformity of the grown crystal domains varied significantly with or without CH₄ promoters. When WSe₂ was grown without CH₄ gas, grain size of the obtained domains was less than 1 µm and there were many multilayer regions (Figure 1c). However, when CH₄ gas was used as a promoter, WSe₂ existed mostly as a monolayer with a grain size of more than 10 µm (Figure 1d). These results clearly show that CH₄ gas acts as a promoter for the growth of WSe₂ crystals.

![Figure 1](image-url)  
**Figure 1.** The schematic illustration of methane-mediated WSe₂ synthesis. (a) Sketch of homemade tube-type chemical vapor deposition (CVD) setup. (b) Schematic image of WSe₂ crystal growth by vapor-solid transport mechanism and its growth morphology difference between (c) without and (d) with methane (CH₄) gas.

As various parameters affect the CVD growth of TMDs, substrate size, carrier gas velocity, weights of precursor powders, growth time, and characterization regions were set as constant [8,10,13,18,19,22,26]. Based on this, Figure 2a–d show SEM images of WSe₂ according to the CH₄ gas ratio. Figure 2a and Figure S1 show that the WSe₂ grain size is less than 1 µm when only Ar gas is used as the carrier gas. Figure 2a and Figure S1 also show some parts of the multilayer WSe₂ regions (dark-colored) with a nucleation density of 1.6 × 10⁵ mm⁻². By increasing the CH₄ gas to 50 sccm, the average grain size of WSe₂ was increased to ~6 µm with a triangular shape and a nucleation density of 5.5 × 10⁴ mm⁻² (Figure 2b and Figure S2). As the flow of CH₄ gas was increased to 100 sccm, the synthesized monolayer WSe₂ showed an average grain size of 9 µm with a nucleation density of 6.8 × 10^4 mm⁻² (Figure 2c and Figure S3). Figure 2d and Figure S3 show that the domain size of a single crystal monolayer of WSe₂ increased up to 80 µm when flowing 150 sccm of diluted CH₄ gas. In this case, the average grain size was 52 µm with a wide distribution due to a lower nucleation density of 156 mm⁻². From a statistical analysis of domain images in Figures S1–S4, grain size and nucleation density of WSe₂ were obtained as a function of the CH₄ gas ratio (Figure 2e and Figure S5). Generally, increasing the CH₄ gas ratio yielded a lower nucleation density of monolayer WSe₂ with a larger grain size. The catalytic effect of CH₄ on the synthesis of large-grain monolayer WSe₂ was similar to the catalytic growth of other 2D materials (graphene, h-BN, MoS₂, WSe₂, etc.) [11,15,32–36].
We also investigated the effects of the CH4 promoter on the morphological and optical properties of synthesized WSe2 via the nondestructive analysis tools of Raman spectroscopy and PL. Figure 3a,b show the typical Raman mapping (at center wavelength: ~252 cm\(^{-1}\)) obtained with and without the CH4 promoter, respectively. When CH4 was used as a carrier gas, the grain size was about 80 \(\mu\)m with a uniform and strong intensity of E\(^{1}\)\(_{2g}\) peak over the synthesized WSe2 crystals (Figure 3a). This result is consistent with the SEM results in Figure 2d. On the other hand, when only Ar was used as the carrier gas, the intensities of the measured E\(^{1}\)\(_{2g}\) peaks were much lower and nonuniform (Figure 3b). Figure 3c shows the differences in the typical Raman spectra of WSe2 crystals grown with and without a CH4 promoter. In the case of CH4-assisted growth, Raman peaks corresponding to E\(^{1}\)\(_{2g}\) and A\(_{1g}\) modes of single-layered WSe2 were observed (Figure S6). When only Ar gas was used, a relatively low E\(^{1}\)\(_{2g}\) peak and an additional small peak at 307 cm\(^{-1}\) (corresponding to B\(^{1}\)\(_{2g}\) resonance mode of WSe2) were observed. In general, the B\(^{1}\)\(_{2g}\) peak is only active on the bilayer or multilayer of WSe2 [5,37]. We also noted that carbon-related Raman signals such as D peak (~1350 cm\(^{-1}\)), G peak (~1600 cm\(^{-1}\)), or 2D peak (~2700 cm\(^{-1}\)) were not observed. These results indicate that CH4 acted only as a promoter during WSe2 synthesis and did not leave other carbon-related residues. We noted that the WSe2 growth temperature (700–750 °C) was too low to form a carbon layer by the reaction of methane on the surface of the SiO2/Si substrate [38]. The optical properties of the synthesized WSe2 and the effect of the CH4 promoter were further investigated using micro-PL with a 532 nm laser.

**Figure 2.** Size control of the WSe2 domain by tuning the methane carrier gas ratio. Typical SEM images of WSe2 grains synthesized on a SiO2/Si substrate with a flow of (a) CH4:Ar = 0:200, (b) CH4:Ar = 50:150, (c) CH4:Ar = 100:100, and (d) CH4:Ar = 150:50 sccm. (e) Edge length (black) and nucleation density (blue) of WSe2 domains as a function of the CH4 gas ratio. The error bars represent the edge length variations of WSe2 domains obtained at the same CH4 gas flow.
Figure 3. Raman and photoluminescence (PL) investigation of the synthesized WSe$_2$ according to the catalytic effects of methane. Raman mapping results of (a) CH$_4$:Ar = 150:50 sccm, (b) Ar gas only as carrier gas, and (c) representative Raman spectrum of each mapping result. PL mapping results of (d) CH$_4$:Ar = 150:50 sccm, (e) Ar gas only as carrier gas, and (f) representative PL spectrum of each mapping result. Raman and PL results were obtained from a micro-Raman instrument with a wavelength of 532 nm laser. Inset is an OM image corresponding to each mapping region.

Figure 3d shows the PL mapping of WSe$_2$ synthesized using a CH$_4$ promoter (CH$_4$:Ar = 150:50). The synthesized WSe$_2$ grain exhibited a uniform PL intensity at the 760 nm wavelength, which is equivalent to the PL value measured with exfoliated and synthesized single-crystal monolayer WSe$_2$ [5,37,39]. On the other hand, when only Ar (200 sccm) was used as a carrier gas, the PL of synthesized WSe$_2$ had a low intensity and showed a wide distribution due to the formation of bilayers and multilayers of WSe$_2$, as shown in Figure 3e. The synthesis effects of CH$_4$ gas were demonstrated from the representative PL spectrum of each PL mapping shown in Figure 3f. Based on these optical property data, it was confirmed that when using CH$_4$ as a promoter in the WSe$_2$ growth process, large WSe$_2$ grains with uniform monolayers can be synthesized.

As shown in the topology images obtained through tapping mode AFM, the thickness of the synthesized WSe$_2$ is uniform to ~0.7 nm, corresponding to the thickness of the monolayer (Figure 4a) [40,41]. A KPFM image of the monolayer WSe$_2$ showed a reduction in surface potential of ~300 meV in WSe$_2$ due to the electrostatic screening effect and charge distribution of WSe$_2$ (Figure 4b) [42]. The work function of the Pt-coated tip was ~4.3 eV, which was obtained by measuring the surface potential of highly oriented pyrolytic graphite (HOPG) (Figure S7). Since the work function of the SiO$_2$/Si substrate was 4.6 eV, the work function of the synthesized WSe$_2$ was estimated to be ~4.3 eV. This value is equivalent to the work function value of the exfoliated monolayer WSe$_2$ [43]. Figure 4c,d show the XPS results of the synthesized monolayer WSe$_2$ with four W$^{4+}$f$_{7/2}$ peaks (W$^{4+}$f$_{7/2}$: 32.8 eV, W$^{4+}$f$_{5/2}$: 34.8 eV, W$^{6+}$f$_{7/2}$: 36 eV, and W$^{6+}$f$_{5/2}$: 38.2 eV) and two Se-3D peaks (Se 3d$_{5/2}$: 55.1 eV and 3d$_{3/2}$: 55.9 eV). The two W$^{4+}$f peaks correspond to the binding energy of W bonded to Se atoms, while the two Se-3d peaks point to the binding energy of Se bonded to W atoms. The two W$^{6+}$f peaks correspond to the binding energy of the W atoms bonded to the O atoms, resulting from the exposure of the synthesized WSe$_2$ to air during the XPS analysis. Additionally, there was no W-4f peak at 32 eV and 34 eV, which represent the 1T phase; therefore, it can be confirmed at the WSe$_2$ of the 2H phase. These results are consistent with previous reports on WSe$_2$ [12,44].
Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/9/11/1642/s1: Figures S1–S4—The SEM results at each synthesis condition for statistical analysis, Figure S5—Raman spectrum of synthesized monolayer WSe$_2$, Figure S6—Surface potential mapping image of WSe$_2$ by Kelvin probe force microscopy (KPFM), Figure S7—The work function of Pt-coated AFM tip and reference HOPG, and Figure S8—XPS wide-range spectra of synthesized WSe$_2$.

Author Contributions: H.-S.J. and J.-Y.L. contributed equally to this work. H.-S.J. and S.-G.K. synthesized the samples. J.-Y.L. and S.-K.S. analyzed and performed the scanning electron microscopy, aAFM, KPFM, and XPS. H.-S.J. and S.-H.H. measured the optical properties (Raman and PL). J.-H.L. and D.W. guided the project and analyzed the results. H.-S.J., J.-Y.L., S.S., J.-H.L., and D.W. wrote the paper. All authors participated in reviewing the manuscript. All authors approved the final version of the manuscript.

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