SCANNING TRANSMISSION ELECTRON MICROSCOPY AND IN-SITU HEATING OF WS_2 AND APPLICATIONS TO GROUP V TRANSITION METAL CHALCOGENIDES

by

HOLLI THRELKELD

(Under the Direction of Tina T. Salguero)

ABSTRACT

Transition metal dichalcogenides are layered materials that have been found to have applications in electronics, catalysis, and optoelectronic devices. Understanding and controlling their growth from amorphous precursors into layered crystalline materials have become important to tuning their functionality and optimizing their synthesis. In this thesis, the formation of tungsten disulfide is explored using in-situ scanning transmission electron microscopy and the resulting data is applied to the design of related experiment to better understand group V transition metal chalcogenides.

INDEX WORDS: Transmission electron microscopy; precursor; transition metal; dichalcogenides; 2D; van der Waals; in-situ

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DEDICATION

To my loving parents, Chris and Jan Threlkeld.

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First, I would like to thank my wonderful parents, Chris and Jan Threlkeld and my sister, Kaitlin Threlkeld for all their love and support throughout this journey. I would not be where I am today if it weren't for your guidance and encouragement. I'd also like to thank my professors from the University of North Georgia, Dr. Nicole Hollabaugh, Dr. Andrew Thomas and Dr. Patricia Todebush for giving me the push I needed to pursue graduate school. In addition, I extend my gratitude to Mr. Tomlinson for being the best high school teacher, introducing me to chemistry and making it FON.

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CHAPTER 1

INTRODUCTION

Transition metal dichalcogenides (TMDCs) have increasingly been studied for the past decade since the discovery of graphene, the monolayer of graphite, in 2004[1]. As science and technology have advanced, it has become evident that there is still much to learn about TMDCs and their properties. With recent advances in sample preparation and increased characterization methods, TMDCs are increasingly being studied for their application in several different fields. Synthesis and analysis of their properties has been of interest to scientists and engineers alike. Due to the range of characteristics displayed by TMDCs, there has been a desire to manipulate them to release their full potential.

TMDCs are a class of layered materials with the general formula MX_2, where M is a group IV-X transition metal and X is a chalcogen from group 16 of the periodic table. These compositions form layers consisting of two hexagonal planes of chalcogen atoms separated by a

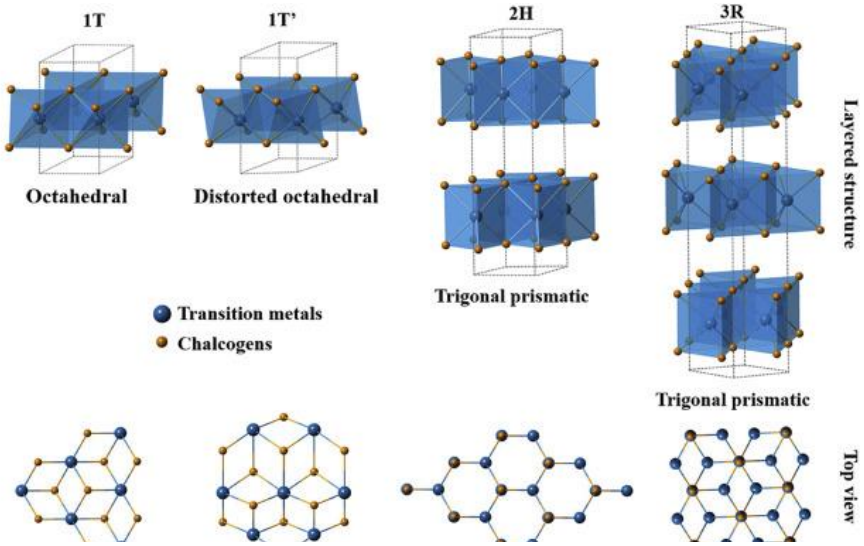

Figure 1: Structural diversity of TMDCs, including four polytypes. (Source: Tran, M. D.; Kim, J.-H.; Lee, Y. H., Tailoring photoluminescence of monolayer transition metal dichalcogenides. Current Applied Physics ***2016,*** 16 *(9), 1159-1174.)*

plane of metal atoms[2]. Six chalcogen atoms are covalently bonded to each metal atom, and the layers are weakly held together by van der Waals forces to form the bulk material[3]. The coordination of the metal atom can occur as either octahedral or trigonal prismatic, which gives rise to the overall symmetry of the TMDC as being either hexagonal, trigonal or rhombohedral as seen in Figure 1[2, 4].

TMDCs have become highly attractive due to their broad range of properties. The layered structure allows for individual layers to be grown and manipulated, and with ever-evolving techniques, the study of single layers have become of interest. Many TMDCs crystallize as ultra-thin sheets and because the layers are held together by weak van der Waals forces, these bulk materials can be easily exfoliated to produce single MX_2 layers[5]. Using information learned from graphene, scientists have found that there are many layer-dependent properties that differ from those of the bulk material including optical, electronic and thermal, among others[2]. The ability to tune a variety of properties by simply reducing the number of layers has made these materials applicable in various fields.

Applications of Transition metal dichalcogenides

One dimensional (1D) and two dimensional (2D) structures have been of increasing popularity because of their tunable properties which range from optical, electronic to physiochemical. These features make TMDCs candidates for applications in energy conversion and storage, electronics and optoelectronics. In addition, they have also been promising alternatives to some precious metal catalysts used in hydrodesulfurization and the hydrogen evolution reaction.

TMDCs have been found to have either metallic or semi-conducting character where the semiconductors have applications in electronics[3]. Ideally materials for transistors have high charge mobilities, high on/off ratios, high charge mobilities and have low off-state conductance. TMDCs, like molybdenum disulfide, have displayed desirable transistor characteristics, such as having tunable bandgaps that enable high on/off ratios, and their extreme thinness allows for more efficient control over switching, which can reduce power dissipation[2].

Optoelectronic devices are devices that are able to generate, detect or control light and include tools such as lasers, LEDs, solar cells photodetectors and displays[2]. Some TMDCs have direct band gaps in the visible region making them attractive for light-absorbing materials like those utilized in thin film solar cells[6]. By using intercalants[7] and adjusting the thickness of the layers[8], the bandgap as well as the optical absorbance can be tuned, enhancing their photovoltaic properties. For flexible and transparent optoelectronics, such as wearable technology and displays, a wide variety of components are required each with their own specific properties. In addition to their tunable bandgaps, TMDCs are thin and processable, giving them the potential to be useful in flexible optoelectronics[2].

Beyond their applications in electronics, TMDCs are currently of interest in the field of catalysis. Hydrodesulfurization is an industrial process used to remove sulfur to produce ultra-low sulfur diesel fuel. Molybdenum disulfide catalysts promoted with cobalt and nickel[9] have proven to desulfurize fuel as well as be useful in the hydrogen evolution reaction (HER)[10]. Edge sites of the layered materials are the active sites for the catalytic reactions, therefore there has been drive to maximize exposure of the edge sites in order to increase the overall activity[10]. Likewise, niobium disulfide has been shown to exhibit excellent catalytic activity towards the

HER due to its unique 2D structure and highly exposed active sites[11]. Both examples aim to be alternatives for current noble metal catalysts like platinum.

The applications of TMDCs extend far beyond those mentioned and continue to make an impact in the fields of material science and electronics. Moving forward, it is important that the synthesis of these 2D materials is refined so that it can be scaled up for commercialization and that the growth of the layers can be controlled. Research using TMDCs continue to reveal more fundamental physics and chemistry, helping us better understand their unique properties and how to maximize their potential.

Synthesis of TMDCs

One commonly employed technique for synthesizing TMDCs is chemical vapor deposition (CVD), which is used to form high-quality TMDCs as large-scale films. In CVD the film is grown by a series of chemical reactions between gaseous molecules of the precursor with the substrate[12]. The substrate, or object to be coated with the film, is placed in a chamber and heated. While the substrate is heated, a carrier gas consisting of hydrogen, nitrogen, argon or a mix of these and the precursor is passed through the chamber. As the gas flows, chemical reactions take place near and on the heated substrate resulting in the deposition of the film on the surface of the substrate[13]. Chemical by-products as well as unreacted precursor gas exit the chamber. Because this technique can be used with a variety of materials and has a wide range of applications, many variations of CVD have been developed including metal oxide CVD, metal halide CVD and metal-organic CVD[3].

A second technique used to synthesize TMDCs is atomic layer deposition (ALD). ALD is a modified CVD technique where the precursors are injected separately into the growth chamber.

Each cycle begins by the injection of the first precursor and allowing it to react and bond to the substate. Next, the chamber is purged with inert gas and the second precursor is injected into the growth chamber and subsequently purged with an inert gas. Because there are only active sites on the surface of the substrate, one cycle should result in the deposition of a single monolayer lining the substrate[14]. This would allow for the modification of the number of layers simply by the number of cycles[15].

TMDC nanosheets can also be synthesized from bulk material using methods of exfoliation. Scotch tape can be used to pull off single layers for small scale applications. Techniques like sonication-assisted liquid exfoliation or intercalation-exfoliation are better suited for larger-scale applications, however[15]. In liquid phase exfoliation a bulk material is sonicated in organic solvents which results in the reduction of the number of layers. Some important considerations of this technique are the starting mass of the bulk material, the solvent, the sonication power and sonication time[16]. Intercalation exfoliation works by inserting ions between layers in the bulk material then transferring the material to water where byproducts, like hydrogen gas, are expelled and the van der Waals interactions are broken to yield the exfoliated sheets. Exfoliation methods have proved to be advantageous in the synthesis of monolayer TMDCs.

The last notable synthetic technique is thermolysis where a precursor undergoes a decomposition reaction to form the TMDC. The precursor typically consists of a cation that dissolves in solution, leaving a transition metal anion that decomposes with increasing temperature to give the final TMDC product along with gaseous byproducts[17]. This technique has become of interest due to its ease, its lack of a sulfurizing atmosphere and its relevance to in-situ electron microscopy methods, which allows film growth to be observed in real time[18].

Thesis Objectives

The goal of this thesis is to investigate potential experiments focused on the growth of group V transition metal dichalcogenides using in-situ electron microscopy techniques. The study will begin with the synthesis of a precursor that can undergo a decomposition reaction to yield the desired TMDC. Then analysis of the reaction intermediates and products will be accomplished using in-situ STEM experiments and analytical techniques.

CHAPTER 2

IN-SITU HEATING AND ELECTRON MICROSCOPY OF WS_2

Introduction to in-situ Electron Microscopy

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) have recently been used to study the growth mechanisms of nanomaterials. These key tools help scientists characterize the often complex and dynamic changes in material morphology, atomic structure, electronic state and chemical composition. Due to its ultrahigh spatial resolution, *in-situ* S/TEM has helped scientists view the lattice structure of TMDCs as well as investigate lattice defects and how they influence the growth of the 2D material.

Advances in *in-situ* S/TEM have enabled this technique to be more widely used to study 2D materials like TMDCs. Recently, S/TEM has been employed to elucidate growth mechanisms in nanomaterials owing to high spatial resolution and the ability to mimic growth environments[19]. In addition, the development of micro-sized heating sample chips has decreased the sample drift during thermolysis experiments, allowing for data to be collected at temperatures up to 1200 °C[19]. *In-situ* S/TEM experiments are carried out by applying external stimuli or conditions to a sample while it remains under constant observation through the microscope. These stimuli or environments, which may include temperature, pressure and/or gaseous atmospheres, are typically applied in stages through specialized sample holders while the electron beam from the TEM illuminates the sample[19]. The resulting images give details related to structure and morphology, which provide insight into the nucleation and formation of 2D crystals. In addition to imaging, the samples can be analyzed by various spectroscopic

techniques, including energy dispersive spectroscopy (EDS) and energy electron loss spectroscopy (EELS).

For example, to study the temperature-dependent growth and evolution of materials, *in-situ* S/TEM utilizes sample holders fitted with heating elements to control the temperature of the sample as data are collected. Heating elements can typically reach up to 1,200 °C and display high temperature stability, which allow for imaging with lattice resolution at elevated temperatures[19]. Such heating experiments have been applied to TMDCs by many groups. Fei et al. observed the growth of MoS_2 flakes from the decomposition of ammonium thiomolybdate ($(NH_4)_2MoS_4$) as temperature increases[20]. The solid precursor $(NH_4)_2MoS_4$ decomposes at ~400 °C into MoS_2, and MoS_2 structures begin to grow layer-by-layer[20]. As the temperature increases, more precursor can be added to enlarge the MoS_2 flakes. In addition to these initial discoveries, Kondekar et al. investigated the effect of nickel on the dynamic growth of MoS_2[18]. The group used the same precursor as Fei but added varying amounts of nickel. They found that small amounts of nickel resulted in the formation of larger crystals but adding large amounts of nickel would suppress growth and lead to Ni-sulfide by-products instead[18].

For the purpose of this study, the goal is to use *in-situ* STEM experiments to monitor the dynamic formation and growth of TMDCs. Using the widely studied MoS_2 and WS_2 as inspiration, potential precursors are identified for in-situ that can lead to niobium and tantalum dichalcogenides. In comparison to group VI TMDCs, group V TMDCs have not been as widely investigated at the nanoscale, therefore the development of *in-situ* TEM experiments will provide valuable information about the evolution of their morphologies and properties.

Sample Preparation: Experiment 1

The tungsten disulfide precursor solution was prepared by dissolving 100 mg of ammonium tetrathiotungstate ($(NH_4)_2WS_4$) in 100 mL dimethylformamide (DMF) to yield a .1 wt% solution. The ammonium tetrathiotungstate quickly dissolved in the DMF resulting in a light green solution that was applied to the silicon nitride chip using a "paint brush" method where the solution is absorbed by a small piece of paper and brushed onto the chip. The chip was then left to dry for 20 minutes so that excess DMF could evaporate. Once the chip was dry, it was placed into the holder (Figure 3 and 4) and placed into the TEM instrument[21].

All images were taken using a Hitachi SU9000EA STEM microscope (Figure 2) operating at 30 kV and using a silicon nitride sample-holding heating chip. Once the holder has been prepared, it was inserted into the instrument where analysis began. The temperature was raised to 300 °C and images were taken after heating. Next, the temperature was increased to 600 °C and held constant for one hour. Images were taken at this temperature and it was then raised again to 800 °C with a one hour hold followed by imaging. Once 800 °C was reached and final images were taken, the sample was brought back to room temperature and more images were taken. Transmission mode and secondary electron (SE) mode images are shown. In transmission mode the image is generated from electrons passing through the sample while SE images are created by the detection of electrons that have been knocked-off from the sample[22]. Transmission mode images give insight into the inner structure such as morphology while SE provides information on the sample's surface and composition[22]. After the experiment, the images were used to carry out Energy Dispersive Spectroscopy (EDS) to determine the constituents of the final TMDC material.

Figure 2: Picture of the Hitachi SU9000EA STEM instrument. (Source: hitachi-hightech.com)

Figure 3: A) Sample holder for the Hitachi SU9000EA. B) Close up of the sample holder where the chip is housed.

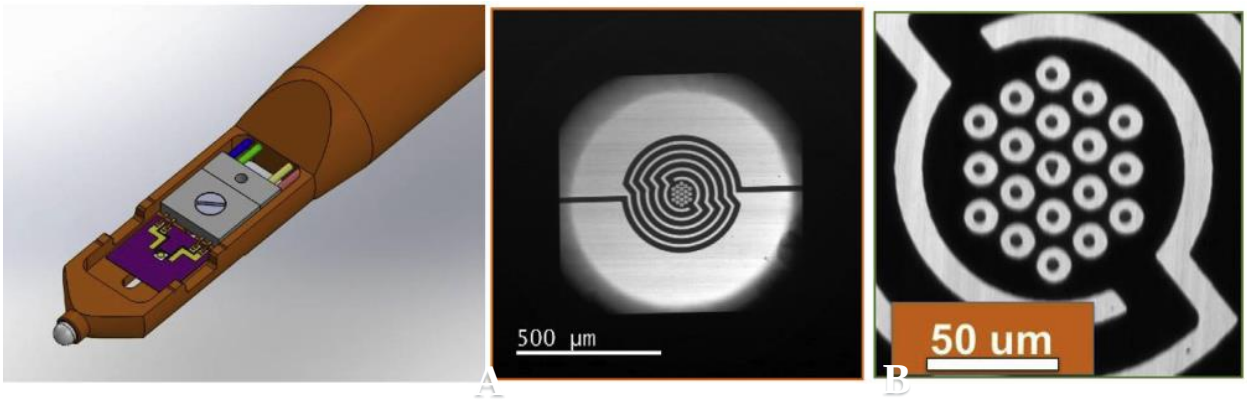

Figure 4: Hitachi schematic of the sample holder for the SU9000EA STEM: A) Schematic of the sample holder, and B) and C) Close up images of the Norcada heating chips. (Source: El-Zoka, A. A.; Howe, J. Y.; Newman, R. C.; Perovic, D. D., In situ STEM/SEM study of the coarsening of nanoporous gold. Acta Materialia ***2019,*** *162, 67-77.)*

Results and Discussion: Experiment 1

To investigate the dynamic growth of WS_2, an in-situ experiment was conducted in which ammonium tetrathiotungstate was dissolved in DMF and heated inside a STEM using a silicon nitride (SiN_x) chip. The Norcada heating chip contains a coil that leads from the sample holder to the sample wells that allow for electricity to pass through, controlling the temperature of the sample. The solution was "brushed" on to the chip using a small piece of Kimwipe to prevent damaging the chip. This precursor is advantageous because it does not require additional sulfur and is easily applied to the surface of the chip. The chip was allowed to dry, then was placed into the microscope and slowly heated to 300 °C to remove any solvent. Images were also taken at this temperature indicating that the precursor is still amorphous. The temperature was increased to 600 °C for one hour then raised to 800 °C for one hour and images were taken at both temperatures. Once imaging was complete at 800 °C, the sample was returned to room temperature for more imaging.

Conclusions: Experiment 1

Images from this experiment utilizing the "paint brush" method revealed that even though there was formation of product at 800 °C, there was not very much precursor deposited on the chip to begin with. In addition to depositing more starting material on the chip, it is important to test at temperatures >800 °C to ensure sufficient time and energy for the precursor to decompose and transform. Imaging and EDS showed the formation of the 2D sheets of the WS_2 product, but due to the limited amount of starting material, an improved experiment was planned.

Sample Preparation: Experiment 2

To load more precursor onto a second chip, a micropipette was used to inject one microliter of solution onto the chip. Then the chip was left to dry, placed into the holder and transferred into the STEM instrument.

All images were taken using a STEM- Hitachi SU9000EA operating at 30 kV and using a silicon nitride chip to house the sample. Once the chip was inserted into the holder, it was placed into the instrument for imaging to begin. The temperature was raised to 300 °C and images were taken after a one hour holding time at this temperature. This process was repeated for temperatures of 600 °C, 800 °C and 1000 °C. After imaging at 1000 °C the sample was returned to room temperature and more images were taken. The next part to the experiment was to heat at a high temperature for a longer time period. The sample was heated to 1000 °C overnight and, after images were taken, the sample was returned to room temperature for more imaging and EDS to determine the chemical composition of the products.

Results and Discussion: Experiment 2

In order to deposit more material on the chip, a micropipette was used in this trial. Initial STEM images show significant quantities of precursor on the chip (Figure 5) using this modified method. It was observed that the precursor before the start of the experiment appeared heterogeneous. The precursor should be more uniform and consistent. This could be due to the solvent used. The solubility in DMF could be poor causing more of a suspension of the particles in DMF rather than being dissolved in the solvent.

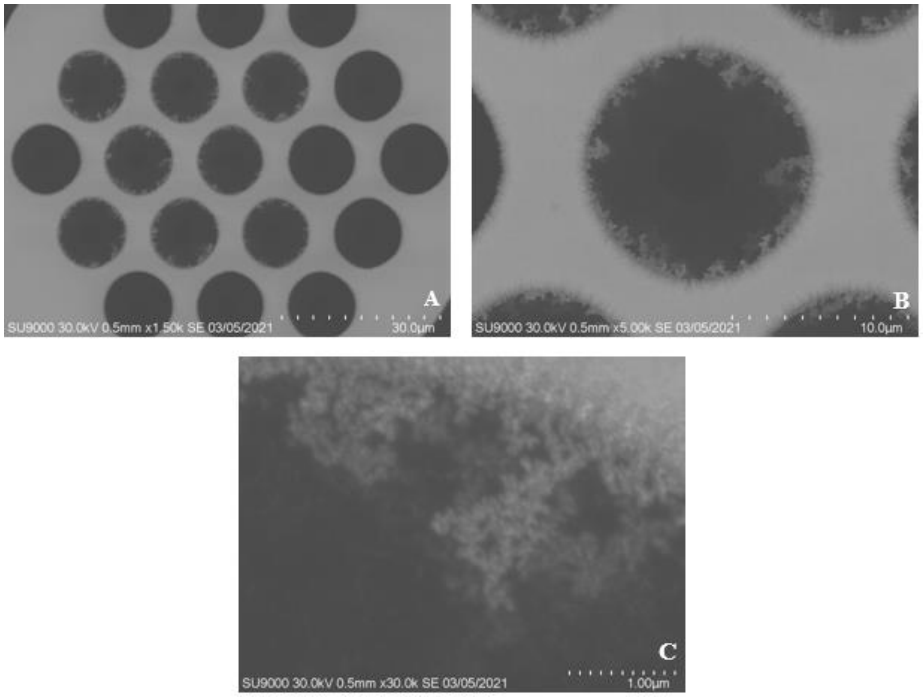

Figure 5:STEM images showing the WS2 precursor deposited on the chip at room temperature: A) low magnification view showing many SiN "windows" in the ceramic chip; B) and C) showing higher magnification views of the dried precursor.

With this confirmation, the temperature study began. At 300 °C and 600 °C there was no significant change to indicate product formation. Once the temperature was raised to 800 °C the formation of the WS_2 product began confirmed by the observation of more defined particles being formed. For this experiment the temperature was raised to 1000 °C to determine if a higher temperature would increase the WS_2 growth. At a temperature of 1000 °C WS_2 particles were

observed as shown in Figure 6. Using ImageJ software analysis, the particles ranged from ~100-150 pm. For each temperature there was a holding time of 1 hour before increasing the sample to the next temperature. Since there was particle growth at 1000 °C, it was important to investigate whether holding at 1000 °C for a longer time would cause WS_2 particle size enlargement (ripening). The sample was returned to room temperature and re-heated to 1000 °C for two hours. After this treatment, images showed that the longer time at 1000 °C caused an increase in WS_2 particle size from ~100-150 pm to ~75-125 nm as seen in figure 7.

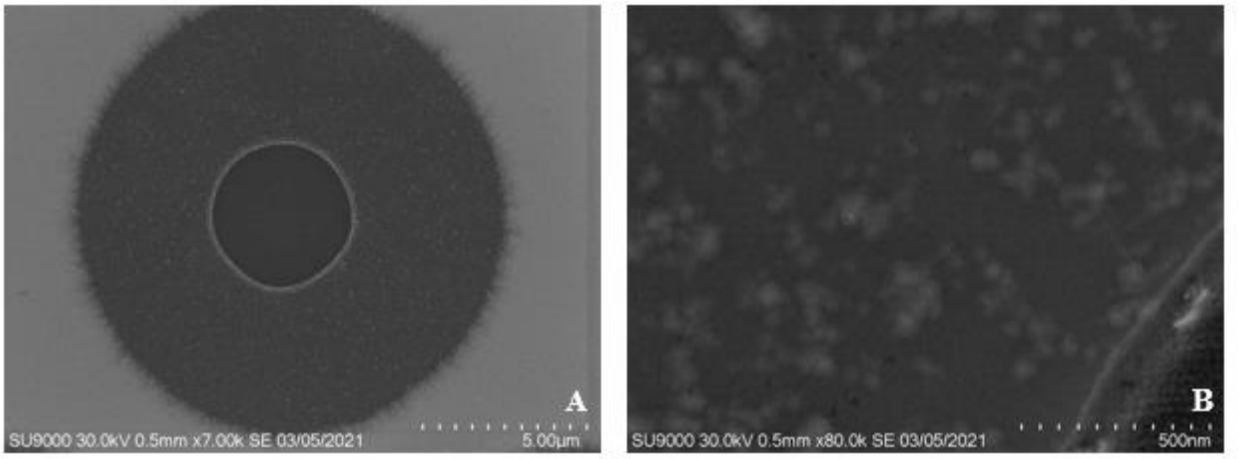

Figure 6:SE (secondary electron) images of WS2 at 1000 °C: A) Shows single SiN window, and B) shows a higher magnification view of product particles.

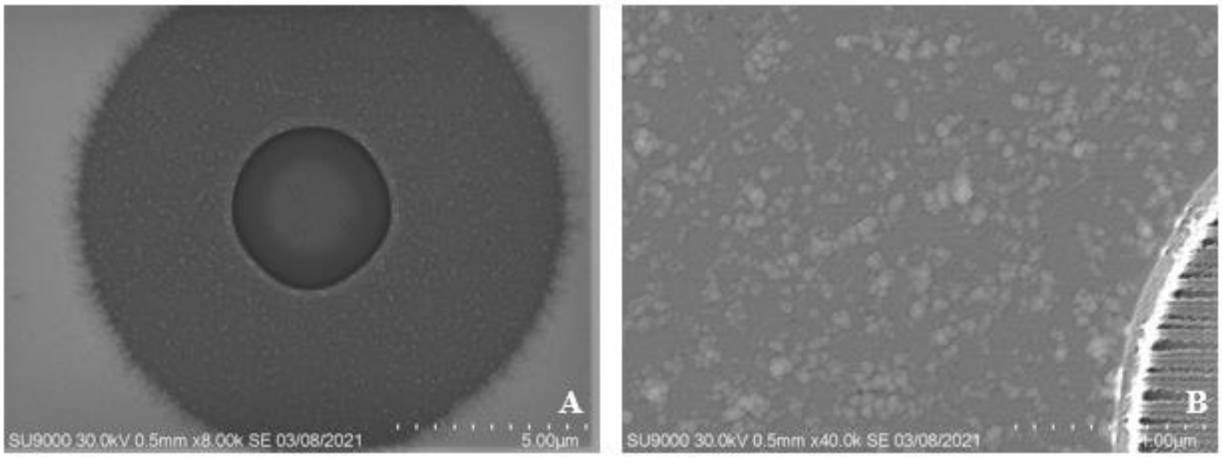

Figure 7: SE images of WS2 after heating at 1000 °C for two additional hours: A) Shows single SiN window, and B) shows a higher magnification view of the particles after additional heating.

Once the sample was heated and all images were taken, EDS was performed to confirm the formation of WS_2 particles. As seen in Figure 8, analysis of the EDS profile reveal that the particles formed were composed of tungsten and sulfur. The presence of nitrogen and silicon can be attributed to the chip being comprised of these elements. Oxygen is present due to minor oxidation during thermolysis.

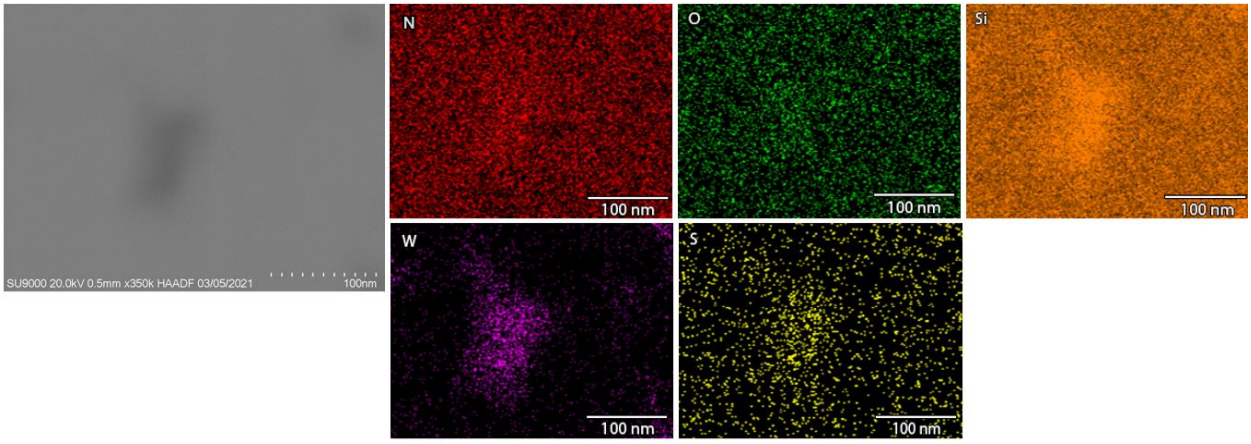

Figure 8: STEM image and EDS profiles for a single, representative product particle.

STEM images captured rope-like formations spanning across the wells of the chip (Figure 9) that formed during this experiment. As presented in figure 10, EDS was performed on the rope-like formations which are shown to be carbon and oxygen rich. This could be due to the voltage being used, contamination of the chip in the drying process, or an effect of heating the chip again after it had been cooled to room temperature. Residual DMF, when exposed to the electron beam, could possibly cause the formation of the carbon and oxygen rich ropes.

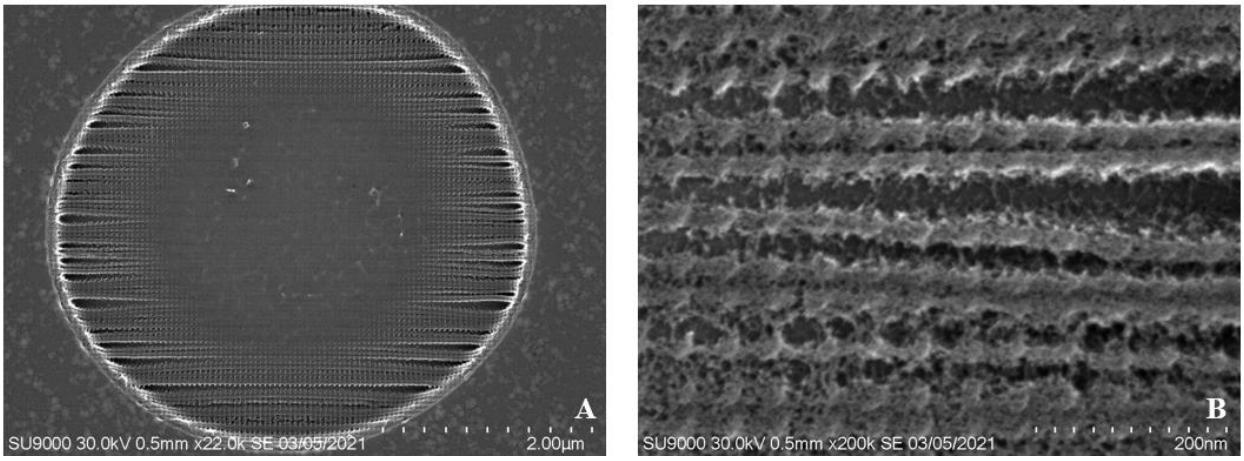

Figure 9: SE images after heating at 1000 °C showing unexpected rope-like formation: A) shows single SiN window, and B) shows higher magnification of the rope-like formation.

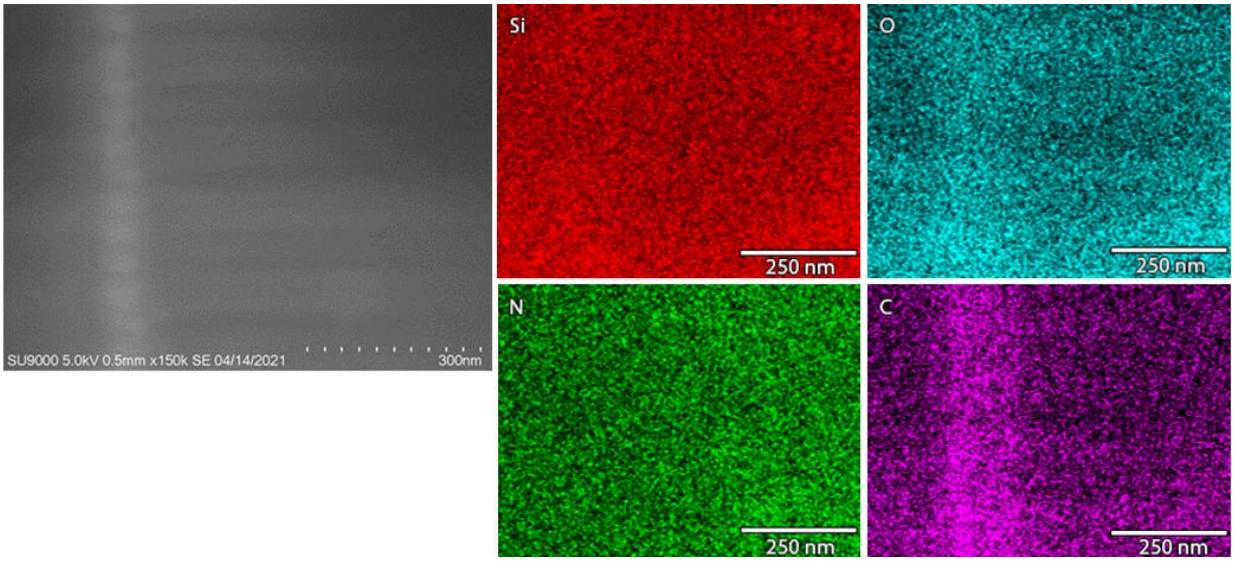

Figure 10: STEM image and EDS profiles for the rope-like structures formed during the second experiment.

Inspiration for this experiment came from McDowell and co-workers at the Georgia Institute of Technology who investigated the effect of nickel on MoS_2 growth using in-situ TEM experiments[18]. In their case, imaging was performed using a STEM instrument operating at 300 kV. The STEM used to conduct the WS_2 experiment here was operated at only 30 kV, however, which should result in reduced knock-on damage and increase the scattering, which should

improve the contrast of the resulting images[23]. To understand how the different voltages impact the growth and stability of these TMDCs, future studies should include direct comparison between the 300 kV STEM and 30 kV STEM conditions. Precursor solvent also can play a role, so another way to improve the WS_2 trials would be to use regular STEM imaging to evaluate different solvent systems prior to conducting in-situ STEM experiments using the expensive heating chips. This could also reveal details about the morphology of the precursor and ensure that it is homogeneous when initially deposited onto the chip. Lastly, there could be contamination during sample preparation which can be reduced by using a solvent that dries quickly or using an inert atmosphere during drying time.

Conclusions

WS_2 particles can be grown from the decomposition of ammonium tetrathiotungstate in DMF using in-situ STEM heating. The first experiment revealed that it is important that enough precursor get deposited onto the chip. It also led to testing at a higher temperature for a longer length of time to assess its impact on the formation of WS_2 sheets. In the second experiment the initial amount of precursor was increased by using a pipette to deposit the precursor instead of using the "paint brush" method. Secondly, raising the temperature to 1000 °C resulted in the unexpected formation of oxygen and carbon rich rope-like structures. Both experiments demonstrated the formation of WS_2 particles.

In addition to these findings, there are more experiments that can be carried out to improve the synthesis of 2D WS_2 using in-situ electron microscopy, like probing the effect of the voltage used and finding the optimal solvent system that reduces chances for contamination and allows for a uniform mixture that can be easily deposited on the chip.

CHAPTER 3

DESIGN OF IN-SITU EXPERIMENTS USING ELECTRON MICROSCOPY TO STUDY GROUP V TRANSITION METAL CHALCOGENIDES

Introduction

In 2010 the Nobel Prize was awarded to Andre Geim and Konstantin Novoselov for their ground-breaking research concerning graphene. Since their discoveries concerning the unique properties of graphene, there has been a spark in the interest of 2D ultrathin materials like the TMDCs. According to SCOPUS data beginning in 2012, there has been a large increase in TMDC-related publications, with molybdenum chalcogenides (MoS_2, $MoSe_2$, $MoTe_2$) being the most widely researched, as shown in Figure 11.[5]

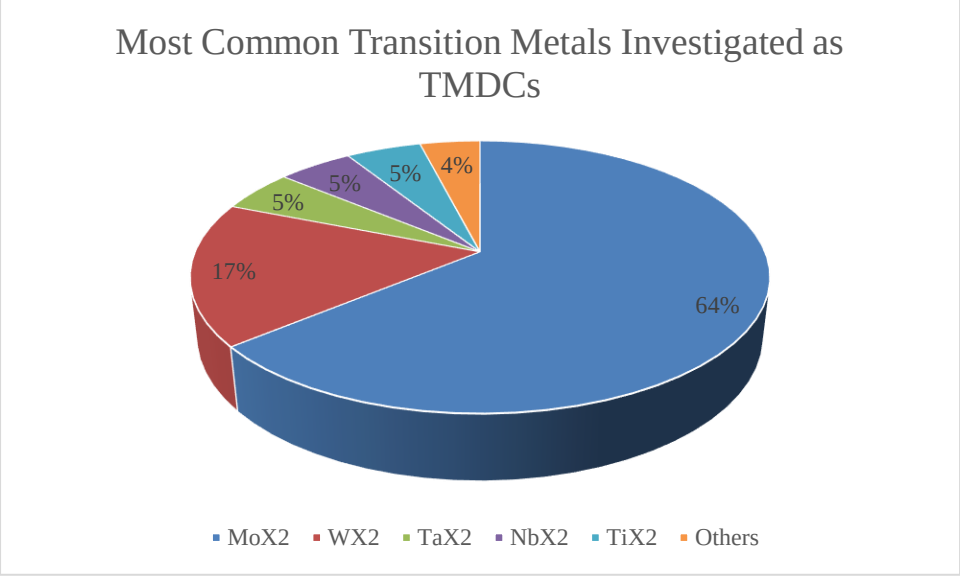

Figure 11: Chart of SCOPUS data from 2000-2017 reporting the most common transition metals being investigated as TMDCs. (Source SCOPUS, Elsevier B.V.: Amsterdam, The Netherlands)

Overall, MoS_2 is responsible for over half of TMDC publications followed by tungsten-based dichalcogenides leaving group V based TMDCs underexplored. Group V TMDCs have different properties when compared to their group VI counter parts. For example, many group V TMDCs have metallic or semi-metallic character, whereas most group VI TMDCs have semiconducting character. Further knowledge about group V TMDCs is not only important from an application standpoint but also in the developing more fundamental knowledge about the properties of 2D chalcogenide materials. Therefore, studies of their synthesis and dynamics are essential to revealing the full potential of group V TMDC materials. Here the focus is niobium disulfide.

Niobium Disulfide

NbS_2 is a layered material with four different phases: two that are stoichiometric and two that are non-stoichiometric. Both the stoichiometric (NbS_2) and non-stoichiometric ($Nb_{1+x}S_2$, where x is ~0.35) forms as the 2H and 3R polymorphs (Figure 1)[24]. The non-stoichiometric phase consists of excess niobium between the layers, is stable and can be easily synthesized by slight modifications of the CVD parameters due to its dependence on the pressure[25, 26]. In addition to the phases it forms, NbS_2 is a metallic dichalcogenide that displays superconductivity at transition temperatures of 1.7 to 6.3 K[27]. The non-stoichiometric phase can accommodate the intercalation of extra niobium between the layers which has been exploited for the use of cathode material in secondary batteries[26]. Furthermore, NbS_2 lacks an electron in the d bands giving rise to its unique magnetic and electronic properties[24]. This feature, coupled with its highly active basal-plane sites, has made it a potential candidate to replace current precious metal catalysts in the hydrogen evolution reaction (HER)[24, 28]. Its applications reach beyond the HER and extend to

a catalyst for petroleum purification, sensors and as cathode material[27]. Facile preparation of stoichiometrically stable NbS_2 nanosheets has prevented it from being widely studied. Also, it is difficult to control the number of layers and the thickness therefore a novel synthesis route for NbS_2 is needed to unlock the full potential of this metallic TMDC.

Sample Preparation

The sample preparation for an in-situ TEM experiment is important to reduce contamination and to optimize growth of the 2D material. Important aspects of the precursor are (i) that it can decompose to form the TMDC product within a realistic temperature range and (ii) its solubility in various organic solvents is sufficient for good precursor loading. Solvent choice is also crucial because the solvent should dry quickly at low temperatures during the setup/experiment.

When considering NbS_2, there are a few options for single-source precursors. One example is $[NbCl_4\text{-}(S_2\text{-}i Pr_2)][NbCl_6]$. This compound can be synthesized by the reaction of niobium pentachloride ($NbCl_5$) with diisopropyl disulfide in dichloromethane[29]. However, this precursor, has a low volatility and is easily hydrolyzed to form thin films of Nb_2O_5 and NbS_2, which is a potential short coming[29]. Studies for this precursor were conducted at 500 °C which resulted in a mixture of NbS_2 and the hydrolyzed product. Increasing the temperature of the experiment and conducting it in vacuum may possibly help form more of the desired NbS_2 product.

Using mixed solutions of $NbCl_5$ with either $S(SiMe_3)_2$, tBu_2S_2, *t*BuSH or $HSCH_2CH_2SH$ can form crystalline NbS_2 films[26]. The sulfur sources *t*BuSH, $HSCH_2CH_2SH$ and tBu_2S_2 show the formation of films at temperatures of 250 °C, 350 °C and 400 °C respectively indicating that

these precursors are extremely volatile and therefore not optimal to use for in-situ heating STEM experiments. $S(SiMe_3)_2$ begins to form the NbS_2 films at 600 °C lending this mixed solution to be the optimal for STEM experiments.

Another potential set of single-source precursors are derived from $NbSCl_3$ giving $NbSCl_3(S^nBu_2)$ and $NbSCl_3(nBuS(CH_2)_3S^nBu)$[30]. These precursors are good candidates due to their volatility and the presence of easily removable ^{n}Bu groups[30]. Product formation began at 700 °C for both precursors and both produced thin NbS_2 films with uniform morphology. There was no major oxidation by-product, and there was no evidence for residual chlorine in the films[30].

In addition to niobium disulfides, niobium diselenide films have been synthesized using the single-source precursor $NbSe_2Cl_3(Se^nBu2)$[30]. Films using this precursor were obtained in a temperature range of 600-700 °C. There was no detectable chlorine contamination which makes this precursor a candidate for in-situ S/TEM experiments.

$NbCl_5(Se^nBu_2)$ was synthesized by the reaction of $NbCl_5$ with Se^nBu_2 in dichloromethane and was developed as a single-source precursor for CVD[31]. Substituents with β-hydrogen atoms were selected in order to lower the lattice energy of the molecule, leading to a favorable volatility[31]. Product formation began between 600-750 °C giving rise to the 3R polytype $NbSe_2$ film. Small amounts of the Nb_2O_5 impurity were found but can be eliminated with careful exclusion of trace moisture. There is no evidence of a chlorine impurity.

Experiments using STEM

In order to use these precursors for in-situ S/TEM experiments, an appropriate solvent would need to be identified. Once a good solvent was confirmed, the precursor could be

dissolved and applied to the chip. Secondly, temperatures and hold times would need to be determined so that the films can be grown adequately. Knowing that the various precursors grow films between the temperatures of 500-700 °C, it would be suitable to steadily increase the temperature to evaporate the solvent and allow the NbX_2 (X= S, Se) films to grow slowly as the temperature rises. Another aspect to take into consideration would be by-products from the decomposition of the precursor and contamination from sample preparation. In addition the formation of hydrolysis by-product must be considered, requiring extra care when preparing the sample and instrument for the experiment. The chip would need to be prepared in an inert environment and experiment run in-vacuo. Using these parameters as guides, a NbX_2 (X= S, Se) film could be formed using in-situ S/TEM.

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