Real time optical observation and control of atomically thin transition metal dichalcogenide synthesis†

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Understanding the mechanisms involved in chemical vapour deposition (CVD) synthesis of atomically thin transition metal dichalcogenides (TMDCs) requires precise control of numerous growth parameters. All the proposed mechanisms and their relationship with the growth conditions are inferred from characterising intermediate formations obtained by stopping the growth blindly. To fully understand the reaction routes that lead to the monolayer formation, real time observation and control of the growth are needed. Here, we demonstrate how a custom-made CVD chamber that allows real time optical monitoring can be employed to study the reaction routes that are critical to the production of the desired layered thin crystals in salt assisted TMDC synthesis. Our real time observations reveal the reaction between the salt and the metallic precursor to form intermediate compounds which lead to the layered crystal formation. We identified that both the vapour–solid–solid and vapour–liquid–solid growth routes are in an interplay. Furthermore, we demonstrate the role H₂ plays in the salt-assisted WSe₂ synthesis. Finally, we observed the synthesis of the MoSe₂/WSe₂ heterostructures optically, and elucidated the conditions required for both lateral and vertical heterostructure syntheses.

Chemical vapour deposition (CVD) synthesis of two-dimensional (2D) transition metal dichalcogenides (TMDCs) involves deposition of gaseous precursors onto a substrate to facilitate the crystallization in the desired crystal structure.1–5 In a typical CVD synthesis, a transition metal containing precursor is placed in a tube furnace with a chalcogen precursor and a target substrate. The Ar/H₂ mixture carries the vaporised chalcogen precursor and the metal compounds to form atomically thin layers on the target substrate. Salts are also added to the conventionally used metal oxide precursors to form more volatile intermediate compounds.6–8 This increases the monolayer formation rate and allows the synthesis of otherwise difficult to synthesize 2D TMDCs.9 The setup described above has been used to produce atomically thin TMDC crystals in various morphologies. However, optimization of the growth parameters requires blind trial and errors, and even the optimized recipes offer limited control in terms of number of layers, crystal phase and morphology.

There are two growth modes in CVD synthesis of TMDCs. (1) Vapour–Solid–Solid (VSS): Vaporized precursors are adsorbed on the substrate and form crystals via surface diffusion and bond formation at an elevated temperature,10 and (2) Vapour–Liquid–Solid (VLS): Supersaturated liquid droplets containing the constituent elements form the crystals.11 Fig. 1(a) depicts these growth modes. Despite many studies on the CVD growth mechanisms of few layer TMDCs, it is unclear which growth mode prevails under different growth conditions. The greatest challenge in understanding the on-going processes during the growth is the inaccessibility of the tube furnace for real time observations. To analyse the intermediate products leading to the desired crystal growth, these products must be captured by shutting off the furnace and quenching the synthesis by a rapid cool down. Although there are reports on real time visual observation of graphene12–14 Y₂BaCuO₅ and15 vanadium dioxide nanocrystal synthesis, due to the complexity of the growth process no such observations have been made for TMDCs.

To explore the synthesis of atomically thin TMDCs, we built a custom-made CVD chamber that allows real time optical observation and control of multi-precursor crystal growth. Fig. 1(b) shows a schematic of the chamber. Our investigations of the CVD growth mechanisms of atomically thin TMDCs rest on the ability to control four separate alumina heaters while...
monitoring the growth substrate under an optical microscope. This ability allows the chamber to be used as a multi-zone chamber. One heater dedicated for the growth substrate is directly located under a 0.5 mm thick sapphire window for optical observations. A 40× ultra-long working distance (4.4 mm) objective is employed to have a high resolving power while maintaining a large enough hot zone above the substrate. The other heaters are dedicated for the growth precursors and their separation to the substrate heater can be adjusted within the chamber (see the ESI† for details).

We focus on salt assisted synthesis of WSe₂ monolayers on an oxidised Si chip as a demonstration of the versatility of our chamber. Fig. 1(c) shows a series of optical images obtained during the synthesis at 790 °C (see ESI Movie 1†). WSe₂ crystal formation via VSS and VLS modes can be observed in real time. Fine mesh grains of WO₃ and NaCl are placed on heater 2 and Se on heater 1. The substrate heater and heater 2 temperatures are increased simultaneously. When they reach 600 °C, the temperature of heater 1 is brought to 300 °C, above the melting point of Se. At the same time H₂ is introduced to aid the growth of the monolayers. We use atomic force microscopy (AFM), Raman and photoluminescence (PL) intensity maps to characterize the samples. Photoluminescence (PL) maps obtained from typical VSS crystals show that they are high quality WSe₂ monolayers (ESI Fig. S5 and S6†).¹⁷ To understand the possible crystal formation routes, we placed a 250 µm³ large grain of NaCl surrounded by smaller grains of WO₃ on a SiO₂/Si chip on the substrate heater and observed the dynamics of the intermediate compound formation before WSe₂ growth. Optical images captured during the heat up show the intermediate stages of the reaction between WO₃ and NaCl (Fig. 2(a)-(f)). Firstly, we observe a turquoise liquid formation in the vicinity of the WO₃ particles at as low as 600 °C. This is consistent with the previously
reported thermogravimetry and differential scanning calorimetry measurements on NaCl–WO₃ mixtures. At this early stage, when we stop the synthesis and perform scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy (EDX) mapping, Na and Cl on the WO₃ grains are detected (see Fig. S8 in the ESI†). This clearly indicates that NaCl sublimates and condenses on WO₃. At higher substrate temperatures, more liquid forms and its colour changes from turquoise to beige. Considering that both NaCl and WO₃ have melting points above 800 °C, the liquid formation is a product of the reaction between the two. Especially above 730 °C, as time goes on, no solid WO₃ grains remain as a result of the reaction with NaCl (see ESI Movie 2†). As reported previously in the literature¹¹ and as illustrated later in the text, this reaction has a significant role in both VLS and VSS crystal syntheses.

Once the liquid is fully formed, we cool down the chamber and immediately perform X-ray photoelectron spectroscopy (XPS) on the solidified liquid to determine its chemical composition. XPS surveys on the solidified liquid show that it is composed of Na, O, W but not Cl. High resolution XPS spectra of Na 1s, O 1s and W 4f binding energies exactly match with the values reported for sodium tungstate, Na₂WO₄ (Fig. 2(g)). The measured Raman spectrum is in good agreement with the reported spectrum for Na₂WO₄ in the literature (Fig. 2(h)). When we consider the chemical reaction between NaCl and WO₃ the second product of the reaction can be WO₂Cl₂.⁹,¹¹

\[
2\text{WO}_3 + 2\text{NaCl} \rightarrow \text{WO}_2\text{Cl}_2(g) + \text{Na}_2\text{WO}_4(l)
\]  

(1)

At above 600 °C, the temperature where we observe the liquid formation, WO₂Cl₂ is in the gaseous phase. As the reaction between vapour NaCl and WO₃ begins, WO₂Cl₂ forms and leaves the chamber with the carrier gas. This explains why we
don’t observe any Cl both in XPS and EDX analysis of the later stage molten product. Also, as discussed later in the text, by controlling the presence of WO2Cl2 in the chamber, we can lead the growth to follow either the VLS or VSS mode.

With the unique abilities we have with our custom-made CVD chamber, we investigated the possible monolayer WSe2 formation routes from both liquid and gaseous intermediate compounds. First, we prepared a mixture of NaCl : WO3 in a 1 : 2 weight ratio to study how molten Na2WO4 forms WSe2 monolayers. A 1 : 1 molar ratio of NaCl : WO3 (based on reaction (1)) corresponds to a 1 : 4 weight ratio, yet the salt rich mixture results in liquid Na2WO4 with a minimum solid content as some salt sublimes during the heat up. A grain of the mixture is placed on an oxidised silicon chip and then heated to 750 °C in an Ar environment on the substrate heater to form liquid Na2WO4. After the liquid formation, we introduced Se. However, this didn’t result in WSe2 synthesis and the liquid remained unchanged as the time went on. Although we tried introducing Se vapour at various substrate temperatures ranging from 700 to 900 °C, we didn’t observe WSe2 formation. Thus, we deduce that H2 plays an essential role in WSe2 formation.

Although there are numerous reports22–27 on the effect of H2 in atomically thin TMDC synthesis, its function in the salt assisted growth is not ubiquitous. To elucidate the role of H2 in monolayer formation, we first tested the sole effect of H2. When we introduce H2 into the molten Na2WO4, cubic crystals varying in colour from yellow to orange emerge. XPS and Raman measurements show that these crystals are sodium tungsten bronzes (Na1xWO3, x < 1) of various Na ratios (see ESI Fig. S9†).28 Accordingly, we determine that the temperature at which H2 dosed during the TMDC synthesis is critical to prevent premature reduction of sodium tungstate to sodium tungsten bronze.

Curiously, when we introduce H2 into Na2WO4 after 20 minutes of Se exposure, we don’t observe WSe2 formation. XPS and EDX analyses (Fig. 3(a) and (b)) of the Na2WO4 liquid exposed to Se for 20 minutes without H2 show that no Se dissolves in Na2WO4. Even when we add Se to the NaCl : WO3 mixture, no Se is detected in the liquid droplets. We would like to note that when H2 is introduced over hot Se vapour above 300 °C, H2 reacts with Se to form H2Se gas.29 H2Se formation during the synthesis can be imperative in WSe2 growth.

We performed a series of controlled experiments to unravel any possible effect of H2Se on WSe2 formation. First, we evacuated the chamber and flushed it with Ar several times. Then, we filled the chamber with a 5 : 1 ratio of Ar : H2 gas. For the VLS mode synthesis, H2Se and H2 gases react with the liquid intermediate compound Na2WO4 to form WSe2 following the proposed reaction:

\[
\text{Na}_2\text{WO}_4(\ell) + 2\text{H}_2\text{Se}(g) + \text{H}_2(g) \rightarrow \text{WSe}_2(s) + 3\text{H}_2\text{O}(g) + \text{Na}_2\text{O}(s)
\]

Here, H2 is also needed as a reducing agent to reduce W6+ in Na2WO4 to W4+ in WSe2. For the VSS mode, the gaseous

![Fig. 3](image-url) Effects of Se exposure on Na2WO4. (a) High resolution XPS spectra of the Na2WO4 liquid droplet obtained after 20 minutes of exposure to Se. Na 1s, O 1s, Se 2p, and W 4f peaks match exactly with Na2WO4 spectra and no Se 2p peaks exist in the spectrum. (b) SEM image and EDX maps corresponding to the labelled elements are obtained from the solidified Na2WO4 liquid droplet exposed to Se for 20 minutes. The Se Lα1 map shows a faint background as the tail of the W Lα1 peak extends through Se Lα1 energy. Scale bar is 20 µm.
intermediate product \( \text{WO}_2\text{Cl}_2 \) reacts with \( \text{H}_2\text{Se} \) and \( \text{H}_2 \) to form WSe\(_2\) crystals. The chemical reaction of the adsorbed molecules that produce WSe\(_2\) can be written as:

\[
\text{WO}_2\text{Cl}_2(\text{ads}) + 2\text{H}_2\text{Se}(\text{ads}) + \text{H}_2(\text{g}) \\
\rightarrow \text{WSe}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 2\text{HCl}(\text{g})
\] (3)

We would like to note that the crystals grow at a much faster rate in the VLS mode compared to the VSS mode. This observation can be described qualitatively as follows: the VSS mode requires gaseous molecules (\( \text{WO}_2\text{Cl}_2 \) and \( \text{H}_2\text{Se} \) in the case of WSe\(_2\)) to be adsorbed by the substrate surface and crystal nucleation requires a seed to begin. On the other hand, in VLS mode once the nucleation begins, crystal growth is fuelled by excess supply of constituent precursors and governed by the kinetic effect.\(^{32}\) These two proposed reactions are critical to understand the effect of each growth parameter that leads to the WSe\(_2\) synthesis.

The ability to control the dominant growth mode could enable directed growth of 2D materials for bottom up device fabrication and high-quality crystal synthesis. When the reaction between the metal–oxide and the salt begins, the VSS precursor is released in the gaseous form and adsorbed by the substrate surface. If there is no \( \text{H}_2 \) and Se present in the chamber, in time, the adsorbed precursor molecules are desorbed from the substrate surface. As the reaction between the salt and the metal–oxide slows down due to consumption of the reactants, partial pressure of the VSS precursor decreases as well. High enough partial pressure of the VLS precursor in the chamber is needed to condense liquid droplets on the target substrate. Several parameters such as separation of the substrate from the precursor heater, carrier gas flow rate and the precursor heater temperature significantly alter the VLS precursor condensation rate. Controlling the temperature and time when \( \text{H}_2 \) and Se are introduced into the chamber allows one to achieve one growth mode over the other. As an example, for WSe\(_2\), introducing \( \text{H}_2 \) and Se when the temperature of the precursor heater is around 600 °C will most dominantly result in the formation of VSS crystals. Delaying the time of \( \text{H}_2 \) and Se by about 10–15 minutes after the temperature of the precursor heater reaches 700 °C results in the formation of VLS crystals predominantly. This level of control is hard to achieve in a tube furnace based CVD chamber as any change in the precursor temperature will either effect the substrate temperature or the separation between the substrate and the precursor needs to be adjusted at a cost of reducing the amount of precursor that reaches the substrate.

The methodology we presented here can be applied to any other TMDC and their heterostructures that can be synthesized in a CVD chamber. Indeed, we tested the chamber to synthesize other selenium based TMDCs such as MoSe\(_2\)\(^{27,33–36}\) and its lateral and vertical heterostructures with WSe\(_2\).\(^{37}\) Our ability to control the heaters independently enables \textit{in situ} control of the heterostructure synthesis. We started by observing the heterostructure formation in real time. 10 mg Se and 10 mg MoO\(_3\) are placed on heaters 1 and 3, respectively. Less than a mg, a 1 : 10 mixture of NaCl : WO\(_3\) is placed at a corner of the substrate to enhance the mass transport of \( \text{WO}_2\text{Cl}_2 \) (Fig. 4(a)). First, the temperature of the substrate heater is ramped up to 550 °C while those of heaters 1 and 3 are at 300 and 600 °C, respectively. At this stage, a 7 : 1 mixture of Ar : \( \text{H}_2 \) is introduced into the chamber to promote the formation of H\(_2\text{Se}\) for MoSe\(_2\) synthesis. After obtaining several micrometres large MoSe\(_2\) monolayers, we shut down heater 3 and the \( \text{H}_2 \) flow. Then, we ramp up the substrate heater to start the WSe\(_2\) synthesis. Once the temperature reaches the desired growth temperature, \( \text{H}_2 \) is reintroduced for WSe\(_2\) formation until the end of the synthesis.

A series of real time optical microscopy images given in Fig. 4(b) captured at 700 °C shows the time evolution of the vertical heterostructure. We observed that upon heating, small droplets of Na\(_2\)WO\(_4\) form at the edge or at the centre of the MoSe\(_2\) monolayers, but never in between (see the ESIF†). After the re-introduction of \( \text{H}_2 \), the WSe\(_2\) layer nucleates from the liquid precursor. Unlike the monolayer TMDC synthesis, vertical layers form at a very slow rate. Fig. 4(c)–(l) show Raman, PL spectra and AFM height traces of the vertical and the lateral heterostructures. The final temperature of the substrate heater determines whether the heterostructure will form vertically or laterally. Our studies show that substrate temperatures below 725 °C mostly yield vertical, while above 750 °C mostly yield lateral heterostructures. This observation can be explained by the kinetic nature of the crystal formation. As the mentioned temperatures are well above the reaction temperature for the NaCl : WO\(_3\) mixture, there are plenty of VLS and VSS precursors available for the crystal nucleation. Thus, substrate temperature determines the heterostructure type rather than the precursor supply unlike the previous reports.\(^{38,39}\)

In summary, we demonstrated that our custom-made CVD chamber can be used to monitor and control the synthesis routes in real time. We showed that both VSS and VLS routes can be employed to grow selenium based TMDC crystals. In the VSS route, H\(_2\text{Se}\) and \( \text{H}_2 \) react with metal-oxychloride to form the monolayers while in the VLS mode a liquid composed of the alkali metal, transition metal and oxygen reacts with H\(_2\text{Se}\) and \( \text{H}_2 \) to form the monolayers. We realize that by timing when \( \text{H}_2 \) and Se are introduced, it is possible to control the growth route. Such a degree of control over the synthesis route allowed us to synthesize both lateral and vertical heterostructures of WSe\(_2\) and MoSe\(_2\) with \textit{in situ} control. We would like to emphasize that although the intermediate products and the reaction routes may differ among various TMDCs, the methods we present here will still be applicable. Furthermore, the CVD chamber we reported in this article can be modified to investigate the synthesis mechanisms of other materials that utilize a CVD chamber for the growth. Optical observations can be accompanied by other spectroscopic measurement techniques that can be incorporated onto the chamber to provide real time spectroscopic information about the intermediate phases.
Methods

The CVD chamber is machined out of a 6061-aluminium alloy. There are three body pieces that form the chamber: bottom plate, reactor and lid. The bottom plate houses the water circulation channels and the cooling water makes direct contact with the reactor when the two pieces are bolted together. The lid allows easy access to the reactor chamber. There are water jackets within the lid as well. The chamber body temperature is maintained at or near room temperature. A closed-cycle chiller supplies water to the cooling channels embedded within the chamber body and the lid. Outside the chamber, the temperature of the hottest regions remains below 50 °C. The optical port on the lid is a 0.5 mm thick sapphire disk and it is directly located above the substrate heater. Electrical connections for temperature control are made via hermetically sealed feedthroughs. There are two separate gas inlets, one for Ar and the other for H2 and a single exhaust at the opposite end of the chamber. Gases are dosed through mass flow controllers. The chamber can reach down to 10⁻³ mBar using an oil rotary vane pump. Heater temperatures and gas flow rates are controlled via a LabView software. Detailed pictures of the chamber are given in the ESI†

Author contributions

TSK conceived the experiments. HRR and TSK designed the CVD chamber and assembled it. HRR and TSK performed the experiments. NM and OÇ helped characterizing the samples. All the authors discussed the results and contributed to the writing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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