

THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

A PRESYNTHESIS METHOD FOR INDUCING SELECTIVE GROWTH IN TWO
DIMENSIONAL AND LAYERED MATERIALS

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SPRING 2017

A thesis
submitted in partial fulfillment
of the requirements
for a baccalaureate degree
in Chemical Engineering
with honors in Chemical Engineering

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ABSTRACT

Developing a process for inducing selective growth in two dimensional layered materials (TDLMs) will allow for direct and non-destructive shaping of thin film transition metal dichalcogenides (TMDs). The process discussed here within utilizes a substrate surface functionalization to inhibit TMD growth in very specific, selected areas. The polymer functional layer (PFL) employed is garnered from conventional photolithography processes and can be used for multiple different growth methods, substrates, and materials. This pre-synthesis functionalization allows for designation of lateral growth pattern, shape, and size of the material without the need for post-synthesis mechanical modification, which can damage material lattice integrity at the cutting interface, adversely affecting TMD transport properties. Utilizing the method will allow for inducing nearly 100% selective area growth of materials synthesized via chemical vapor deposition (CVD), enabling non-destructive shaping of said materials for usage in photoelectrics, photovoltaics, and field effect transistors.

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ACKNOWLEDGEMENTS

This research was conducted with use of facilities in the Millennium Science Complex provided by Penn State University and the Department of Materials Science. In particular, the labs of Dr. Joshua Robinson and Dr. Joan Redwing were utilized for experiments.

A large portion of the work was done in tandem with or furthered by Brian Bersch, Yu-Chuan Lim, Ganesh Bhimanapati, and Dr. Sarah Eichfeld. Special recognition is extended to Dr. Sarah Eichfeld for being the primary advisor/overseer of the project and lending direction, advice, and support throughout the process.

Additionally, special thanks is given to the assistance and advice from Max Wetherington, Tanushree Choudhury, Zak Al-Balushi, Xiaoten Zhang, and Dr. Joshua Robinson.

Chapter 1

Introduction

Transition metal dichalcogenides (TDMs) are of interest for their potential use as semiconductors in electronic and optoelectronic devices. This is in particular due to their direct band gap of 1.65 eV when synthesized with monolayer thickness¹. Additionally, via heterostructure layering, the band gap can be refined to achieve a broad range of desired band gaps, which enables many new electronic applications^{1,2,3,4}. Furthermore, these materials are inherently nanoscale and can carry large amounts of current, which makes them interesting for use as the channel material in transistors (to potentially replace silicon)².

Many synthesis techniques exist which can be utilized to grow the two dimension materials, from powder vaporization, to epitaxial growth and chemical vapor deposition (CVD)^{1,6,7,8}. The latter has been found, in particular, to be highly scalable and very effective for formation of large, consistent, and device-ready monolayered films¹. Through manipulation of temperature, pressure, growth time, precursor flow rates, and substrate type, the size and quality of the materials can be optimized to provide for the appropriate/desired characteristics¹.

While growth techniques have been extensively explored, achievement of full selectivity has long been sought after. Most procedures, though resulting in high quality material, have no means for shaping said films. As the commercialization of such materials require that they can be modified to very specific shapes and sizes (image the intricacy of a circuit board), mere general growth is unacceptable on its own. Multiple methods have been researched for providing a solution to this general-growth problem, from channel confinement to reactive etching^{9,10}. These,

however, fail to provide for an easy and 100% selective material creation without needing extensive modification of synthesis processes, or do not allow for the retainment of material integrity on at all locations.

The following sub-chapters highlight the specific material synthesized, growth techniques, and selectivity procedures, respectively, in more detail.

Tungsten Diselenide

TMDs are atomically thin (~one atom of thickness) semiconductors which exist in the form MX_2 ; M is a transition metal (such as tungsten, molybdenum, etc...) and X is a chalcogen (sulfur, selenium, or tellurium). The general form of the thin material lattice formed by these materials can be seen below, in **figure 1**.

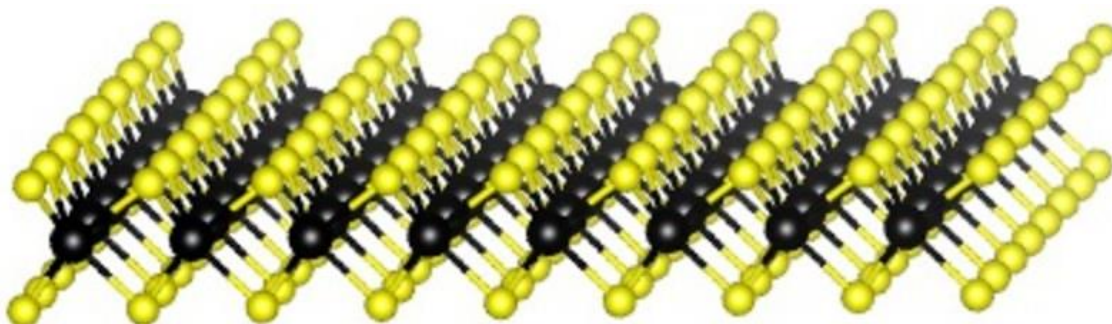


Figure 1: Illustration of typical TMD material lattice. The black atoms represent the M, while the yellow represent the X in the MX_2 form of TMD.

Though several TMDs are currently being investigated in an array of projects in our lab, tungsten diselenide (WSe_2) was the primary one utilized in this thesis' experiments. WSe_2 , like all TMDs, is useful due to direct band gap, extreme thinness (and therefore light weight),

absence of dangling bonds, and P/N junction type reversibility (achieved via doping by electrode)^{1,11}. Through heterostructural layering, as previously mentioned, tunable band gaps may be achieved, allowing for a variety of control on different devices made of this material. Further, it has application as an LED material, since, due to the p/n reversibility and band gap modification, multiple different colored LEDs could be made from the same material¹.

WSe₂ is also highly efficient with respect to charge transferring, able to conduct charge carriers at very high speed^{1,2}. In fact, the efficiency related to WSe₂ electron-hole transfer, when set in a p/n MoS₂/WSe₂ heterojunction is as high as 99%, furthering the assertion that it is an ideal material for many electronic related uses^{2,3,4}.

The potential for large scale commercial use of these TMDs in general, and WSe₂ in particular, provided the direct motivation for the achievement of selective growth. As the material is in line as a primary candidate for use in highly efficiency electronics, physical shaping of its boundaries becomes very important in terms of implementation feasibility.

Synthesis Details

There are many synthesis techniques currently used to grow high quality TMDs. This section will highlight an overview of the three most commonly used general fabrication methods: exfoliation, molecular beam epitaxy (MBE), and chemical vapor deposition (CVD). It should be noted that all methods do indeed result in monolayered TMDs, but each have their own advantages and disadvantages when compared with the other methods.

Mechanical exfoliation is a comparatively rudimentary method of achieving atomically thin TMDs. This method involves having a bulk form of the desired TMD material and

physically removing thin layers via adhesive tape. This removed layer is then deposited by the tape onto the desired substrate. This, like with graphene, works because the individual layers in bulk form are held together only by van der Waals forces, and this attraction is not as strong as the bond between M and X, allowing the micro cleavage to yield a desired monolayer thickness TMD. The advantage of such a method is in its simplicity. Assuming the bulk material has already been obtained, generating the thin film TMD is simply a matter of using tape; no complex reactors, dangerous chemicals, or high temperatures/pressures are needed. This makes it useful when material is simply needed to be studied, but it lacks the appropriate control needed for usage on large scale production and subsequent application. Uniformity can not necessarily always be achieved, and no control over general size/shape can be implemented with this method¹².

MBE provides for a larger amount of control, yet, expectedly, increases the complexity of the process. MBE functions by heating the substrate of use to high temperatures ($\sim 600^{\circ}\text{C}$) in near vacuum and, via effusion cells, ‘shooting’ beams of gaseous atoms (one with M, one with X) onto the surface of the substrate. The molecules condense once on the substrate, and slowly coagulate together on the surface, forming layer by layer of the desired material. A general schematic of this process can be seen on the next page, in **figure 2**.

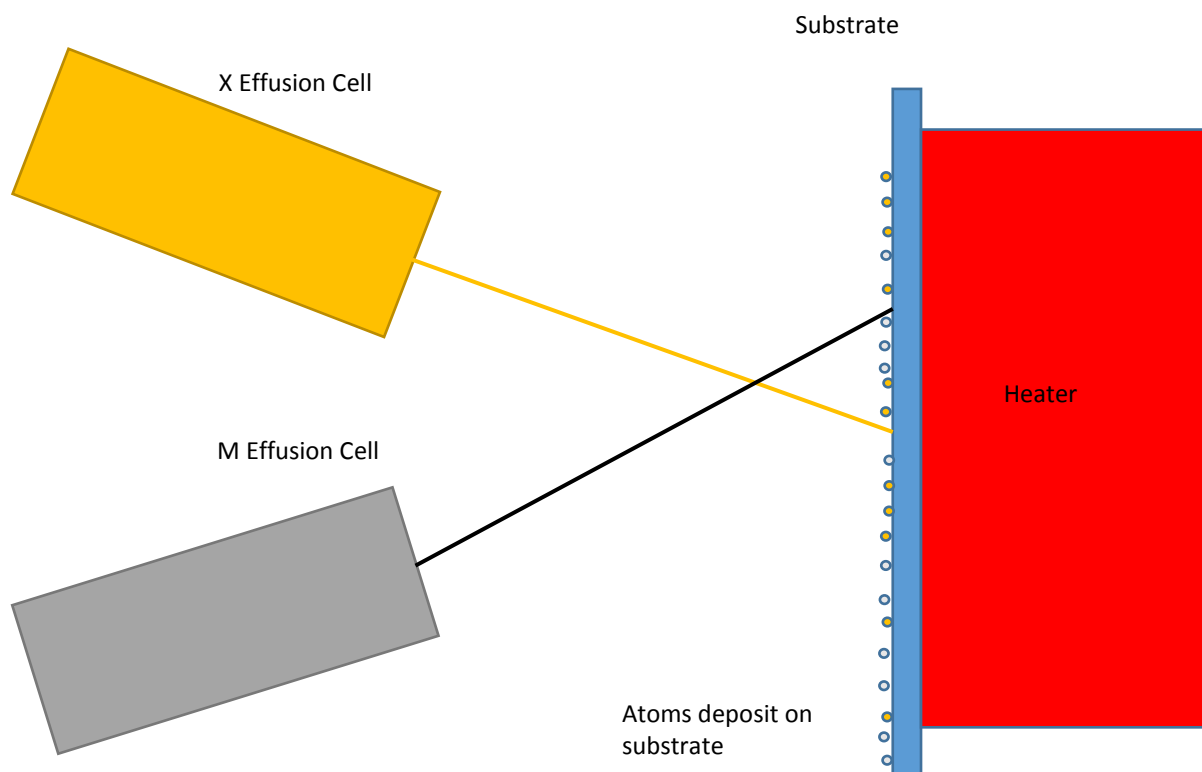


Figure 2: General schematic of MBE process. Illustrates the deposition of atoms to form the thin TMD

While this method obviously requires a special system designed specifically for this purpose, the resultant control afforded is a major advantage. Exact temperatures, pressure, and run time can be monitored and modified to allow for optimization of the process. Such parameters can be tuned and therefore material quality can be controlled and tested repeatedly. Additionally, because the process works inside of a vacuum chamber, a large degree of cleanliness is introduced by utilizing this method, in comparison to mechanical exfoliation. This effectively eliminates the chance for particulates to fall on the surface and interfere or distort the synthesis process, and ensure that the synthesized material lattice contains relatively few

impurities and contaminants. Since even a dust particle could cause a significant amount of interference, this is a huge advantage^{5,13}.

The last synthesis method to be discussed is CVD. Though not *solely* used for thin films, CVD is commonly used in the semiconductor industry to produce the desired TMDs. In general, this method has been shown to provide for excellent material quality, and largely controllable, highly scalable, synthesis¹. It functions by allowing volatile precursor materials, often delivered via carrier gas, to react and deposit onto a substrate in a heated reaction chamber to produce the desired thin film. A general schematic can be seen below, in **figure 3**.

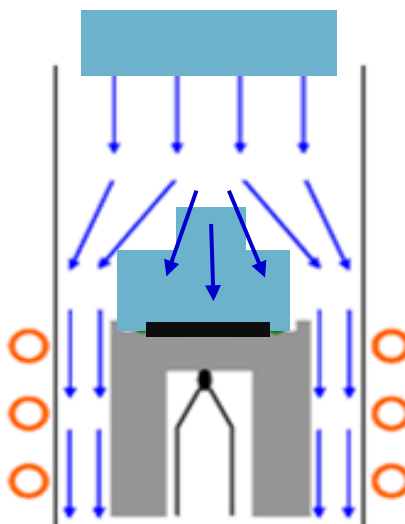


Figure 3: General schematic of CVD process. Blue lines indicate gaseous flow of precursor materials and carrier gas flowing/depositing over and near the (black line) substrate

The major advantage of this method is, in addition to its commercial scalability, its allowance for process control. The user has the ability to determine growth temperature, growth pressure, growth time, exact M/X ratio (by tuning the carrier gas rate and vapor pressure of precursor material bubblers), overall flowrates, and cooling time. Though this creates a lot of

potential variability, with so many different alterable parameters, it also allows for a great deal of optimization potential. Since all parameters directly impact the type of growth achieved, each can be altered to find the set of inputs which return the best quality, and largest quantity of desired TMD. It is for these reasons that this experiment utilized this synthesis method as its basis for material fabrication. It is, thus, described in greater detail in the “Methods” section of this report¹.

Current Selectivity Methods

Selectivity, for the purposes of this report and in general, refers to the ability of the user to grow/synthesize the desired TMD specifically in some predetermined regions and have total inhibition of growth in the other regions. With this, the user can *select* the shape/size/pattern they want their material to be grown, which lends itself to many possibilities.

The desire for a method to introduce this selectivity in the synthesis process for TMDs is not a new one. With most of the promising applications for TMD implementation dealing with electronics or photovoltaics, the need for finely shaped and sized materials is a barrier to use in mass production. Circuitry, transistors, LEDs, etc... all require intricate electrical work to function properly and also need to fit in with all other components of a system that they are connected to. Because of this, they must have specific shapes and sizes to fit appropriately in these applications and, thus, there has already been a great deal of research into methods that can provide said selective growth of the TMDs.

The first existing process analyzed was the use of confined channel growth of gallium nitride (GaN) on silicon dioxide (SiO₂) (Leung et al). This process utilized a literal channel to

physically confine the areas in which the desired material could grow⁹. This method, though technically capable of confining growth to a specific area, was insufficient for use in TMDs for a few reasons. The primary reason is that the channel design confines the growth in such a way that it can only continue in one direction. As seen in **figure 4** (Leung et al), the growth can essentially only be selectively set in a single, one dimensional direction: straight forward.

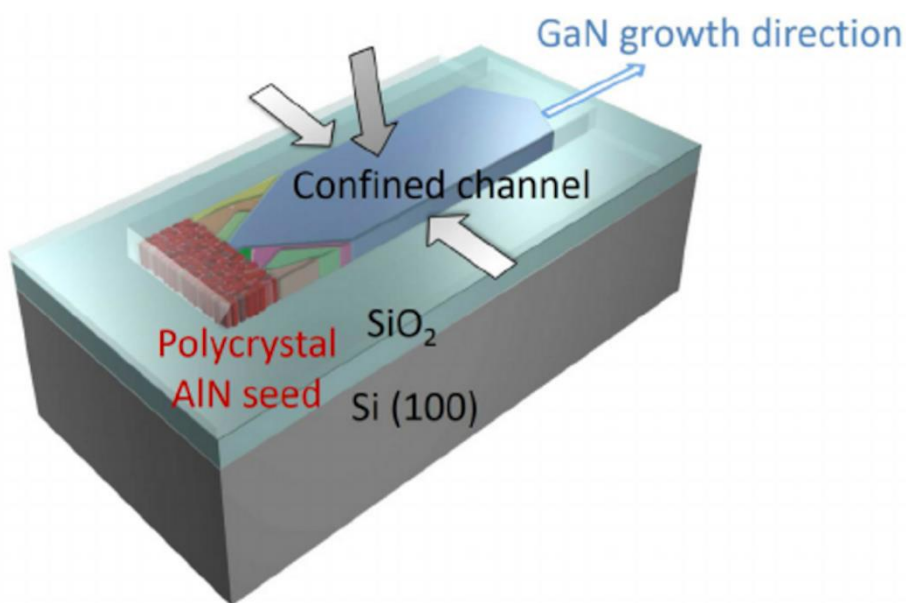


Figure 4: (Leung et al) Graphic depicting the selective area growth achieved by the confined channel. Note that growth can only continue straight forward, confined sideways.

The process also needs to have a defined starting point, set with the polycrystal AlN seed viewable in the figure. Further, the channel has a depth, meaning that it is confined on the top side. Not only would this not work with the general CVD process, it would not yield the one atom thick layers desired for TMDs.

Another process analyzed was the use of selectively etching the grown material with a potassium hydroxide (KOH) solution, post synthesis¹⁰. As with the previous method, there are

some issues (and it should be noted, this was performed with GaN in a specific configured, truncated pyramid, not a TMD). Chen et al demonstrated that the use of wet etching the already-grown GaN would etch the “N-polar side walls, while leaving the Ga-polar top surface intact”⁷. This technically works as a method for achieving selective growth in general, but fails for usage with TMDs for a few reasons. The primary issue is that it is a post-synthesis method. The process functions by selectively etching an already grown material. Even ignoring the fact that it worked very specifically with GaN, we sought to develop a pre-synthesis method to avoid damaging material integrity/transfer properties. This meant expressly avoiding any physical method of alteration to the material after it had been synthesized.. Further, the KOH selectively etched the side walls and left the top unaltered. This is really not possible for a one atom thick TMD. There is hardly a distinction between the sides and top of the material lattice in terms of height, and so this method (even if a post-synthesis method had been desired) would not have worked. This type of process, therefore, was insufficient for the desired result.

The use of an absorbent as a directing agent was also researched. Lu et al reported achieving selective growth of $W_{18}O_{49}$ nanowires by utilizing polyethylene glycol as structure defining compound¹⁴. At first glance, this appeared to be potentially useful as process that could be used for TMDs. The issues of the previous papers (one dimensional growth restriction and post-synthesis implementations) were absent. However, upon closer inspection, this process, too, was unfit for usage as a TMD selective area growth promoter. The primary issue was due to the synthesis process involved with the $W_{18}O_{49}$ nanowires. They were fabricated utilizing a solvothermal process, with which the polyethylene glycol could draw synthesis to due to selective absorption to the growing crystals. This is plainly an entirely different process from CVD and such a method would most likely not be transferable. Additionally, introducing a new

agent (polyethylene glycol or similar) would likely alter the deposition process in the CVD reaction chamber; significant effort is exerted (see “Methods”) to keep the system free of contaminants and to ensure the only species present during synthesis are precursor materials and hydrogen. This new species would, therefore, likely cause problems.

Another paper looked at, interestingly enough, did not even deal with selective area growth as a goal. Rather, Lloyd et al explored the usage of surface functionalization as a method to attain a desired result. Specifically, they utilized UV photodecomposition of their substrate of choice (zinc acetate) to promote a seed layer for the growth of zinc oxide (ZnO) nanowires¹⁵. The paper was of particular interest because of the usage of UV light to induce surface functionalization. It was strikingly close, though very different in terms of desired result, to the method presented in this paper. Though this report utilized the UV light remove a polymer which caused the functionalization in certain areas, it was useful to analyze other processes that took advantage of changing surface chemistry to effect the synthesis of a desired material.

These processes analyzed, though novel and useful in their own right and for their own goals, were lacking in several different areas and did not satisfy the need for a simple, easily-integratable, pre-synthesis method for inducing repeatable, high quality, user desired selective growth of any shape and size in an industrially scalable synthesis process. Thus, we sought to find one.

Chapter 2

Methods

The utilized synthesis method, as previously described, was metal organic chemical vapor deposition (MOCVD), in which two bubbler-held precursors (dimethyl selenium (DMSe) and tungsten hexacarbonyl ($\text{W}(\text{CO})_6$)) were reacted for a prescribed amount of time at around 500°C to form the desired monolayered tungsten diselenide (WSe_2).

The process began with the cleaning of double side-polish sapphire substrates to remove unwanted particulates from the surface of the material. A roughly $1\text{ cm} \times 1\text{ cm}$ square was mechanically cut from a large wafer using a diamond scribe. These pieces often looked like small shards of glass, as can be seen in **figure 5**.

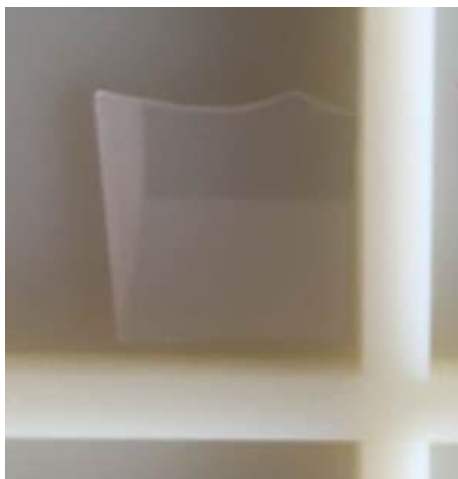


Figure 5: Image of a standard $\sim 1\text{ cm}^2$ sapphire substrate. Note the edges are not perfect as diamond scribe cleavage is not exact.

The general schematic of the overall cleaning procedure can be seen below, in **figure 6**.

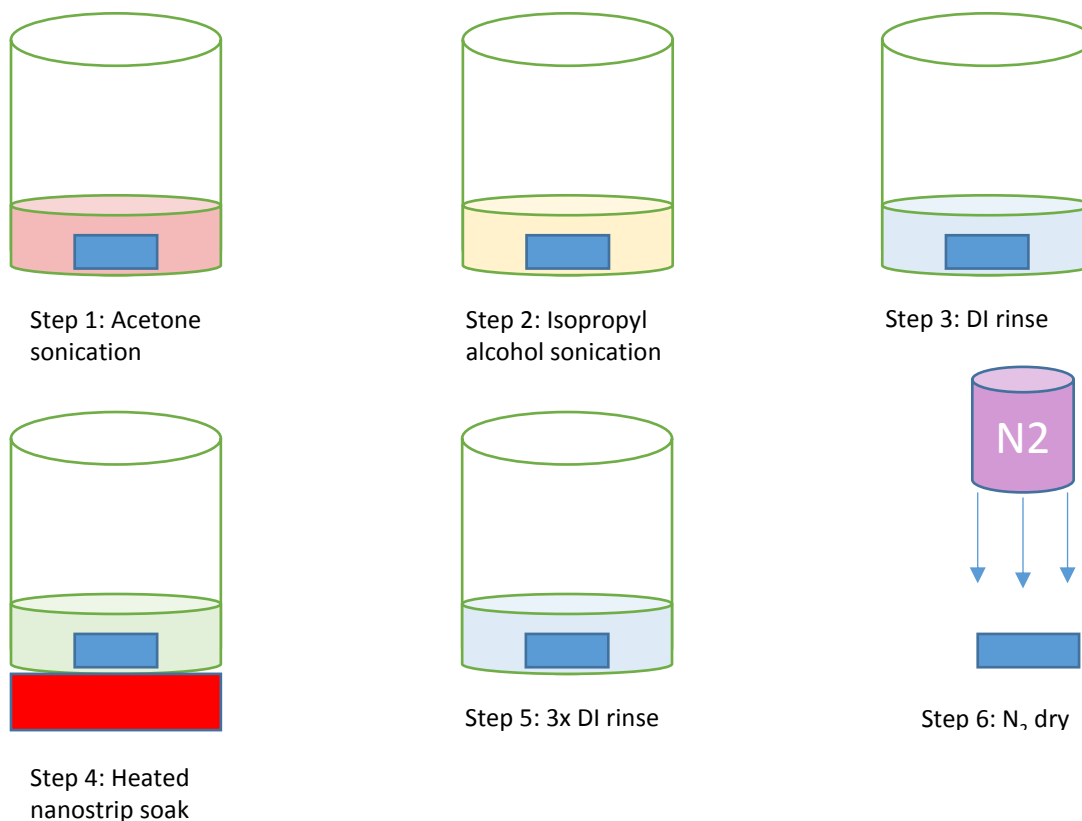


Figure 6: General cleaning process schematic. All sonications were 10-15 minutes

The piece, often with (1-4) other pieces, was placed in a container with acetone and sonicated for 10-15 minutes. This was done to remove any organic substances, including oils, and dust particulates from the surface, which can interfere with the synthesis process. The pieces were then placed immediately into a different container containing isopropyl alcohol (IPA) and sonicated again for 10-15 minutes to remove the acetone (specifically preventing dried acetone from remaining on the surface). The pieces were further placed in deionized water (DI) and sonicated again before being placed in a nanostrip solution at 80°C and left for 10 minutes to allow for removal of all remaining containments. Finally, the pieces were repeatedly DI rinsed

and blow dried with an N₂ gun to complete the cleaning process. Samples were eyed to ensure that no organic residue was left over on the sample, which could potentially happen if acetone was allowed to dry before being submersed in IPA, among other ways.

Following the cleaning procedure, and cleanliness verification, the samples were run through a standard lithography process to introduce the surface functionalization needed to inhibit the growth in the desired regions. After a 5 minute O₂ reactive ion etch, the samples were spun with photoresist. They were subsequently exposed to UV light through a mask and chemically developed to remove the resist from the exposed regions, leaving behind a PFL. It was this mask which allowed for the creation of any desired growth pattern achieved later during synthesis. As the mask could conceivably be in any shape, this lent itself to allowing the user to create any desired pattern. To further remove the residual polymer from these exposed regions, the samples were treated with an O₂/He plasma. These regions were now clear of all leftover polymer and were therefore ready to contain the growth. Finally, the unexposed regions (as of this point, not cleaned) were treated with a photoresist stripper and then rinsed with isopropanol and deionized water. This process resulted in a ~2nm thick polymer/functional layer on top of the UV unexposed regions of the sample, which was ultimately the responsible mechanism for inducing the selective growth by inhibiting nucleation/synthesis in the regions covered with the residual polymer⁸. A general diagram of the process can be seen on the next page, in **figure 7**.

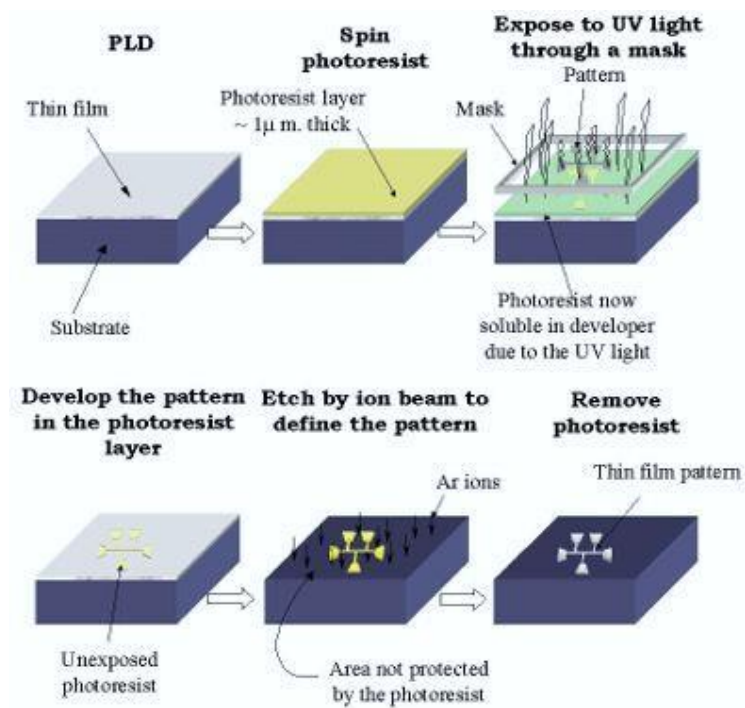


Figure 7 : General schematic of the photoresist lithography process utilized to leave the growth inhibiting polymer layer in desired regions. Note that this schematic does not show the reactive ion etching or plasma steps involved.

To prepare the system for the forthcoming synthesis process, a hydrogen bake was routinely implemented directly beforehand. The system was purged of oxygen and sealed off from the environment. After flushing the reactor chamber with hydrogen, the bake was performed at high temperatures (900°C) at low pressure for ~30 minutes. The purpose of this was to rid the system of any residual precursor chemicals (potentially from previous growth runs) and expel any moisture that may have built up in the chamber or on the side walls of the quartz liner tube used to house the system. Both of these potential contaminants would negatively affect any subsequent syntheses and were necessarily cleared before each run.

It should be noted that though baking was certainly effective and done prior to each run, it was not sufficient on its own to continuously keep the liner tubes themselves perpetually clean. As a result, the liner tubes were periodically replaced with clean ones to reduce contamination. The dirty ones were left in a nitric acid solution, often overnight, to break down the selenium and tungsten deposits on the sides. Following the nitric acid soak (and shaking), they were rinsed several times with DI water, dried with an N₂ gun and then set aside on a clean cloth for the next rotation.

With the functionalized surface ready to inhibit growth, due to the residual layer resulting from the afore described lithography process, and the system cleared of previous contaminants, the substrates were loaded into the reaction chamber on a graphite crucible. After pumping the system to get rid of oxygen (which could potentially reacted with the precursors at high temperatures) and purging multiple times with inert nitrogen, the system was brought to ~750 torr in hydrogen and raised to the desired growth temperature over a designated period of time (often 15-30 minutes to ensure controlled ramping and avoidance of overshooting, which could potentially alter conditions at growth). The temperature ramping was achieved through coupling of the graphite crucible with the heating coils on the outside of reaction chamber; a picture of this system can be seen, on the next page, in **figure 8**.

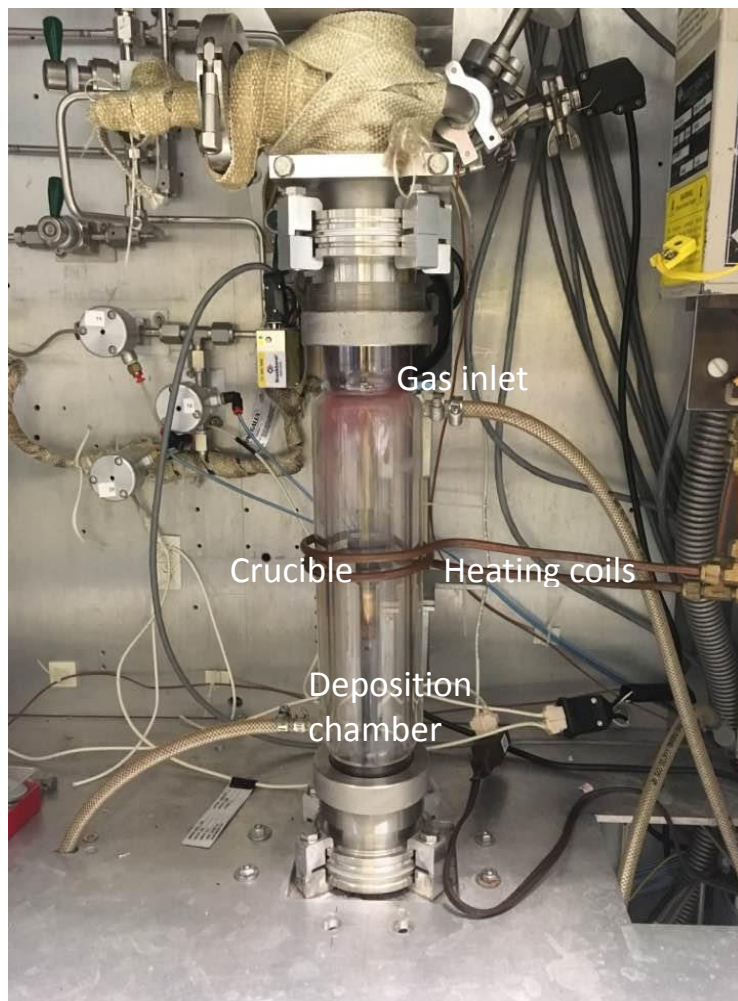


Figure 8: Picture of the reactor chamber of the CVD system (bubblers not pictured).

Note the heating coils on the outside of the containment chamber. One can see the graphite crucible resting on top of its stand right around the height of the coils.

Once the desired temperatures stabilized, the precursor bubblers were opened. Hydrogen, utilized as a carrier gas, was sent through each bubbler to carry small amounts of each precursor into the reaction chamber. (Each bubbler was held at a specific temperature to ensure the vapor pressure within would provide the appropriate amount of each chemical to be carried by the hydrogen passing through.) Once in the reaction chamber, the precursors were “cracked” by the

high temperatures, releasing the elemental W and Se into the system and allowing them to deposit on the sapphire substrate held on the heated graphite crucible. Nucleation sites formed over the surface and the lateral growth of the material began. This continued until the allotted growth time passed, at which point the bubblers were closed. A general schematic of the reaction chamber can be seen below, in **figure 9**.

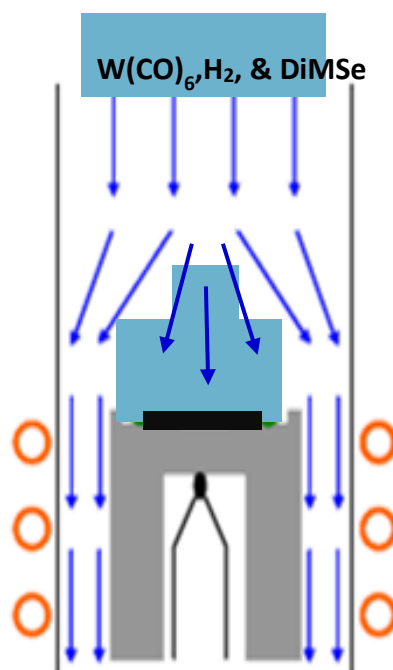


Figure 9: A general schematic of the reaction chamber, showing the hydrogen gas carrying the two precursors over the heated crucible/substrate where they deposit to form monolayered WSe₂.

The system was allowed to cool from the growth temperature to the safe-to-open room temperature. After inducing positive pressure via nitrogen flow (to prevent oxygen from entering the chamber) the samples were removed and immediately placed in tight plastic containers,

which were themselves placed in a nitrogen box, to prevent oxygen induced material degradation. Each sample was left in this level of containment until ready to be characterized.

To ensure correct material synthesis, as well as achievement of expected selectivity, several characterization methods were utilized. The first of these was atomic force microscopy (AFM), which was used for topographical/visual analysis of grain size, shape, and pattern. Secondly, scanning electron microscopy (SEM) was employed to gain finer detailed images of the surface and look closely for selectivity boundaries and quality. Raman spectroscopy was implemented to identify chemical compounds via identifiable fingerprints to ensure appropriate species were present. Photoluminescence (PL) was also used for layer thickness analysis, to ascertain whether or not the film had been synthesized in the desired 1 atom deep thickness. The combination of these several characterization methods allowed for proper analyzation of the process' effectiveness and repeatability.

Chapter 3

Results and Discussion

After conducting the experiments and completing their subsequent sample characterizations, it became evident that the method designed was able to reliably and consistently provide for selective growth of WSe₂ on sapphire.

The first method used was atomic force microscopy (AFM) which provided a topographical map of the sample surface. This data was multifaceted. Not only did it very clearly outline if the material had been grown selectively, as a distinct barrier between growth and inhibition was visible, but it also provided insight to individual grain size, particulate count, and, via Nanoscope software analysis, material height (which could be used to confirm monolayer thickness). A specific example of such an image can be seen in **Figure 10**, below.

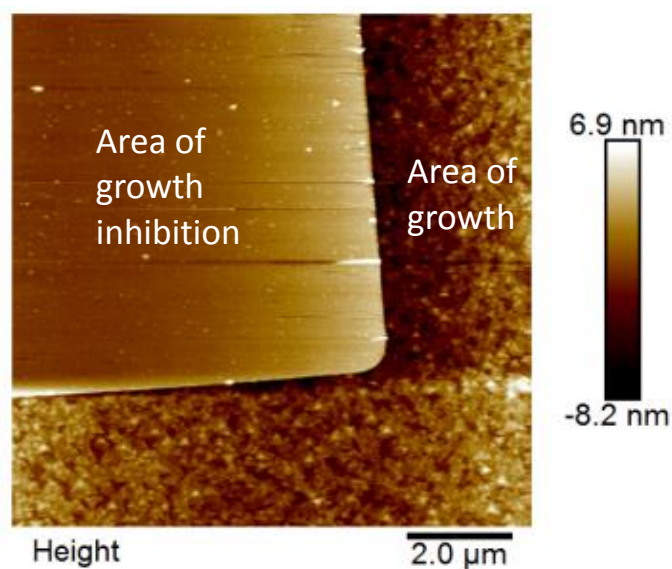


Figure 10: AFM image of WSe₂ (the small triangular grains) on a sapphire substrate. Note the clear definition between the clear area of growth inhibition and that of growth.

As shown in the figure, the distinction between the area of synthesized material and the area of inhibited growth afforded by the surface functionalization is clear and defined. The specific reason for the difference in height (the image shows the inhibited area as significantly higher up than the growth area) is due to a specific set of trench etchings into the sapphire's surface. This is because the initial purpose of the experiment was to induce sidewall synthesis; however this trench etching was immediately found to be unimportant in the selectivity process (once the surface functionalization was identified as the source of inhibition) and all subsequent growth runs/lithography processes did not include this.

As it is difficult to see in **Figure 10**, the specific triangular shape of the individual WSe₂ grains is shown up close below in **Figure 11**. Note that **Figure 10** contains a large amount of densely packed grains which harder to differentiate in the zoomed out image.

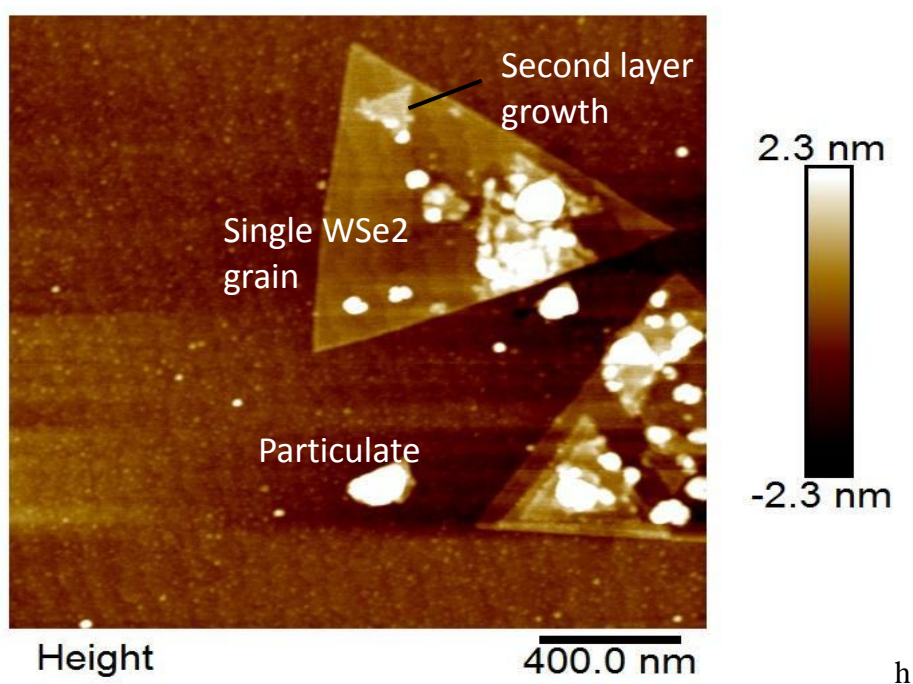


Figure 11: AFM image close up of the individual triangular WSe₂ grains on sapphire substrate. The high elevation (white) dots are random particulates on the surface.

The image in **figure 11**, it must be noted, is not from a selective growth sample and serves purely to illustrate the general size/shape of the WSe_2 as grown. In all selective growth samples, these triangles are what make the regions of growth. It is important to note, as well, that the vertical nucleation present on the grains that was common in most samples. Both triangular grains contain other, smaller, triangles on top of them which lead to additional layers of material being grown on nucleation sites on top of already synthesized grains. This was not ideal as these added layers move the material farther away from its two dimensional (and thus direct band gap) state. Work has, and continues to be done, to eliminate this vertical growth.

To further analyze this growth/inhibition boundary, and to ensure its consistency and reliability, samples grown in the aforementioned manner were also run under scanning electron microscopy (SEM), which could provide an additional, more defined/higher resolution, visual of the sample surface. The excellent degree of selectivity can be seen below, in **figure 12**.

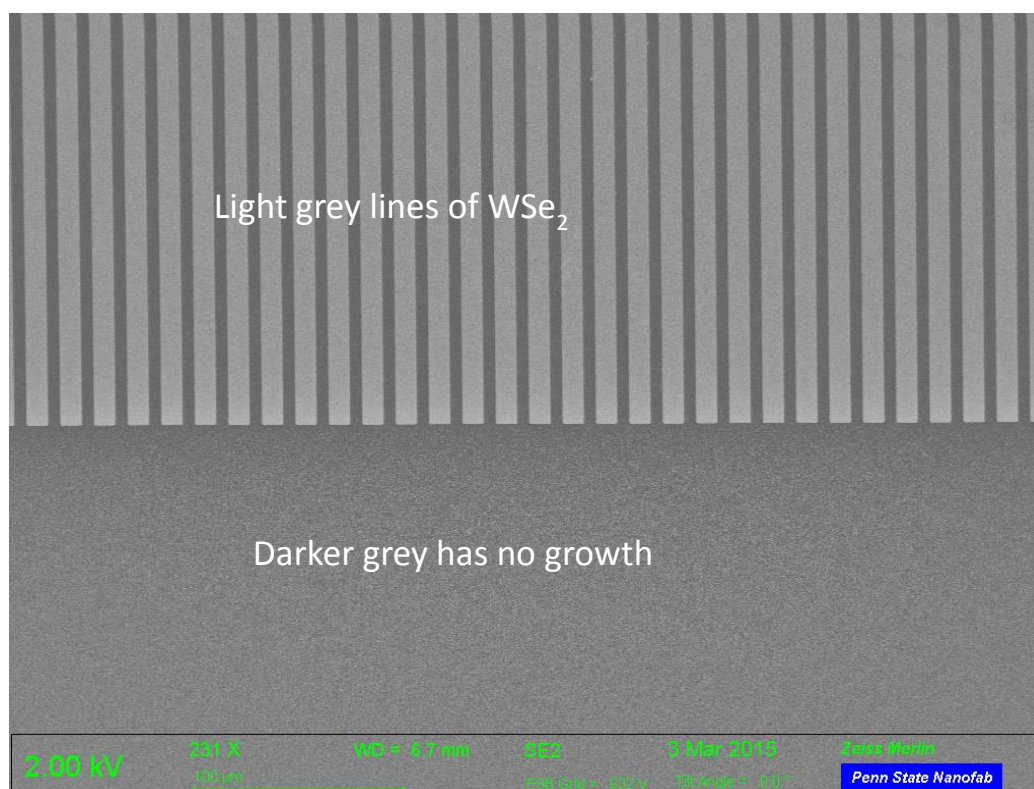


Figure 12 (previous page): SEM image of a selective growth sample. The lighter grey lines indicate areas of growth, while the darker lines show areas of inhibition.

The figure, though clearly indicating the selective nature of the sample, highlights a minor problem with the technique that still needs to be resolved. The functionalization of the surface via the photoresist residue is clear and works well towards the top of the sample (where the vertical lines are). However, towards the bottom of the sample the growth becomes indiscriminant. This area was also functionalized to inhibit the growth, but a smattering of growth appears. The WSe_2 in this region is thin, relatively spread out, and not particularly uniform. This issue arose in regions farther away from the functionalized/non-functionalized boundaries (such as the vertical lines in the figure) and resulted in indiscriminant smaller amounts of nucleation/growth in these areas. This still must be worked on.

The areas where the boundary was distinct, as previously discussed, and well defined.

Figure 13 shows an SEM image of this area up close.

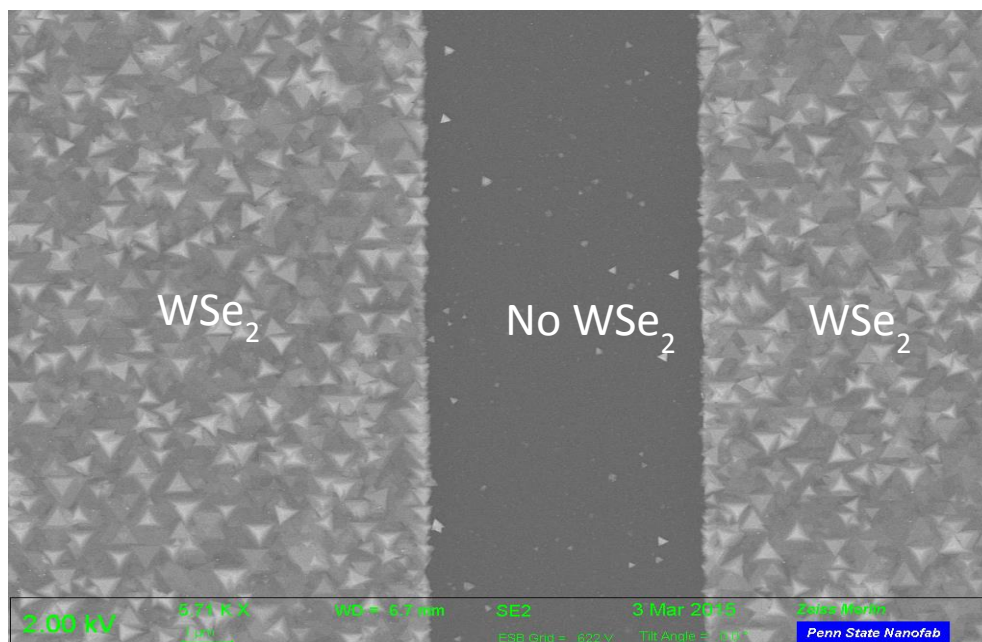


Figure 13 (previous page): SEM image of boundary between growth (non-functionalized) and inhibition (functionalized) region

Though there is a *few* WSe₂ grains located in the region of inhibition, the straight borderline between the two regions is sharp. The vast majority of growth can clearly be seen on either side (left or right) of the darker region down the middle. The stark difference between the regions furthers the assertion that process works as intended and can be used (in any shape, size, or orientation) to achieve pre-synthesis specified regions of nucleation.

Lastly, each sample was characterized using Raman spectroscopy and photoluminescence (PL). Raman spectroscopy could be used to define a fingerprint of the materials on the sample, through which the specific species could be identified. Though it is highly unlikely that any other triangular shaped material could possibly have been synthesized, Raman was utilized to make sure that the synthesized species was indeed WSe₂. Additionally, it could be used to identify which functional groups were present in the inhibition designated region, specifically left over from the photolithography process. The figures on the following page indicate the Raman spectroscopy results run on samples in the growth region, and spectroscopy results in the inhibition region.

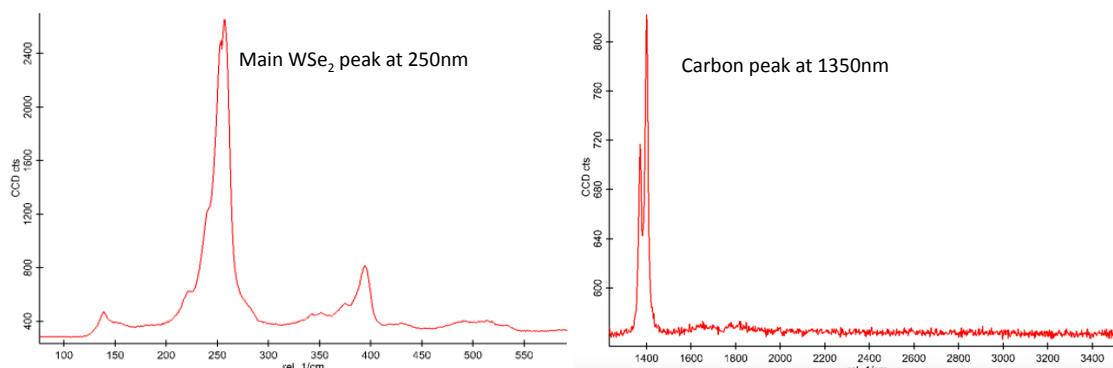


Figure 14: (Left) Shows a Raman spectrum of a sample. Notice the main WSe₂ peak located at around $\sim 260 \text{ cm}^{-1}$. (Right) Shows a Raman spectrum of a region of inhibition. The peak at 1350nm is an indicator of the carbon-based polymer residual layer

The figure illustrates, chemically, the stark contrast between the growth/inhibition regions on the sample surface that SEM and AFM confirmed visually. The WSe₂ peaks were present, as expected, in the growth region but notably absent in the inhibited/functionalized region. Similarly, the carbonyl (C=O) functional group resulting from the residual polymer layer from the photoresist, and ultimately responsible for the growth inhibition on the surface where desired. This data, in particular, largely led to the verification that it was indeed the carbon based functionalization of the surface which directly led to the WSe₂ inhibition and not some other mechanism.

The PL conducted also provided some important conclusions. Though it was already clear with the other characterization methods that selective growth had been achieved, it was important to make sure that the desired product material was still synthesized to yield the correct parameters. Chief of these was the requirement that the WSe₂ film was at or around one layer depth, to take advantage of the aforementioned direct band gap at this thickness; even entirely perfect selectivity would have been unusable had the material not come synthesized one atom

thick. Though the AFM analysis could give general depth based on the topography, to ensure that direct band gap was consistently achieved, PL was utilized. The peak (figure unavailable) was located at $\sim 750\text{nm}$, which ensured the band gap was direct and therefore the material still functioned appropriately.

Chapter 4

Conclusions

With all characterization results verified over several different samples, it became clear that the process did indeed work as expected and could provide for any selective growth pattern that the user desired. Additionally, the synthesized material (WSe_2) remained functionally sound, keeping its desired band gap property and remaining at around 1 atom thickness. The method also hardly introduced any additional steps, the few of which were not complicated and did not require alteration of the actual synthesis process. Only a small lithography step, implemented before growth, was required to provide the desired result. Due to the simplicity associated with the process, the ease of implementation (no alteration of synthesis method), the inexpensive nature of its use, and, most importantly, the method's effectiveness, the facile route to the selectivity could be used in a vast amount of synthesis processes currently utilized in the two dimensional realms of research and product development. The high quality selectivity would allow for synthesis of like materials in any orientation/shape, which would be hugely beneficial in circuitry applications, for example, and serves to only further the feasibility of usage of such materials in similar fields.

Chapter 5

Future Work

Though the process was shown to work repeatedly and effectively with WSe₂ on sapphire substrates, more work needs to be conducted on different TMD/substrate combinations. For example, some work on epitaxial graphene (EG) was briefly investigated before it was determined that, without modification, the process did not work on this substrate. This is probably due to the fact that the plasma etch damages the surface of the EG, creating non-homogeneity in the surface morphology, which interfered with the general nucleation process for the TMDs. This part of the process is not a problem with sapphire substrates as the etch merely cleans the sapphire, but would require some modification to work on other substrates like EG and those similar.

Work has also been done other TMDs (chiefly MoS₂, molybdenum disulfide) but this was not included in this report as it was done after my involvement in the project. It should be noted, however, that the process showed high quality results with this material as well (though, still, only on sapphire) and could be extrapolated to work with other common TMDs. These, though, do need to be more fully investigated and will be in the future.

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Publications

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Awards & Scholarships

Dean's List- 2013-2017

Penn State Millennium Scholarship

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Hispanic Scholarship Fund Scholarship

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Inventors Incentive Award, PSU IDN 2015-430