Scalable low-temperature synthesis of two-dimensional materials beyond graphene

Azimkhan Kozhakhmetov\textsuperscript{1,4}, Riccardo Torsi\textsuperscript{1,4}, Cindy Y Chen\textsuperscript{1,4} and Joshua A Robinson\textsuperscript{1,2,3}\textsuperscript{a}

\textsuperscript{1}Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States of America
\textsuperscript{2}Two-Dimensional Crystal Consortium, The Pennsylvania State University, University Park, PA 16802, United States of America
\textsuperscript{3}Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA 16802, United States of America
\textsuperscript{4}A.K., R.T. and C.Y.C. contributed equally.

E-mail: jrobinson@psu.edu

Keywords: 2D materials, transition metal dichalcogenides, low temperature synthesis, CVD, MBE, ALD, solution-based synthesis

Abstract

Two dimensional (2D) materials are of interest for a wide range of applications, including low-power electronics, catalysis, optoelectronics, and quantum information. Scalable synthesis is the foundation of a 'Lab-to-Fab' transition, where significant advances in material scalability over the last few years is made possible via common industrially adopted thin film deposition techniques. To date, elevated temperatures and crystalline substrates are the major enablers of electronic-grade 2D materials, but these parameters may not always meet state-of-the-art manufacturing requirements due to the high thermal budget and necessity to transfer the 2D films to secondary substrates. Hence, large-scale, high-quality low-temperature (<500 °C) synthesis methods are being pursued by a variety of research groups. This review highlights low-temperature synthesis and properties of 2D materials beyond graphene such as transition metal dichalcogenides, with emphasis on correlating large-scale vapor, liquid, and solid source growth methods with structural, morphological, compositional, and transport properties. In addition to reviewing traditional thin-film synthesis techniques, we discuss solution-based processes compatible with spin or spray coating, summarize typical techniques for evaluating material quality, and present grand challenges faced at this kinetically limited growth regime.

1. Introduction

The absence of band gap in graphene initiated the pursuit of other two-dimensional (2D) materials for a variety of next-generation technologies\cite{1–3}. 2D transition metal dichalcogenides (TMDCs) have emerged as a core topic of interest in the semiconductor community and include a wide range of properties: from metals (NbS\textsubscript{2}, TaS\textsubscript{2}) to semiconductors (MoS\textsubscript{2}, WSe\textsubscript{2}) to superconductors (NbSe\textsubscript{2}, TaSe\textsubscript{2})\cite{4–7}. Pioneering studies on fundamental properties of 2D TMDCs utilized mechanical exfoliation via adhesive tapes, where weak interlayer van-der Waals forces enable the peeling of individual molecular layers from bulk crystals grown by chemical vapor transport. As a result, numerous ‘proof of concept’ devices with great potential are demonstrated and since then large-scale manufacturing has been actively explored to take the next step towards batch production\cite{8–14}. Scalable synthesis of 2D TMDCs will be a global key technological driver to revolutionize our materials world across various industries from digital electronics, photovoltaics, and batteries\cite{15–19}.

Metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD) have enabled significant progress in the large-scale synthesis of TMDCs (e.g. MoS\textsubscript{2}, WS\textsubscript{2}, and WSe\textsubscript{2}), on various substrates\cite{20–22}. The progress primarily lies in the utilization of elevated growth temperatures (>700 °C) or high-temperature post-growth annealing and crystalline substrates\cite{14, 21}. However, many applications of 2D TMDCs preclude the use of a high thermal budget and
Figure 1. Successful realization of scalable, application-grade, low temperature 2D TMDCs will enable to potentially integrate them in the following targeted areas: flexible electronics, catalysis. Reprinted with permission from [45]. Copyright (2016) American Chemical Society. Batteries (adapted from [30]), heterostructures, sensors, and Si CMOS circuitry (adapted from [26]).

single-crystal substrates. For example, relentless scaling of transistors in silicon CMOS chips has faced insurmountable challenges and various interdisciplinary efforts are dedicated to investigating novel device architectures to comply with Moore’s law [23, 24]. The integration of 2D TMDCs with Si CMOS technology at the back-end-of-line (BEOL) is considered an alternative strategy to increase the multifunctionality and performance of the circuit (figure 1) where wafer-scale synthesis at temperatures < 500 °C will be a first major step towards realization [25, 26]. Moreover, flexible electronics may benefit from the development of the large-scale low-temperature synthesis of 2D crystals [27]. Conventionally, organic, amorphous thin-film transistors (TFTs) are used for flexible electronics but exhibit low carrier mobilities. In contrast, semiconducting 2D TMDCs exhibit orders of magnitude higher mobility values and can enable the launch of a new era of integrated flexible nanoelectronics based on 2D TFTs [28]. Since 2D thin films must be deposited on soft and foldable polymer substrates where the glass transition temperature of the polymer must be taken to account, the role of scalable low-temperature synthesis processes becomes significant.

The broad spectrum and intrinsic high absorption efficiencies of 2D TMDCs make them ideal candidates as active layers for ultrathin photovoltaic devices [31, 32]. Traditional photovoltaic materials become fragile when thinned below < 10 nm where surface effects start to dominate resulting in the increased rate of nonradiative recombination losses, ultimately lowering the efficiency [33, 34]. Beyond individual layers, 2D heterostructures constructed by stacking disparate 2D crystals on top of each other can yield highly efficient, ultrathin photovoltaics [32]. Such heterostructures must maintain large-scale uniformity, with pristine interfaces, during all processing steps to maximize the performance of the devices [35, 36]. However, the current-state-of-the-art 2D TMDC devices utilize mechanically exfoliated flakes, not directly grown heterostructures, that are typically < 100 μm [2, 31, 37]. Moreover, the majority of synthetic heterostructures are grown via powder-based (solid source) CVD synthesis techniques that utilize elevated growth temperatures (> 600 °C), are not well reproduced from lab-to-lab, and often do not yield uniform, coalesced films [38–41]. Therefore, significant efforts remain to realize a truly scalable process that can produce uniform heterostructures at the wafer (or bucket in the case of solution-based processes) scale.

Beyond optoelectronics, the high surface to volume ratio and ability to controllably functionalize the surface of 2D basal planes expand the horizon of possible applications to sensor, catalyst, and battery technologies [42–44]. Current industry benchmarks either suffer from high cost of materials (Pt, Ir for hydrogen evolution reaction catalysts) or have limited operational windows (selectivity, environmental stability) and cycle lifetime [45, 46]. Industrial-scale, low-cost, environmentally stable devices based on 2D materials can be realized if scalable manufacturability of high-quality starting materials is achieved. Since production lines vary across different technologies, aforementioned low-temperature thin-film deposition
techniques (MOCVD, MBE, ALD) are less likely to be utilized in catalysis and battery technologies. Therefore, alternative low-temperature roll-to-roll and solution-based synthesis of 2D crystals must be developed and are briefly reviewed here.

In this review article, we highlight the most common scalable, low-temperature growth methods based on MOCVD, ALD, MBE, and solution-based approaches, and discuss their corresponding structural, compositional, and transport properties. Moreover, challenges are discussed, and we summarize different alternative approaches to overcome these temperature limits by introducing various growth promoters and catalysts. The purpose of the review paper is to introduce recent advances in the low-temperature synthesis of 2D materials beyond graphene and focus on their potential applications.

2. Synthesis

2.1. Vapor phase synthesis methods

Vapor phase synthesis utilizes vapor/gas-based precursors, carried by hydrogen or inert gases to the reaction chamber where they react and form a film on a substrate. Vapor phase synthesis methods are classified based on the chemistry of the precursors utilized and the mode of vapor transport; however, gas phase synthesis is summarized by: (i) evaporation and transport of precursors to growth zone (ii) decomposition of precursors and diffusion of reactants to substrate (iii) migration of reactants on substrate (iv) nucleation (v) crystal growth (vi) desorption of reactants from substrate [52]. While these steps describe a complex, dynamic environment, the ability to precisely control process parameters enables the production of epitaxial, wafer-scale 2D films. Perhaps the most impactful process parameter in vapor phase synthesis is the growth temperature. Typically, high growth temperatures yield a thermodynamically, mass-transfer-limited process, while low growth temperatures are characterized by a kinetic, surface-reaction controlled process [53]. The growth temperature also affects nucleation density and grain size. At low growth temperatures, reactant surface adsorption is significantly higher compared to high temperatures, dramatically increasing nucleation events and hindering grain size [54]. Higher adsorption at lower temperatures also impacts the relative attachment and desorption rates, which controls the film growth rate. Attachment requires adatoms to diffuse along the substrate, reach a domain edge, and incorporate into the growing grain. Attachment rate will therefore be dictated by the density of adatoms, and the ability for the adatoms to overcome the substrate diffusion energy barrier ($E_{diff}$). The latter can be represented by the Maxwell-Boltzmann relation [53]:

$$D = D_0 e^{-\frac{E_{diff}}{k_B T}}$$

where, $k_B$ is Boltzmann’s constant, $T$ is temperature, and $D_0$ is a temperature independent pre-exponential factor. Desorption, on the other hand, is governed by the adsorption energy ($E_{ad}$)—when the absolute value
of the adsorption energy is high, the desorption rate is slow. From transition state theory the desorption rate can be written as [54]:

\[ r_{\text{des}} = \nu_0 e^{\frac{E_{ad}}{kT}}, \]

where, \( \nu_0 \) is the pre-exponential factor. Since the adsorption energy is generally \( \sim 10 \times \) higher than the diffusion energy barrier and both phenomena are governed by Arrhenius relationships, and the adsorption rate far exceeds the desorption rate at lower growth temperatures [54]. The difference in the adsorption and desorption rates results in high precursor conversion rate and the growth of small fractal-shape domains typically observed in low-temperature vapor-phase synthesis [55]. Adsorption/desorption equilibrium is only approached at higher growth temperatures, where larger, triangular (in the case of TMDCs) domains grow due to increased adatom surface mobility. Additionally, at low growth temperatures the relatively low lateral growth rate and enhanced nucleation density increases the chance for nucleation on the basal plane rather than on the substrate which makes it challenging to control layer number and subsequent layer properties [48]. While most electronic-grade films are grown at high temperatures, various approaches can achieve high-quality films at low temperatures (<500 °C) (figure 2(a)). Herein, we define ‘application-grade’ materials as films that meet the performance targets for applications shown in figure 1, which may be very different from application to application. For instance, metrics such as defect density requirements can vary widely based on the application, where CMOS requires the lowest defect density possible, catalytic and sensing applications often rely on defects for high performance. In this section we review the techniques that demonstrate promise for growth of application-grade thin films of 2D TMDCs at low-temperatures: (i) powder-based chemical vapor deposition (P-CVD) (ii) metal organic CVD (MOCVD), (iii) MBE, and (iv) ALD.

2.1.1. Powder-based chemical vapor deposition (P-CVD)

P-CVD of crystalline 2D layers is generally achieved via the evaporation and subsequent reactions of powdered precursors located inside the growth chamber. Powder-based CVD is considered the simplest and most inexpensive technique to create 2D monolayers, often consisting of a horizontal, hot-wall, quartz tube furnace connected to mass flow-controlled carrier gas lines. The modesty of the set-up has made P-CVD the most common method of synthesizing large-area domains for probing fundamental phenomena in 2D TMDCs. The low vapor pressure of transition metals makes their use as powdered precursors impractical, therefore the identification of transition metal-containing compounds with appropriate vapor pressures is critical. The evaporation of transition metal oxide powders in a reducing chalcogen environment is an effective approach [56–60]. In the case of MoS₂, the simplest combination is the vaporization of S powders that reduce MoO₃ to volatile suboxide MoO₃₋ₓ, which then further reacts in the S environment to form MoS₂ [61]:

\[
\text{MoO}_3 + \frac{x}{2} S \rightarrow \text{MoO}_{3-x} + \frac{x}{2} \text{SO}_2
\]

\[
\text{MoO}_{3-x} + \frac{7-x}{2} S \rightarrow \text{MoS}_2 + \frac{3-x}{2} \text{SO}_2
\]

Nevertheless, the vapor pressure of these oxide precursor powders remains low, requiring a growth temperature > 700 °C for most P-CVD experiments (figure 2(a)) [61]. As a result, P-CVD is not typically considered a practical technique for low-temperature synthesis. This may be partially addressed by the use of molten alkali salts, which are shown to increase the lateral grain size to > 100 µm and reduce the growth temperature to 600 °C for many TMDCs [62–67]. The physical phenomena that causes this sizeable effect, which was first employed in the low-temperature production of ceramics powders [68], is still a topic of discussion. One possible explanation is that molten salts act as a catalyst on the edges of the growing TMDC grains effectively promoting lateral growth. Another prominent hypothesis is that the molten alkali salts combine with the metal oxide precursors to form volatile metal oxycarbides and/or eutectic intermediate compounds, such as Na₂MoO₃, that effectively increase the mass flux enabling growth at lower temperatures [69]. A similar effect was exploited by Gong et al [47], by mixing tellurium powder with a metal or metal-oxide precursor (MoO₃ for MoS₂ and W for WS₂ growth) to increase precursor volatility and lower the energy barrier for sulfurization. Te-assisted P-CVD growth of monolayer MoS₂ and WS₂ islands led to 50 µm domains (figure 2(c)) at 500 °C, with no apparent tellurium contamination from x-ray photoelectron
spectroscopy (XPS) analysis. The same group also achieved monolayer MoS2 on a polyimide substrate at 450 °C by using (NH4)2MoO4 powder as the Mo precursor [70]. In this process H2 was added to the carrier gas mix to facilitate the decomposition of (NH4)2MoO4 to MoO3, H2O, and NH3. The MoO3 originating from this decomposition is more kinetically active than crystalline MoO3 powder and the gas produced during the decomposition process assists in mass transport of the MoO3 for reaction with S at lower temperature. Along with optimizing precursor combinations, controlling nucleation density by seeding the growth substrate can promote lateral growth and larger grain sizes. Planar aromatic molecules are commonly used seeding promoters [71–73] that have shown enhancement of layer growth over island growth. This effect is hypothesized to originate from both an increase in surface adhesion forces and the lowering of energy barrier for nucleation in the presence of planar aromatics on the growth substrate [71]. Nevertheless, even in seed-promoted synthesis, the growth temperature is ultimately limited by the kinetics of precursors decomposition and reaction. In addition to the limitations originating from source selection, the P-CVD method does not allow for precise control over precursor evaporation. This limitation leads to inhomogeneous precursor diffusion and reaction rates affecting the nucleation density over the growth substrate. This has often led to poor layer coverage and thickness uniformity in films grown by P-CVD with the presence of a deposition plume on the growth substrate often observed [74]. Another less-discussed limitation of P-CVD is its poor reproducibility across different growth furnaces with disparate results being reported even between individual researchers in the same lab [75]. While low-temperature synthesis of TMDs via P-CVD is possible, the inability to independently and precisely control precursor concentration affects the uniformity of the growth film over large areas—likely limiting the technique to academic laboratories.

2.1.2. Metal–Organic Chemical Vapor Deposition (MOCVD)
MOCVD is achieved by precisely vaporizing organometallic compounds and transporting them to the growth chamber via a carrier gas. Unlike the case of P-CVD, MOCVD is not limited to a horizontal, hot-wall experimental set-ups, but can also be carried out in cold-wall reactors. Cold-wall reactors limit the area of thermal heating to the substrate, effectively limiting undesired gas-phase reactions of precursors before they reach the substrate. Organometallic compounds are often employed as precursors, because their vapor pressures are orders of magnitudes higher than those of their metallic constituents [76]. Furthermore, many organometallic precursors used in MOCVD process decompose below 400 °C thus enabling low-temperature synthesis. This enables precursor flux to be finely tuned by placing the organometallic compounds in temperature-regulated bubbler manifolds that precisely control carrier gas (usually H2 and N2) flow rates. Precursor purity and decomposition pathway under growth conditions must be carefully considered to yield carbon contamination-free films at the desired temperatures [76]. Metal oxycarboxyls like Mo(CO)6 [77–79] and W(CO)6 [79–81] yield MOCVD-grown epitaxial films of Mo(S,Se)2 and W(S,Se)2, respectively, with excellent layer control down to the monolayer, sharp triangular grains up to a few microns in size, and competitive transport properties at a wafer scale [82]. Generally, MOCVD grown layers are obtained at high temperatures (>800 °C), high pressures (>100 Torr), and in chalcogen-rich environments confirming kinetic Monte Carlo (kMC) and reactive force Field (ReaxFF) simulations of the vapor-phase growth process [54, 83–85]. The high-level of control, adequate precursor options, and scalability of MOCVD make it an excellent candidate for synthesis of 2D materials for applications with a limited thermal budget (figure 2(a)). Early reports of low-temperature (<500 °C) MOCVD growth, however, exhibited films with poor layer number control, and grain sizes on the order of a few nanometers [86, 87]. This undesirable morphology can be attributed to: (i) high adatom/molecule attachment rates that lead to high nucleation density and (ii) low adatom surface diffusion that results in small, irregularly shaped grains. Similar to P-CVD, alkali salts are effective at enhancing lateral growth at low-temperatures [79, 88, 89]. The expected effects of higher growth rates and larger grain sizes are observed due to the more favorable reaction pathway and enhanced adatom surface mobilities. Mun et al [89] introduced a controlled NaCl flux during the MOCVD growth of MoS2 to realize a uniform nanocrystalline film on a polyimide (PI) substrate at a growth temperature of 250 °C. The relatively high field-effect mobility and on/off ratio values of 10 cm2 V−1 s−1 and 105 respectively, demonstrate the potential for these films in flexible electronics applications. While alkali salts enhance the layer-by-layer growth mode and lead to larger grains, loss of epitaxy and high-density of particles on the film have also been observed [88]. Using a combination of time-of-flight secondary ion mass spectroscopy (ToF-SIMS) mapping and XPS, Zhang et al [88], demonstrate the presence of Na interfacial layer between the growth substrate and the TMDC film, which initially lowers the energy barrier for domain-edge bonding and effectively increases the growth rate. As the interfacial layer increases and saturates the surface, substrate adhesion becomes unfavorable, introducing a high density of multilayer particles. Furthermore, the use of alkali metals within the process precludes its
BEOL-compatibility due to the adverse impacts of alkali ions on electronic performance from the creation of charge trap states [3, 71, 75, 90, 91]. It is worth noting that degrading effects were also found to be present after layer transfer [33]. Substrate modification via seeding [92] and annealing [93] has also been employed in MOCVD synthesis to manipulate nucleation density and enable larger grains. In both these studies the objective of the substrate treatment is to reduce the nucleation density and facilitate larger grain growth.

The high-level of source flow control possible in MOCVD was demonstrated by Kalanyan et al [94], who developed a pulsed precursor injection process with bis(tert-butylinido)bis(dimethylamido)-molybdenum (N’Bu2(NMe2)2)Mo and diethyl disulfide Et2S2 as the molybdenum and sulfur source respectively. This highly regulated method yielded a polycrystalline film with excellent thickness control in the 1–25 nm range and a fast growth rate of 0.12 nm pulse−1 at a substrate temperature of 591 °C. Kang et al [79], exploited the high-source flow control possible in MOCVD by introducing incredibly small amounts of precursors (0.01 sccm for molybdenum hexacarbonyl and 0.4 sccm for diethyl sulfide) into the reaction chamber for MoS2 synthesis. This enabled the suppression of nuclei density and the synthesis of wafer-scale, monolayer MoS2 with large grain sizes and electron mobility of 30 cm² V⁻¹ s⁻¹. Nevertheless, the growth was carried out at 550 °C, again making it incompatible for BEOL processes. Very recently, moderate improvement in the electronic properties of BEOL-compatible WSe2 was achieved by carefully controlling the Se:W ratio to create large-area, polycrystalline WSe2 with domain size of ~200 nm (figure 2(d)) [48]. As a result of the optimized growth conditions, the electronic transport properties of the film displayed a 100 × improvement compared to ones grown at similar temperatures with a ON current of 4 μA µm⁻¹ and an ON/OFF ratio of 10⁶. Although MOCVD is promising for TMDC synthesis on substrates with a low thermal budget, its lower temperature limit is imposed by the decomposition of the precursors used. This issue is avoided in MBE, where small fluxes of elemental precursors are precisely directed towards the growth substrate.

2.1.3. Molecular beam epitaxy (MBE)

MBE traditionally utilizes thermal or electron-beam evaporation of solid-source precursors to synthesize epitaxial films on crystalline substrates, and differs from other synthesis techniques in three primary ways: (i) the precursors used are elemental, (ii) the precursor fluxes are several orders of magnitude lower compared to other vapor-phase synthesis methods and (iii) the growth occurs at high-vacuum (10⁻¹⁰–10⁻⁷ Torr). MBE is extensively used for growth of ultra-thin films because of the excellent control over source flux and the ability to utilize in situ characterization methods such as reflection high energy electron diffraction (RHEED). Koma et al [95–99] pioneered synthesis of layered chalcogenide films on van der Waals substrates and pseudo- van der Waals passivated 3D substrates well before the boom of the 2D-materials field. The latter reignited the interest in the MBE growth of TMDs after Koma’s initial work. However, the growth of large-area, uniform, monolayer 2D films via MBE is difficult. In a typical MBE system effusion cells are used for controlled evaporation of metals, however, the high melting temperature of transition metals such as Mo and W necessitates the use of electron-beam evaporation. The challenge in the growth of TMDs films via MBE is the result of the large difference in vapor pressure between the metal and chalcogen components. The sticking coefficient of chalcogenides (especially S) on the growth surface is very low under ultra-high vacuum conditions which results in sub-stoichiometric layers particularly at high growth temperatures which are beneficial to promote metal surface diffusion and large grain sizes. As a result, most MBE experiments are typically carried out well below 500 °C (figure 2(a)), but often suffer from poor film morphology, with small (<30 nm), non-coalesced domains in the monolayer regime. To address the low metal surface mobility, MBE growth of TMDs is generally carried out on van der Waals materials such as epitaxial graphene, highly oriented pyrolytic graphite (HOPG), and mica which all exhibit low surface migration barriers compared to traditional 3D substrates. Yue et al [100]. Utilized kMC calculations to theoretically guide experimental efforts to lower the nucleation density and enhance lateral growth of WSe2 on a variety of van der Waals substrates. Similar to MOCVD, the ultimate path was to reduce the metal flux (to 10⁻⁹ mbar) and increasing the substrate temperature (up to 550 °C) in a chalcogen-rich environment. This enabled micrometer-scale domains, significant improvement beyond previous report, but the films still suffered poor coalescence and layer control at the monolayer limit [100]. Beyond the current optimization efforts for improving surface uniformity, MBE is a flexible synthesis tool for 2D layer growth because it can provide a large variety of precursors to grow many different types of 2D layers at low temperatures. Because of this there are a number of TMDCs demonstrated by MBE including MoSe2 (figure 2(e)) [100, 101], HfSe2 [102], SnSe2 [103], WTe2 [104], HfTe2 [105], and MoTe2 [106].

2.1.4. Atomic layer deposition (ALD)

ALD enables low-temperature synthesis of atomically thin materials with angstrom-level thickness control. ALD utilizes a sequential process in which gaseous chemical precursors are alternatively pulsed for a specific
time and allowed to react directly on the substrate surface towards completion. In between each precursor pulse, inert gas purge steps are employed to remove reaction by-products and excess precursors, as a way to maintain self-limiting reactions. Furthermore, the sequential process of precursor reactions and purging steps establish one ALD cycle, which can be tuned to precisely control the film thickness. As a result, ALD offers advantages such as excellent film uniformity over a large area and high conformality over three-dimensional structures. ALD is typically conducted at temperatures below 350 °C, which is an operating range essential for electronic devices requiring BEOL-compatible conditions. The advantages of ALD enabled this technique’s widespread application for materials in microelectronics, photovoltaics, and energy storage [107].

The two common modes of ALD are thermal and plasma-enhanced ALD (PEALD). Surface reactions in thermal ALD are solely driven by thermal energy where higher deposition temperatures are required to increase the reaction rate of precursors. High thermal budget and limited reactivity of gaseous species have led to the development of PEALD where an RF-plasma source is used to generate highly-reactive radicals during the growth. The enhanced reactivity allows for the reduction of deposition temperature and thereby enables the realization of practical applications using materials synthesized through PEALD. While the reduction in temperature is beneficial, PEALD is nevertheless accompanied by limitations such as reduced conformality. For example, in trenched structures, the radical concentration decreases from top to bottom of the trench, resulting in deposition inhomogeneity [108].

ALD is also capable of synthesizing a wide range of materials, ranging from oxides, nitrides, fluorides, chalcogenides, and high-order compounds [109–111]. Of particular interest are 2D materials such as graphene, boron nitride (BN) and TMDCs that can be synthesized on a wafer-scale. ALD of MoS₂ is accomplished by sequentially reacting Mo(CO)₆ with H₂S at 120 °C–200 °C, resulting in small grains of MoS₂ layers (figure 2(f)), where a subsequent anneal at 500 °C–900 °C under a H₂S atmosphere improves crystallinity and reduces oxygen impurities [50]. Increase in domain size and coalescence of the film usually results in the reduction of the density of grain boundaries, which leads to improved structural and transport performance of the devices [112, 113]. Furthermore, ALD of MoS₂ is reported on Si, SiO₂/Si and c-plane sapphire substrates using various metal and chalcogen precursors such as Mo(CO)₆, MoCl₅, Mo(NMe₂)₄, Mo(thd)₃ (thd = 2,2,6,6-tetramethylheptane-3,5-dianato), and H₂S and (CH₃)₂S, respectively at 60 °C–480 °C [114–120]. The deposited films share similar features and are a strong function of the growth temperature. Amorphous MoS₂ are observed at < 150 °C, while nanocrystalline films with an average domain size of 50–150 nm are obtained at > 250 °C [114–120]. Moreover, polycrystalline WS₂ is obtained via PEALD using WF₆ and H₂S as metal and chalcogen sources, respectively at 300 °C [121–123], where successful integration with the current Si technology in a 300 mm pilot line was demonstrated [123]. Preliminary electrical measurements suggest WS₂ films grown via ALD are promising for future BEOL integration of 2D TMDCs—where improving carrier mobility in the 2D channel, reducing the gate leakage, and utilizing better gate dielectrics are critical aspects of achieving a 2D-based BEOL technology [123]. Other members of TMDCs family such as MoSe₂, WSe₂, WS₂, and SnS₂, have also been studied via thermal and PEALD at a temperature range of 90 °C and 390 °C where all the deposited films are nanocrystalline with an average domain size of 100 nm.

ALD operates at the lowest temperature regime among the different vapor-phase deposition techniques and faces challenges in achieving large-crystal domains without the use of a high temperature post-growth anneal that is not compatible with low-temperature synthesis restrictions. Deposited films often adopt the amorphous phase or a mixture of amorphous and nanocrystalline phases due to the reduced thermal energy during the process. Consequently, for applications in which high material crystallinity is a requirement, the extra step of post-growth anneal at high temperatures (>800 °C) poses a challenge in the implementation of ALD for manufacturing of 2D-based channel materials. However, the recent introduction of seed layers prior to PEALD of 2D TMDCs indicate the potential for realization of highly crystalline, impurity-free films with preferred orientations and an outstanding transport performance that may eliminate the need for the high temperature post-growth annealing in the future [127].

2.2. Solution-based synthesis

Solution-based synthesis methods (not to be confused with chemical exfoliation methods [128–130]) are one of the most effective low-cost approaches to create a range of nanostructures including quantum dots, nanowires, and nanosheets, and the field has progressed rapidly to achieve control over nanostructure size, thickness, shape, and composition. Unique advantages of this approach include cost-effectiveness, achievement of freestanding 2D layered nanosheets, and the simplicity in structural tunability. Despite these advantages, solution-based synthesis is particularly challenging for 2D materials because growth processes must be controlled to promote planar directionality during nanocrystal formation. The successful
development of solution-based synthesis of 2D materials can lead to material integration in applications such as energy conversion, nonvolatile memory, and optics [131–133].

The reaction schemes of solution-based synthesis can vary widely depending on the chosen technique. The most prominent solution-based methods for 2D materials are hot injection (figure 3(a)) and one-pot heat-up (figure 3(b)) methods [134]. The general reaction scheme of 2D material hot-injection synthesis begins with heating the mixture of organic solvents and capping ligands up to 300 °C–350 °C (limit determined by the solvent boiling temperature), followed by the injection of precursors into the solution matrix [135]. During the hot injection step, the formation of nuclei can be characterized by LaMer’s nucleation and growth theory, in which a sudden supersaturation of precursors from the rapid injection initiates nucleation [136, 137]. As nucleation occurs, the degree of supersaturation is reduced, shifting the mechanism from nucleation towards growth of nuclei into nanocrystals. Thermodynamics of this process favors the dissolution of smaller nanocrystals into monomers, which are then consumed by the growth of larger nanocrystals. Hot-injection of oleic acid-coordinated WCl6 and CS2 into oleylamine at 320 °C yields monodisperse, circular 1T-WS2 monolayers ~ 100 nm in diameter [138]. This protocol can be modified through the addition of hexamethyldisilazane into oleylamine prior to injection to increase the reactivity of the tungsten precursor, leading to phase tunability and stabilization of 2H-WS2 over 1T-WS2. The wide applicability of hot-injection synthesis has led to the development of other 2D materials such as MoTe2 [139] and MoS2 [132] for applications in non-volatile memory, and WSe2 [140] and SnS2 [141] for photocatalysis and Li-ion battery, respectively. Although the application of hot-injection synthesis is versatile, difficulty in achieving reproducibility and scalability limits this technique to research in laboratories. In particular, the injection time can vary when not automated, causing differences in the initial reaction kinetics from researcher-to-researcher. Additionally, there exists an inherent mixing time to achieve homogeneity in both the precursor concentration and temperature upon injection, making the upscaling of this technique more challenging.

Alternatively, the heat-up synthesis approach can be utilized to circumvent the aforementioned drawbacks of hot-injection synthesis. In heat-up synthesis, the organic solvents, ligands, and precursors are first mixed at low temperature, then heated to break down the precursors into monomers and subsequently induce the nucleation and growth processes [142]. Compared to hot-injection, heat-up synthesis has a longer nucleation temporal window due to its progressive heating process. Since there is no injection of precursors, the reaction temperature can be maintained once the growth temperature is reached, reducing the degree of irreproducibility caused by temperature fluctuations. 2D materials such as MoSe2 [51], MoS2 [143], WS2 [143], and ZrS2 [144] were successfully synthesized via heat-up synthesis. In general, multilayered nanosheets are the most stable forms in the solution synthesis of 2D materials. Capping ligands with different binding energies to the edge facets of 2D materials can be used to control the layer thickness and to
achieve freestanding single-layer nanosheets. In the heat-up synthesis of WSe$_2$ nanosheets [51], W(CO)$_6$ and diphenyl diselenide (Ph$_2$Se$_2$) are reacted with an excess amount of oleylamine at 330 °C, resulting in 4 to 8 layered nanosheets with a lateral size of $\sim$ 50 nm. By changing the capping ligands from oleylamine to oleic acid, 1 to 2 monolayer nanosheets are formed and the domain size increases to $\sim$ 200 nm (figure 2(g)). Due to a lower binding energy to edge facets, weaker binding ligands such as oleic acid yield better control over lateral growth and promotes single-layer nanosheets, resulting in film quality comparable to that of vapor phase synthesis methods. This study highlights an important characteristic of solution-based synthesis: the type and concentration of capping ligands in solution can drastically affect the size and layer thickness of the nanosheets. Although ligands help stabilize nanosheets in solution and prevent agglomeration, they are difficult to remove and can hinder electronic transport, limiting the solution-phase material's applications in catalysis and electronics. Thus, research efforts towards effective ligand stripping methods must be considered to improve the electronic properties of these solution-phase 2D materials.

2.3. Other methods
An alternative, simple, and scalable method to produce high-quality TMDCs is a process known as ball milling. In ball milling, a consecutive collision of stainless-steel balls generates high pressures that enable the grinding of a large quantity of bulk material into powders. The technique is highly employed across various industries (ceramic, mining, steel and etc.) where the milling usually takes place at room temperatures [145]. Recently, Ambrosi et al [146], reported ball milling of bulk crystals of MoS$_2$ with lateral dimensions 10–20 µm into sub-micrometer fine powders where significant enhancement of electrochemical and catalytic performance is observed. Furthermore, M. Cantarella et al [147], demonstrate improved water contaminant absorption properties of ball-milled natural bulk MoS$_2$ crystals which can be valuable for wastewater treatment applications. In both cases, the specific surface area of the powder increases up to an additional 42% as a function of milling. Larger specific surface area leads to the increased density of active edges which are essential for the aforementioned applications [146, 147]. Moreover, a promising successor of ball milling has emerged lately in the 2D community reported by C. Han et al [148], where a new hybrid room-temperature method consists of a cycle of salt-assisted ball milling and sonication-assisted solvent exfoliation of bulk MoS$_2$ and WS$_2$ (figures 4(a)–(c)). The process yield exceeds 20% and exhibits great reproducibility indicating a very promising route towards mass production. As a direct result of a process, ball milling faces several challenges such as undesired impurity incorporation and oxidation 2D TMDCs which turns out to be very crucial in obtaining defect-free TMDCs. However, advances in hybrid ball milling processes might lead to defect reduction and scalable production. Demonstrated processes may be considered as a scalable approach towards high-quality, large-scale films where the obtained materials are limited to certain applications such as catalysis, electrochemistry, and sensors.

Electron beam irradiation is recently emerged as another approach for producing 2D materials. M. S. M. Saifullah et al [149], simultaneously use Mo$_4$S$_8$(C$_4$H$_7$OCS)$_6$ as a single source precursor and as a resist for e-beam lithography where it is prepared by self-assembly method using Mo(CO)$_6$, dialkylxanthogen disulfides and immersion in aromatic hydrocarbon solutions. Room-temperature, dose-dependent e-beam exposure of the precursor/resist displays formation of MoS$_2$ films where the grain size is increased as the e-beam dose increased from 25.2 mC cm$^{-2}$ to 240 mC cm$^{-2}$ [149]. This room-temperature method of forming 2D-TMDCs is promising, and continued advancements in increasing lateral growth of the grains and reducing e-beam exposure times may enable its potential application for scalable production of 2D TMDCs in predefined channel areas.

3. Characterization
While the graphene community has widely accepted Raman spectroscopy as the characterization method of choice to determine material quality through parameters such as the I$_D$/I$_G$ ratio [150–152], the TMDC
community lacks a unified and standard method to determine the quality of the nanosheets. As a result, TMDC-focused reports often have a combination of Raman, photoluminescence (PL), XPS, transmission electron microscopy (TEM), and scanning tunneling microscopy (STM). This makes comparison of film quality and properties across different reports difficult, regardless of synthesis temperature. It is well known that the quality of TMDCs grown by vapor phase synthesis techniques or solution-based synthesis methods is generally not comparable to that of exfoliated flakes and having a complete understanding of the materials properties is necessary prior to device integration [153]. Raman spectroscopy is a well-researched method for the characterization of TMDCs since it is a non-destructive method with no sample preparation necessary and relatively short acquisition times. The information that can be acquired from carefully acquired spectra is rich. Raman has been used for layer number determination [154], quantification of lattice disorder [155], concentration of chalcogen vacancies [156], or layer strain estimation [157]. Photoluminescence is also ubiquitous in the TMDCs field as it can be more sensitive than Raman spectroscopy to factors such as layer number [158], defect concentration [159], and doping [160], where PL peak width is often cited in literature as a measure of overall sample quality [79, 161, 162]. Figures 5(a) and (b) shows the Raman and PL spectra of 2D WSe$_2$ synthesized via different methods and on various regions of the same sample. The data elucidates that while the Raman data only slightly shifts across the various synthesis techniques with the defect-activated LA(M) mode evolving the most, the room-temperature PL response from the different samples is remarkably disparate [153]. This highlights PL as a more sensitive method for probing changes in 2D TMDCs properties; however, film-substrate interaction can have a large impact on PL intensity [163], therefore comparison between films grown via different methods and on dissimilar substrates remains challenging. While most reports utilize room-temperature PL to evaluate layer quality [164], low temperature PL is a more quantitative method for monitoring defect concentration because it eliminated phonon-stimulated optical excitations, and allows for the defect related PL peak to be resolved along with the exciton and trion emission [165, 166]. XPS is another characterization technique often featured in TMDCs literature since it offers direct evidence of nearest neighbor chemical environment. This allows researchers
employing XPS to investigate sample stoichiometry, as well as dopant and impurity concentration [75]. It is non-trivial, however, to make quantitative claims of sample chemistry with XPS since often reference samples are required for accurate peak fitting, and detection limits for impurities are > 0.5% [75]. Figure 5(c) illustrates Mo 3d core level spectra from P-CVD MoS\(_2\) grown under different sulfur concentrations showing peaks originating from intrinsic MoS\(_2\) (i-MoS\(_2\)), defective MoS\(_2\) (d-MoS\(_2\)), and MoO\(_3\) [167]. The contribution from defective/substoichiometric MoS\(_2\) increases as the sulfur concentration during synthesis decreases. AFM and SEM are both ubiquitous techniques in the TMDCs field to examine film morphology with the first being particularly useful for layer number determination and the second one being effective for viewing large sample areas. While visualization of grain boundaries is challenging especially in coalesced polycrystalline films, several methods have been employed that take advantage in their highest chemical reactivity to image them via both AFM and SEM (figure 5(d)) [168–170]. Imaging grain boundaries and measuring grain size is critical for predicting transport properties of TMDC films. As discussed in the sections above a limitation of low-temperature TMDCs synthesis is the small grain sizes which will reduce carrier mobility due to defect scattering [171]. In addition to the standard characterization methods mentioned above, advanced techniques such as TEM and STM can be helpful for comparing materials grown by different processes as they provide direct evidence of crystal structure, point defects, and grain boundaries. Kozhakhmetov et al [48]. for example, imaged BEOL-compatible MOCVD-grown WSe\(_2\) with high-resolution, high-angle, annular, dark field scanning transmission electron microscopy (HAADF-STEM) to show that, even at low growth temperatures, a high number of point defects form with chalcogen vacancies as the dominating defect type. In the same report, STM of a WSe\(_2\)/epitaxial graphene heterostructure demonstrated epitaxy is possible with low-temperature MOCVD synthesis.

4. Conclusion and outlook

This review highlights the recent advances in low-temperature growth of 2D materials beyond graphene, with an emphasis on thin-film deposition techniques. The field continues to progress, and wafer-scale, application-grade materials are constantly improving through the introduction of growth promoters and surfactants to overcome the large kinetic barrier at these temperature regimes. Looking forward, further process development of industrial thin-film synthesis techniques (MOCVD, MBE, ALD) are needed to realize manufacturable, electronic grade materials for flexible electronics and potential integration with Si technology at the BEOL level. Specifically, more efforts must be directed towards wafer-scale crystal growth with precise thickness control and low defect densities. Self-limiting growth of 2D crystal would be an ideal solution in which monolayer, individual domains grow and coalesce into the film without allowing to secondary nucleation happen. The density of bilayer nucleation is directly correlated to the defect densities in the monolayer, growth temperature, pressure, and substrate surface properties. However, self-limiting growth is still quite challenging and other alternative approaches must be pursued. For example, molecular hydrogen gas in MOCVD tends to etch TMDCs during the growth. Since edges of the bilayer domains are more reactive and more exposed to the hydrogen, it will be removed faster compare to the underlying monolayer film. Hence, in-situ selective area etch can be considered as a potential engineering move to control the thickness. Furthermore, monolayer films with reduced defect densities must be developed to preclude the bilayer nucleation by balancing the sticking coefficients and desorption rates of metal and chalcogen atoms during the dynamic growth processes. Also, achieving 100% alignment of individual domains with respect to the substrate will promote coalesced films without anti-phase boundary that serve as nucleation sites for bilayer domains. Last but not least, similar optimizations on room temperature processes such as ball milling and hybrid-balling will enable the design of practical devices for sensors and catalysis by improving the precise control over dimensions of fine powders and minimizing the undesired impurity incorporation.

Acknowledgments

The authors acknowledge funding from Intel through the Semiconductor Research Corporation Task 2746; NEWLIMITS, a center in nCORE as part of the Semiconductor Research Corporation (SRC) program sponsored by NIST through award number 70NANB17H041; and the Penn State 2D Crystal Consortium (2DCC)-Materials Innovation Platform (2DCC-MIP) under NSF cooperative agreement DMR-1539916.

ORCID iDs

Azimkhan Kozhakhmetov  https://orcid.org/0000-0003-4743-8408
Cindy Y Chen  https://orcid.org/0000-0003-1073-4852
Joshua A Robinson  https://orcid.org/0000-0002-1513-7187
[126] Browning R, Kuperman N, Solanki R, Kanzyubba V and Rouvimov S 2016 Large area growth of layered WS\(_2\) films Semicond. Sci. Technol. 31 1–4

[127] Pyeon J et al 2020 Wafer-scale, conformal, and low-temperature synthesis of layered tin disulfides for emerging nonplanar and flexible electronics ACS Appl. Mater. Interfaces 12 2679–86

[128] Voiry D et al 2013 Enhanced catalytic activity in strained chemically exfoliated WS\(_2\) nanosheets for hydrogen evolution Nat. Mater. 12 850–5

[129] Lin H, Wang J, Luo Q, Peng H, Luo C, Qi R, Huang R, Travas-Sejdic J and Duan C G 2017 Rapid and highly efficient chemical exfoliation of layered MoS\(_2\) and WS\(_2\) J. Alloys Compd. 699 222–9

[130] Desai J A, Adhikari N and Kaul A B 2019 Chemical exfoliation efficacy of semiconducting WS\(_2\) and its use in an additively manufactured heterostructure graphene-WS\(_2\)-graphene photodiode RSC Adv. 9 25803–16

[131] Sokolikova M S, Sherrell P C, Palczynski P, Bemmer V L and Mattevi C 2019 Direct solution-phase synthesis of 1T’ WSe\(_2\) nanosheets Nat. Commun. 10 1–8

[132] Son D et al 2016 Colloidal synthesis of uniform-sized molybdenum disulfide nanosheets for wafer-scale flexible nonvolatile memory Adv. Mater. 28 9326–32

[133] Sun Y, Fujisawa K, Lin Z, Lei Y, Monscheim J S, Terrones M and Schaak R E 2017 Low-temperature solution synthesis of transition metal dichalcogenide alloys with tunable optical properties J. Am. Chem. Soc. 139 11096–105

[134] Han J H, Kwak M, Kim Y and Cheon J 2018 Recent advances in the solution-based preparation of two-dimensional layered transition metal chalcogenide nanomaterials Chem. Rev. 118 6151–88

[135] Tedstone A A, Lewis D J and O’Brian P 2016 Synthesis, properties, and applications of transition metal dichalcogenides Chem. Mater. 28 1965–74

[136] Murray C B, Kagan C R and Bawendi M G 2000 Synthesis and characterization of monodisperse nanocrystals and closed-packed nanocrystal assemblies Annu. Rev. Mater. Sci. 30 545–610

[137] LaMer V K and Dinegar R H 1950 Theory, production and mechanism of formation of monodispersed hydrosols J. Am. Chem. Soc. 72 4847–54

[138] Mahler B, Hoepfner V, Liao K and Ozin G A 2014 Colloidal synthesis of 1T-WS\(_2\) and 2H-WS\(_2\) nanosheets: applications for photocatalytic hydrogen evolution J. Am. Chem. Soc. 136 14121–7

[139] Sun Y et al 2016 Layered compounds low-temperature solution synthesis of few-layer 1T’-MoTe\(_2\) nanostructures exhibiting lattice mismatch Angew. Chemie Int. Ed. 55 2830–4

[140] Zhang B-Q, Chen J-S, Niu H-L, Mao C-J and Song J-M 2018 Synthesis of ultrathin WSe\(_2\) nanosheets and their high-performance catalysis for conversion of ammonia to imines Nanoscale 10 20266–71

[141] Huang P-C, Wang H-I, Brahma S, Wang S-C and Huang J-L 2017 Synthesis and characteristics of layered SnS\(_2\) nanosheets via hot injection method J. Cryst. Growth 468 162–9

[142] van Embden J, Chesman A S R and Jassienk J 2015 The heat-up synthesis of colloidal nanocrystals Chem. Mater. 27 2246–85

[143] Alkavilla C, Sarno M, Ciambelli P and Novel W A 2011 Chemistry approach for the synthesis of hybrid 2D free-floating single or multilayer nanosheets of MoS\(_2\)-oleylamine (M=Mo, W) Chem. Mater. 23 3879–85

[144] Yoo D, Kim M, Jeong S, Han J and Cheon J 2014 Chemical synthetic strategy for single-layer transition-metal chalcogenides J. Am. Chem. Soc. 136 14670–3

[145] Bai Y, Zhang J, Wang Y, Cao Z, An L, Zhang B, Yu Y, Zhang J and Wang C 2019 Ball Milling of hexagonal boron nitride microflakes in ammonia fluoride solution gives fluorinated nanosheets that serve as effective water-dispersible lubricant additives ACS Appl. Nano Mater. 2 3187–95

[146] Ambrosi A, Chia X, Sofer Z and Pumera M 2015 Enhancement of electrochemical and catalytic properties of MoS\(_2\) through ball-milling Electroc. Commun. 54 36–40

[147] Cantarella M et al 2019 Mechanical milling: a sustainable route to induce structural transformations in MoS\(_2\) for applications in the treatment of contaminated water Sci. Rep. 9 1–14

[148] Han C, Zhang Y, Gao P, Chen S, Liu X, Mi Y, Zhang J, Ma Y, Jiang W and Chang J 2017 High-yield production of MoS\(_2\) and WS\(_2\) quantum sheets from their bulk materials Nano Lett. 17 7767–72

[149] Saifullah M S M et al 2020 Room-temperature patterning of nanoscale MoS\(_2\) under an electron beam ACS Appl. Mater. Interfaces 12 16762–81

[150] Ferrari A and Robertson J 2000 Interpretation of Raman spectra of disordered and amorphous carbon Phys. Rev. B 61 14093–107

[151] Malard L M, Pimenta M A, Dresselhaus G and Dresselhaus M S 2009 Raman spectroscopy in graphene Phys. Rev. B 73 51–87

[152] Dresselhaus M S, Jorio A, Hofmann M, Dresselhaus G and Saito R 2010 Perspectives on carbon nanotubes and graphene Raman spectroscopy Nano Lett. 10 751–8

[153] McCreary A et al 2016 Distinct photoluminescence and Raman spectroscopy signatures for identifying highly crystalline WS\(_2\) monolayers produced by different growth methods J. Mater. Res. 31 931–44

[154] Li H, Zhang Q, Yap C C R, Tay B K, Edwin T H T, Olivier A and Ballareght D 2012 From bulk to monolayer MoS\(_2\): evolution of Raman scattering Adv. Funct. Mater. 22 1385–90

[155] Migone S, Pollard A J, Bonini N, Brennan B, Gilmore I S, Pimenta M A, Richards D and Roy D 2015 Effect of disorder on Raman scattering of single-layer MoS\(_2\) Phys. Rev. B 91 1–7

[156] Parkin M W, Balan A, Liang L, Das P M, Lamparski M, Naylor C H, Rodriguez-Manzo J A, Johnson A T C, Muenzer V and Dandrid M 2016 Raman shifts in electron-irradiated monolayer MoS\(_2\); ACS Nano 10 4134–42

[157] Wang Y, Cong C, Qiu C and Yu T 2013 Raman spectroscopy study of lattice vibration and crystallographic orientation of monolayer MoS\(_2\); under uniaxial strain Small 9 2857–61

[158] Tongay S et al 2014 Monolayer behaviour in bulk ReS\(_2\) due to electronic and vibrational decoupling Nat. Commun. 5 1–6

[159] Wu Z, Zhao W, Jiang Z, Zheng T, You Y, Lu J and Ni Z 2017 Defect activated photoluminescence in WS\(_2\); monolayer J. Phys. Chem. C 121 12294–9

[160] Zhang K et al 2018 Tuning the electronic and photonic properties of monolayer MoS\(_2\) via in situ rhenum substitutional doping Adv. Funct. Mater. 28 1–7

[161] Mouri S, Miyauchii Y and Matsuda K 2013 Tunable photoluminescence of monolayer MoS\(_2\) via chemical doping Nano Lett. 13 5944–8

[162] Sercombe D, Schwarz S, Pozo-Zamudio O D, Liu F, Robinson B J, Chekhovich E A, Tartakovskii I I, Kolosov O and Tartakovskii A I 2013 Optical investigation of the natural electron doping in thin MoS\(_2\); films deposited on dielectric substrates Sci. Rep. 3 1–6
[163] Wurstbauer U, Miller B, Parzinger E and Holleitner A W 2017 Light-matter interaction in transition metal dichalcogenides and their heterostructures J. Phys. D: Appl. Phys. 50 1–19

[164] McCreary K M, Hanbicki A T, Sivaram S V and Jonker B T 2018 A- and B-exciton photoluminescence intensity ratio as a measure of sample quality for transition metal dichalcogenide monolayers APL Mater. 6 1–9

[165] Tongay S et al 2013 Defects activated photoluminescence in two-dimensional semiconductors: interplay between bound, charged, and free excitons Sci. Rep. 3 1–6

[166] Wu Z. et al 2016 Defects as a factor limiting carrier mobility in WSe2: a spectroscopic investigation Nano Res. 9 3622–31

[167] Kim I S et al 2014 Influence of stoichiometry on the optical and electrical properties of chemical vapor deposition derived MoS2 ACS Nano 8 10551–8

[168] Fan X, Siris R, Hartwig O, Duesberg G S and Niklaus F 2020 Rapid and large-area visualization of grain boundaries in MoS2 on SiO2 using vapor hydrofluoric acid ACS Appl. Mater. Interfaces 12 34049–57

[169] Ly T H et al 2014 Observing grain boundaries in CVD-grown monolayer transition metal dichalcogenides ACS Nano 8 11401–8

[170] Tao L, Chen K, Chen Z, Chen W, Gui X, Chen H, Li X and Xu J B 2017 Centimeter-scale CVD growth of highly crystalline single-layer MoS2 film with spatial homogeneity and the visualization of grain boundaries ACS Appl. Mater. Interfaces 9 12073–81

[171] Pascoe R D 1976 Fundamentals of Solid-State Electronics (New York: Wiley)