2D-1D Semiconductor Heterostructures: Synthesis, Characterisation and Optoelectronic Applications

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1. Abstract

2D materials have become very popular in recent years in the electronics industry. This is due to the unique properties of a 2D material compared to its bulk form. In my project, Chemical Vapour Deposition (CVD) is used to fabricate 2D Transition Metal Dichalcogenides (TMDs) on either a Sapphire or Silicon dioxide (SiO₂/Si) substrate. The characteristics of these TMD flakes are studied through the use of different techniques. Raman Spectroscopy is used to identify the TMD. Photoluminescence Spectroscopy helps determine its bandgap. Atomic Force Microscopy allows me to study the morphology of the TMD flake. Fluorescence Microscopy helps determine the specific areas of fluorescence on the TMD flake. This is followed by a manual stacking of a Cadmium Selenium Sulfide, CdS₀.₈Se₀.₂, nanowire. This forms a heterostructure junction. This junction is made into an optoelectronic device. Lasers of different wavelengths were incident upon the junction through global irradiation and the photoelectrical properties, such as Photoresponsivity, External Quantum Efficiency (EQE) and Photodetectivity, were studied using graphs of current against voltage (IV) and current against time (Ivst).
2. Introduction

Many 2D materials have been used as the building blocks for electronic devices all over the world. A lot of research has been done in recent years to study the properties of these 2D materials. Some examples of these 2D materials are Graphene, Boron Nitride and Transition Metal Dichalcogenides (TMDs).

However, many of these materials face difficulties in being used in optoelectronics. Graphene for example, has a zero bandgap\(^1\). Although this means that the conductivity of graphene is excellent, it also implies that the charge carriers do not have any significant large excitations or relaxations to absorb or emit fluorescence or PL. Boron Nitride on the other hand, has a bandgap that is too large. The bandgap is 5.97eV\(^2\), which corresponds to a wavelength of 208nm, which is in the ultraviolet range of the electromagnetic spectrum. This large bandgap causes boron nitride to have a very low conductivity and behave as an insulator and is used as a dielectric in some cases. Although most of the 2D TMDs have a bandgap corresponding to the visible light range, some TMDs have a low mobility due to the reduction in the amount of charge carriers compared to its bulk form\(^3\). However, through the use of heterostructures, we might be able to overcome some of the disadvantages which individual materials possess.

2.1. Project Description

The first stage of this project was to do a parameter search for the synthesis of thin TMD flakes on different substrates. I will be focusing on synthesizing thin WS\(_2\) flakes on both sapphire and SiO\(_2\)/Si substrates. For synthesis, the Chemical Vapour Deposition (CVD) technique chosen, using WO\(_3\) and Sulphur powders as precursors and argon gas as the carrier gas. Repeated experiments were done to find the optimum conditions for synthesis.

The second stage of this project was to study the characteristics of the WS\(_2\) flakes synthesized. This was done using 4 different techniques. Raman Spectroscopy was used to identify WS\(_2\), Photoluminescence Spectroscopy to determine the bandgap, Atomic Force Microscopy to study the morphology and Fluorescence Microscopy to determine the specific areas of fluorescence on the flake.
The final stage of this project is to study the optoelectronic properties of heterostructures. The two materials chosen were WSe$_2$ and CdS$_{0.8}$Se$_{0.2}$. The reason for this choice was to develop a $p$-$n$ heterostructure junction. These two materials can also be synthesized using the CVD technique. The heterostructure junction was made using the Electron Beam Lithography (EBL) technique and placed on a Side-Brazed Dual In-line Ceramic Package (DIP). This optoelectronic device was used to measure the photocurrent of the heterostructure junction through IV and Ivst plots using lasers of different wavelengths. The Photoresponsivity, External Quantum Efficiency (EQE) and Photodetectivity were calculated using these measurements. These values were compared with that of non-heterostructure junctions.

2.2. Transition Metal Dichalcogenides (TMDs)

Atomically thin sheets of TMDs are a promising class of materials for a range of applications. These materials are made to complement or even replace certain standard materials being used in semiconductor devices currently. One reason for this is due to the direct bandgap the 2D TMDs possess. The concept of a direct bandgap is illustrated in the diagram below.

![Energy profile diagram of direct and indirect bandgaps](image)

Fig 1: Energy profile diagram of direct and indirect bandgaps

Bulk TMDs possess an indirect bandgap. This means that for an electron to transfer from the valence band to the conduction band, a photon and a phonon is needed, as illustrated in the figure above. However, when a TMD monolayer is used instead, the bandgap changes to a direct bandgap. This means that only a photon is needed for the excitation of an electron.
This allows the material to exhibit fluorescence and photoluminescence which is useful for optoelectronics.

Thin 2D TMDs can be synthesized by a few methods. The exfoliation technique can be used, where a thin layer of TMD can be mechanically cleaved off of a bulk TMD using an adhesive tape. This is possible due to the structure of TMDs.\textsuperscript{4} Similar to graphene, TMDs consists of layers of covalent bonds. This can be seen in the figure below which shows the monolayer structure for MoS\textsubscript{2}.

![Atomic structure of monolayer MoS\textsubscript{2}](image)

Fig 2: Atomic structure of monolayer MoS\textsubscript{2}. (© Johnny Wong, University of Twente)

In a bulk TMD, the monolayers are bonded to each other through weak Van Der Waals forces.\textsuperscript{4} This explains why the exfoliation technique is appropriate in synthesizing thin 2D TMDs. However, this technique has a low yield and has little control over the thickness of the TMD flake obtained.\textsuperscript{7}

In my project, I will be using the Chemical Vapour Deposition technique to synthesize 2D TMDs. This technique will be elaborated in the following section of my report.

### 2.3. Chemical Vapour Deposition (CVD)

There are many different variations and modifications that can be applied to CVD. However in my project, I will be using a standard Atmospheric pressure CVD. Below is a diagram showing the different processes during CVD.
The diagram shows the precursors and substrate being placed in a furnace. The furnace has an input of carrier gas. When the temperature is high enough, the precursors begin to vaporize. The precursors are then transported by the carrier gas to the substrate which is placed downstream of the furnace. The precursors are then adsorbed onto the surface of the substrate. On the surface, the precursors can undergo several surface processes such as nucleation and surface diffusion. Through this CVD, various different thin film materials can be synthesized with the use the appropriate precursors.

### 2.4. \( p-n \) junction

Semiconductors conduct electricity through the presence of charge carriers within them. The two possible charge carriers are electrons and holes. To explain these charge carriers, the example silicon will be used.

Silicon is a group IV element, meaning it has 4 electrons in its outer shell. In a pure silicon crystal, the atoms are bonded to each other through covalent bonds, each atom having 4 bonds. When an electron in a bond gains enough energy, it can break free of its bond and become a charge carrier. This also creates a ‘hole’ at its initial electron position.
Fig 4: Diagram of movement of hole within semiconductor

This hole can be filled up by other nearby electrons. However, when a nearby electron takes up the position of this hole, the position which the electron came from will now be a hole. This phenomenon is illustrated in the diagram above. Although a hole is just the absence of an electron and does not carry a charge itself, the presence of this hole allows the nearby electrons to move and therefore creates a current. It should be noted that the flow of electrons in one direction would cause the hole to flow in the opposite direction.

Some semiconductor materials intrinsically have extra free electrons or holes which increases its conductivity. Free electrons and holes can also be introduced into a semiconductor through doping, which is the addition of impurities. A semiconductor which has more free electrons than holes is called an n-type semiconductor. A semiconductor with more holes than free electrons is called a p-type semiconductor. When these 2 types of semiconductors are placed adjacent to each other, a p-n junction is formed.
The above diagram shows what happens in a p-n junction. The excess electrons from the n-type semiconductor combine with the excess holes in the p-type semiconductor for annihilation. However, this process leaves behind positive ions in the n-type semiconductor and negative ions in the p-type conductor. These remaining ions then create an electric field that hinders free electrons from diffusing into the p-type region. This diffusion occurs until the electric field is stronger enough to prevent further diffusion. The region of positive and negative ions is called the depletion region, where the charge carriers are depleted.

A potential difference can be applied across the junction, where the positive terminal is placed at the p-type semiconductor and the negative terminal at the n-type semiconductor. If the potential difference is larger than the electric field in the depletion region, the electrons can overcome the electric field barrier and travel from the n-type to the p-type semiconductor, thus resulting in a current through the junction. This is called a forward bias.

However, if the potential difference is applied in the other direction, where the positive terminal is placed at the n-type region and the negative terminal at the p-type region, the electric field at the depletion region is now enhanced even further, creating an even larger depletion region. There is no current through the junction in this case. This is referred to as a reverse bias.

This shows that a p-n junction behaves as a diode, allowing current to flow in the forward bias direction but not in the reverse bias direction.
3. Methodology

3.1. Synthesis of WS$_2$ through Chemical Vapour Deposition (CVD)

The CVD method was used to grow WS$_2$ flakes on different substrates. One tube furnace was used for sapphire substrates and another tube furnace was used for Silicon dioxide (SiO$_2$/Si) substrate.

3.1.1. Furnace used to synthesize WS$_2$ on SiO$_2$/Si

![Furnace used to grow WS$_2$ on SiO$_2$/Si](image)

Fig 6: Furnace used to grow WS$_2$ on SiO$_2$/Si substrate
The cross section of the furnace used to synthesize WS$_2$ on SiO$_2$/Si is displayed in the diagram below.

![Diagram of furnace cross section](image)

**Fig 7: Cross section of furnace used to synthesize WS$_2$ on SiO$_2$/Si**

WO$_3$ and Sulphur precursor is placed in a ceramic boat each, along with the SiO$_2$/Si substrate. These ceramic boats are then placed in a test tube within the tube furnace. An argon gas canister is attached to the inlet of the tube furnace. The rate of gas flow is controlled by a mass flow controller. The outlet can either be connected to a vacuum pump to achieve lower pressures, or connected to an open tube, keeping the pressure in the tube furnace at atmospheric pressure.

According to Ling et al. $^8$, using a seeding promoter such as perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) on SiO$_2$/Si substrate enhances the synthesis of MoS$_2$ through Chemical Vapour Deposition. The PTAS molecular aggregates act as seeding promoters and initiate the growth of thin layer MoS$_2$ flakes. In my experiment, I made a PTAS solution using a concentration 50μM, stated in a paper written by Lee et al. $^9$ and dropcast it onto the SiO$_2$/Si substrate, followed by drying through heating at 80°C.

The furnace is then set run a certain temperature setting.
3.1.2. Furnace used to synthesize WS\textsubscript{2} on Sapphire

Another furnace with a slightly differing setup was used to synthesis WS\textsubscript{2} on Sapphire.

Fig 8: Furnace used to grow WS\textsubscript{2} on Sapphire

The cross section of the furnace is as such.

Fig 9: Cross section of furnace used to synthesize WS\textsubscript{2} on Sapphire
The setup of this furnace is very similar to the furnace used to synthesize WS$_2$ on SiO$_2$/Si. However, instead of having the Sulphur precursor boat being in the furnace, it is placed outside the furnace, under a heating plate. The heating plate helps to control the temperature of the Sulphur separately. The Sulphur was heated to a temperature of 290°C. According to Peimyoo et al.\textsuperscript{10}, heating the Sulphur separately helps in a more uniform growth of the WS$_2$ flakes.

The gas flow was also controlled by a mass flow controller and the outlet was also open to the atmospheric pressure.

The furnace is then set run a certain temperature setting.

### 3.2. Characterisation of WS$_2$

I used 4 techniques to study the WS$_2$ flakes synthesized. The four techniques are Raman Spectroscopy, Photoluminescence Spectroscopy, Fluorescence Microscopy and Atomic Force Microscopy. Each of these methods helps us to study an aspect of the WS$_2$ flakes.

#### 3.2.1. Raman Spectroscopy

Raman Spectroscopy is a method used to study the molecular vibrational and rotational modes of a sample through Raman Scattering.

![Raman Microscope](image)

**Fig 10:** Raman Microscope used for Raman Spectroscopy

In Raman Spectroscopy, a monochromatic laser beam is incident onto the sample. In my case, the excitation wavelength used was 532nm. Majority of the photons will be elastically
scattered, also known as Rayleigh scattering, which means that they will be the same wavelength as the incident photons. However, there will be a small portion of photons which will be inelastically scattered, which is called Raman Scattering. This is due to the laser photons interacting with the molecular vibrations of the sample. Raman Scattering wavelengths deviate from the excitation wavelength to extents, depending on the vibrational modes present. This gives each material a specific Raman spectrum.

Often after a synthesis process, there are many microscopic objects of different shapes and sizes on the substrate that can be seen optically. Raman spectroscopy can also be used to identify and confirm what is seen.

The graphs of Raman Spectroscopy plot the Intensity of scattered photons against the shift in wavenumber with respect to the incident photon’s wavenumber.

### 3.2.2. Photoluminescence (PL) Spectroscopy

According to Gfroerer\textsuperscript{11}, PL is the spontaneous emission of light from a material under optical excitation. PL Spectroscopy is a non-destructive method used to study the optical properties of a material. A photon of a higher frequency and energy is incident onto the sample. For my PL Spectroscopy, I used an excitation wavelength of 532nm to incident onto the WS\textsubscript{2} flake. This photon causes electrons in the material to excite to a higher energy level, overcoming its bandgap. Following this, the electron will undergo relaxation processes. The relaxation across the bandgap will occur as an emission of a photon, which is the PL observed. PL Spectroscopy plots the intensity of PL detected against wavelength. PL Spectroscopy helped to determine the bandgap of the WS\textsubscript{2} flake.
3.2.3. Atomic Force Microscopy (AFM)

Tapping mode Atomic Force Microscopy (AFM) is a method used to study the morphology of a material’s surface. The setup is as shown above. A cantilever and tip are used as a probe to map out the surface of the sample. When the tip is brought close to the surface, various different forces between the surface and the tip will cause the angle of deflection of the laser to change. These deflections are detected by a photodiode acting as a detector. The photodiode will then feedback to the system to adjust the tip-to-sample distance. This is to prevent the tip from being damaged by the surface. These changes will correspond to the height of the point on the surface, which is then recorded. The cantilever will go back and forth along the surface and slowly plot out the morphology of the surface.

3.2.4. Fluorescence Microscopy

Fluorescence Microscopy is commonly used in today’s research, especially in the fields of Biology. It is very good for visual detection and tracking of certain cells which might exhibit specific fluorescence. Certain dyes can be used to coat certain materials for easy tracking. Fluorescence occurs when photons of a higher energy, compared to that of the bandgap of a material, is incident onto the material. If the photon is within the absorption range of the material, the photon will excite the electron into a higher energy state. The electron will then
release energy through photons and other forms of vibrations. The photon emitted by the electron when dropping back down the bandgap is the fluorescence seen. This is very similar to PL mentioned earlier. In Fluorescence Microscopy however, an optical image of the fluorescence is taken rather than an intensity plot of fluorescence. This helps us to visually see which points on the WS₂ flake emit fluorescence.

3.3. Optoelectronic Device

An optoelectronic device was made to study the properties of the junction through IV and Ivst graphs. WSe₂ flakes were used instead of WS₂ flakes. The reason for this choice will discussed in section 4.3.

3.3.1. Fabrication of Optoelectronic Device

First, Polymethyl Methacrylate (PMMA) is applied onto the substrate containing the WSe₂ flake. It is spin coated and then baked. This material polymer is used as a photoresist. After a layer of PMMA is formed, the substrate is put into an EBL chamber where the electron beam is used to draw out the position desired for the electrode. According to Choi et al.¹², the electron beam causes chain scission within the PMMA which degrades it. The substrate is then placed in photoresist developer which dissolves away only the degraded PMMA. Following this the substrate is washed with DI water and dried with Nitrogen gas. The substrate is then put into a thermal evaporator with 2 heating sources within it, one with Gold (Au) and the other Palladium (Pd). A layer of Palladium of 20nm thick is deposited on the substrate followed by 80nm of Gold. Following this, Acetone is used to remove the remaining PMMA on the substrate, leaving behind Pd/Au electrodes at the desired positions. The process is finished off by washing the substrate in DI water and dried with Nitrogen gas.

For my device in particular, a CdS₀.₈Se₀.₂ nanowire was stacked on top of a WSe₂ flake, as can be seen in the figure below.
Fig 12: Optical image of Optoelectronic Device on a Sapphire substrate

The CdS$_{0.8}$Se$_{0.2}$ nanowire and WSe$_2$ flake was highlighted in green and blue for easier observation. The two electrodes of interest are labelled Electrode 1 and 2.

CdS$_{0.8}$Se$_{0.2}$ nanowire is also prepared using the CVD technique, except that the precursors used are CdS and CdSe powder. The reason for using CdS$_{0.8}$Se$_{0.2}$ over CdS, CdSe or even CdS$_{0.65}$Se$_{0.35}$ is that CdS$_{0.8}$Se$_{0.2}$ has the better optoelectronic properties such as a higher “ON/OFF” ratio.$^{13}$

The substrate is then placed in a Side-Brazen Dual In-line Ceramic Package (DIP) where the electrodes can be electrically connected to copper wires for easier use, as can be seen in the picture below.
3.3.2. Measuring Photocurrent

Above is the setup on the optoelectronic device. The current runs through Electrode 1, through the CdS$_{0.8}$Se$_{0.2}$ nanowire, pass the heterostructure junction into WSe$_2$ and then through Electrode 2.

The electrodes are connected to a sourcemeter which provides a sweeping DC bias voltage and measures current simultaneously. The measurements were done at room temperature and in ambient conditions. Different broad beam lasers were being used for the measurements.
The lasers were mounted on a tripod stand and incident upon the substrate, ensuring that the entire heterostructure junction and the electrodes contact with the WSe$_2$ flake and CdS$_{0.8}$Se$_{0.2}$ nanowire are uniformly illuminated. This is called global irradiation. Measurements were done for both dark current and with laser incidence of different wavelengths.

Besides IV graphs, current against time (Ivst) graphs were measured as well. During the measurement, the laser used is being blocked and unblocked approximately every 5 seconds. The “ON” state refers to when the laser is unblocked and “OFF” when the laser is blocked. This way, the difference between dark current and the current under illumination can be measured.
4. Results

4.1. Synthesis of WS$_2$ with CVD

A majority of my time spent on this project was on doing parameter searches for the optimum conditions for growth of WS$_2$ on sapphire and SiO$_2$/Si. Approximately 160 CVDs were done in this project. It was very difficult to find optimum conditions as it was difficult to get consistent results with apparently the same parameters. It was probably the case that there were a few parameters I was unaware of that affected the growth of the TMD flakes. These parameters were not controlled and therefore leading to apparently inconsistent results. Across time, I did manage to find out a few of these parameters, but definitely not all. However, I did manage to find my best set parameters that have been giving me rather consistent growth for sapphire and SiO$_2$/Si substrates. Although definitely not with 100% consistency for good growth, this was the best set of parameters I could find out during my time doing this project.

4.1.1. Synthesis on SiO$_2$/Si substrate

There were many variations being made in the parameter search for synthesis of WS$_2$.

4.1.1.1. Position of substrate

The substrate was placed at different distances away from the WO$_3$ precursor within that ceramic boat for different CVDs. It was even placed at different positions in between the ceramic boats along the test tube. For the SiO$_2$/Si substrate, there is only 1 side which is used for the synthesis of TMD flakes. For many of these positions along the furnace, the substrate was tested both facing up and facing down. The size of the substrate was also varied for some of the positions. We discovered that the optimised position for the SiO$_2$/Si substrate was to place it face down, right above the WO$_3$ precursor, as shown in the figure below.
The WO₃ precursor, though cannot be seen in the picture, is below the SiO₂/Si substrate. The SiO₂/Si substrate is balanced above the precursor, supported by the sides of the boat. Due to the boat being V shaped, the substrate’s distance above the WO₃ precursor can be altered by changing the width of the substrate, as can be seen in the “Cross section of WO₃ boat” diagram above. This made it difficult to obtain consistent results as the size of the substrate was altered through manual breaking. Breaking the substrate into the exact size and width desired required a lot of skill. The growth WS₂ flakes on the substrate is very sensitive to the height of the substrate above the WO₃ precursor. If it was too low, the WS₂ flakes would become thicker with more black particles covering it. These particles are suspected to be WS₂ particles, which are always seen in the ceramic boat after CVD, taking over the position of the WO₃ precursor. These particles however, cannot be removed by blow drying it with nitrogen gas. A picture of this is shown below.
If it was too high, the WS\textsubscript{2} flake growth would be lesser and smaller. I found that the ideal height above the WO\textsubscript{3} precursor was approximately 2-3mm. 1mm would be too low and 4mm would be too high.

**4.1.1.2. Position of precursor**

The position of the precursor on the boats always remained the same. They were always placed at the corner of the boat, towards the side downstream of the furnace. The optimised positions of the ceramic boats were based on the temperature profile within the tube furnace.

The furnace does not experience a uniform temperature throughout its entire length. The edges of the furnace will experience a slightly lower temperature due to cooling from the environment outside the furnace. This is shown in the temperature profile diagram below.
This temperature profile was taken from a similar tube furnace of the same structure. The preset temperature was 950°C, which was achieved at the centre portion of the furnace. Therefore, the boat containing the WO$_3$ precursor and the substrate are positioned such that the WO$_3$ precursor and substrate are aligned to the centre of the furnace. This is to ensure that the temperature the substrate and WO$_3$ precursor experienced was as close to the temperature settings as possible. The position of the sulphur boat is near the edge of the furnace, along the temperature gradient of the temperature profile, meaning that the temperature experienced is very dependent on the position of the boat. Through varying the position and comparing the growth of WS$_2$ flakes on the SiO$_2$/Si substrate, I found that if the Sulphur was placed too far away from the WO$_3$ precursor, there would be lesser growth. If I placed the Sulphur too near, the WS$_2$ flakes would be too thick. I experimentally found that the optimised distance between the centre of the furnace and the Sulphur precursor was approximately 36cm. This is illustrated in Fig 7 in section 3.1.1.

4.1.1.3. Amount of precursor
The amount of precursor was also experimentally optimised. For some of my synthesis processes, this was observed on my substrate.
According to Rong et al.\textsuperscript{14}, these are WS\textsubscript{2} nanowires being formed. The formation of these nanowires indicates that the sulphur precursor is either introduced too late or there was not enough WO\textsubscript{3} precursor. For this furnace, the sulphur precursor was not separately heated from the WO\textsubscript{3} precursor, making it difficult to control how the sulphur precursor is heated without affecting the heating of the WO\textsubscript{3} precursor. Therefore, the amount of WO\textsubscript{3} precursor was altered instead. On the other hand, if there was too much sulphur precursor, the WS\textsubscript{2} flakes would be too thick. An image of thick WS\textsubscript{2} flakes can be seen in Fig 16 in 4.1.1.1. This knowledge made it a lot easier to optimise the amount of precursors needed for the CVD. The optimised amount of WO\textsubscript{3} was 20mg and sulphur was 240mg.
4.1.1.4. Temperature

The optimised temperature setting used is shown in the diagram below.

![Temperature Setting for SiO2/Si substrate](image)

Fig 19: Temperature settings of furnace of SiO2/Si

The temperature, starting at room temperature, was raised to 105˚C at a ramping speed of 40˚C/min and dwelled at that temperature for 30min. This was done so that all the air, water vapour and other impurities would be flushed out by argon gas. Following that, the temperature was raised to 750˚C at a ramping speed of 28˚C/min and dwelled at that temperature for 15min. The dwelling time is the growth stage for WS2 flakes. Following that, the furnace was left to cool to room temperature by the argon gas flow and natural cooling.

The ramping speed leading to the growth stage was varied between 15-40˚C/min. Faster ramping speeds led to thicker flakes and slower speeds led to lesser flakes. The growth stage temperature was also varied between 600-850˚C. Both lower and higher growth stage temperatures led to lesser flakes. The growth stage time was also varied between 1 second to 40 min. It was difficult to observe a clear pattern for growth stage time as results were very inconsistent.

4.1.1.5. Gas supply and pressure

Throughout the whole process, the tube furnace is supplied with argon gas at 50sccm at room temperature and atmospheric pressure. At approximately 6 hours after the start of the CVD
process, the tube furnace would be approximately 350˚C. This is when the argon gas supply is stopped and the tube furnace is left to cool through natural cooling.

The rate of gas supply input was varied from 50-200sccm. Using faster rates led to thicker flakes. The pressure within the tube furnace was also varied between 0.57Torr to atmospheric pressure. Lower pressure was achieved through connecting the outlet of the tube furnace to a vacuum pump. Lower pressures led to lesser flake growth.

4.1.1.6. Cleaning substrate using Piranha solution

One of the suspicions for bad growth of WS$_2$ flakes was that the substrates used were not clean enough. Therefore, the substrates were washed in Piranha solution before using it for CVD. The Piranha solution consists of aqueous Sulphuric Acid and Hydrogen Peroxide. The concentrations of Hydrogen Peroxide and Sulphuric acid used were 30w/w and 98%w/w respectively. The ratio of volume of Sulphuric Acid to Hydrogen Peroxide was 3:1. The substrate was left inside the solution for approximately 16 hours. The substrates were then taken out, washed with DI water and dried with nitrogen gas. However, we found that this caused even less WS$_2$ growth. I speculate that it is because certain particles can acts as nucleation sites for the WS$_2$ flake. I did not use the Piranha solution in my ideal parameters for growth of thin WS$_2$ flakes.

4.1.1.7. Si$_3$N$_4$

In the later portion of my project, we tried to use the WS$_2$ flakes on SiO$_2$/Si substrate to make an optoelectronic device. However after running some tests, we realized that current could flow through SiO$_2$/Si surface itself, meaning that the current was not isolated to the WS$_2$ flake or CdS$_{0.8}$Se$_{0.2}$ nanowire. This meant that the dielectric layer on the SiO$_2$/Si was spoilt. We speculate that it is probably due to the high heat during the CVD process. I started using Si$_3$N$_4$ instead of SiO$_2$/Si for my CVD process, using the same parameters. There was successful growth of thin WS$_2$ flakes. However, I did not have time to make an optoelectronic device out of it due to time constraints.
4.1.1.8. Best Parameters

In summary, the best parameters I determined experimentally are as follows.

<table>
<thead>
<tr>
<th>TMD grown:</th>
<th>WS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate used:</td>
<td>SiO₂/Si</td>
</tr>
<tr>
<td>Position of substrate:</td>
<td>2-3mm above WO₃, facing down</td>
</tr>
<tr>
<td>Position of precursors:</td>
<td>WO₃: centre of furnace</td>
</tr>
<tr>
<td>Amount of precursor:</td>
<td>WO₃: 20 mg</td>
</tr>
<tr>
<td>Gas supply &amp; pressure:</td>
<td>Gas: 50 sccm argon</td>
</tr>
</tbody>
</table>

**Temperature settings**

<table>
<thead>
<tr>
<th>End temp (°C)</th>
<th>Ramping Speed (°C/min)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>105</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>750</td>
<td>28</td>
<td>55</td>
</tr>
<tr>
<td>750</td>
<td>0</td>
<td>70</td>
</tr>
</tbody>
</table>

Fig 20: Table of parameters for CVD on SiO₂/Si substrate

There were a lot of CVD carried out across the duration of my project. Approximately 80 CVDs were carried out for SiO₂/Si substrate.
Below are some optical images of the progress made across the duration of my project.

Fig 21: Improvements in CVD growth results in chronological order, with a) being the earliest and d) being the latest.

It can be seen in a) that the WS\textsubscript{2} flakes are completely covered in WS\textsubscript{2} particles. Adjustments were made to slowly reduce the growth of these particles. In c), there is minimal particle growth, but the WS\textsubscript{2} flakes still remain very thick. Finally in d), there are some bluish green triangles present, which are the thin WS\textsubscript{2} flakes desired.

Below is an optical image of one of the biggest WS\textsubscript{2} thin flakes grown using the best parameters, approximately 40 μm in length.
Thin areas of flakes are indicated by a blue colour whereas the thicker areas are indicated by a whiter colour.

4.1.2. Synthesis on sapphire substrate

A majority of knowledge of CVD growth on SiO$_2$/Si substrate can also be applied to CVD on sapphire substrate. I started off using the growth parameters that Peimyoo et al.$^{10}$ used, making adjustments across the duration of my project to optimize it to the tube furnace I was using.

4.1.2.1 Position of substrate

Unlike SiO$_2$/Si substrate, we found that the optimum position of the sapphire substrate is to be placed face up beside the WO$_3$ precursor.
The position of the sapphire was varied along the ceramic boat. It was consistently observed that the edge of the sapphire closest to WO$_3$ precursor always had the most flake growth. If the substrate was placed further away from the precursor, there would be lesser flakes grown. If the sapphire was placed face down, there will be more WS$_2$ particles grown. Below is an optical image consisting of thin flakes, thick areas and WS$_2$ particles.
4.1.2.2. Position of precursor
The WO$_3$ precursor was always placed at the corner of the ceramic boat, towards the side downstream of the furnace. Due to the amount of Sulphur precursor and the size of its ceramic boat, the Sulphur precursor always took up the entire ceramic boat. Following the same principle as with CVD using SiO$_2$/Si, the WO$_3$ precursor and sapphire was positioned in the centre of the furnace ensuring it experiences the most accurate temperature. Since for this CVD the Sulphur precursor is separately heated by a heating plate, there was no need to adjust the position of it. The Sulphur precursor was placed 25 cm away from the centre of the furnace and the WO$_3$ precursor.

4.1.2.3. Amount of precursor
Using the same knowledge for growth on SiO$_2$/Si substrate, I found the optimum amount of precursors used is 20 mg of WO$_3$ and 200 mg of Sulphur.

4.1.2.4 Temperature

![Temperature Setting for Sapphire substrate](image)

Fig 25: Temperature setting for CVD on sapphire substrate

The temperature is first kept at 25°C for 1 min to flush out the air, water vapour and other impurities from the chamber. The temperature is then raised to 550°C at a ramping speed of 25°C/min for 21 mins. When the WO$_3$ precursor hits 550°C, the Sulphur precursor begins to heat by a separate heating plate to 290°C. The temperature of WO$_3$ precursor then continues to rise to 800°C at a ramping speed of 6.25°C/min for 40 min. The growth stage then begins, dwelling at 800°C for 20 min. This is followed by cooling through the argon gas and natural
cooling. After approximately 3 hours, the WO$_3$ precursor reaches approximately 400°C. This is when the heating plate beneath the Sulphur precursor is turned off.

The ramping speed for the WO$_3$ precursor from 550°C to 800°C was varied between 5-10°C/min. A higher ramping speed caused thicker flake growth. The growth stage temperature was varied between 750-850°C. Using a higher temperature caused lesser flake growth. However, 750-800°C seemed to have equally good growth. The growth stage duration was also varied between 10-20 mins. A shorter duration caused lesser flake growth.

4.1.2.5. Gas Supply and Pressure

Through the whole CVD, the chamber is supplied with 200sccm of argon gas at atmospheric pressure. Approximately after 6 hours after the start of the CVD, the chamber will reach between 100-200°C. The gas supply is turned off and the tube furnace is left to cool by natural cooling.

The argon supply was varied between 100-200sccm. A lower rate would lead to lesser growth of WS$_2$ flakes.

4.1.2.6. Sulphur-rich environment.

Across the course of my project, the test tube used for CVD was changed a total of 3 times. It was noticed that every time it was changed, the growth of WS$_2$ flakes would decrease drastically, giving a relatively clean sapphire substrate after CVD. Since this always coincided with the changing of a new test tube, we suspect that a test tube with more condensed Sulphur was better for CVD. A picture of the test tubes used for both CVD processes are shown below.

![Fig 26: Condensed Sulphur in test tubes used for CVD](image_url)
The amount of condensed Sulphur is proportional to the number of CVDs it has undergone. It takes approximately 7 CVDs for a new test tube to obtain sufficient condensed Sulphur for the growth of thin WS\textsubscript{2} flakes. I suspect this creates a Sulphur-rich environment for the WO\textsubscript{3} precursor and sapphire substrate, helping the growth of WS\textsubscript{2} thin flakes.

4.1.2.7. Best parameters

In summary, the best parameters I concluded with are as follows.

<table>
<thead>
<tr>
<th>TMD grown</th>
<th>WS\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate used</td>
<td>sapphire</td>
</tr>
<tr>
<td>Position of substrate</td>
<td>Right beside WO\textsubscript{3}, facing up</td>
</tr>
<tr>
<td>Position of precursors:</td>
<td>WO\textsubscript{3}: centre of furnace</td>
</tr>
<tr>
<td>Amount of precursor:</td>
<td>Wo\textsubscript{3}: 20mg</td>
</tr>
<tr>
<td>Gas supply &amp; pressure:</td>
<td>Gas: 200sccm argon</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>End temp (°C)</th>
<th>Ramping Speed (°C/min)</th>
<th>Time (min)</th>
<th>Heating plate temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>550</td>
<td>25</td>
<td>22</td>
<td>290 (start when WO\textsubscript{3} 550°C)</td>
</tr>
<tr>
<td>800</td>
<td>6.25</td>
<td>62</td>
<td>290</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>82</td>
<td>290</td>
</tr>
<tr>
<td>400(approx)</td>
<td>4(approx)</td>
<td>180(approx)</td>
<td>0 (switch off heating plate)</td>
</tr>
</tbody>
</table>

Fig 27: Table of parameters for CVD on sapphire substrate

Compared to the CVD using SiO\textsubscript{2}/Si substrates, the improvements in growth were not as obvious across time. The quality of growth on sapphire substrate fluctuated a lot more. However, here are some examples of non-ideal WS\textsubscript{2} flakes.
Fig 28: a) Bright areas represent thick areas on the flakes. b) Black WS$_2$ particles present.

The images a) and b) shows an example of a substrate with thick WS$_2$ flakes and black WS$_2$ particles respectively. An image using the best growth parameters is shown below.

![Optical image of thin WS$_2$ flakes using best parameters](image)

Fig 29: Optical image of thin WS$_2$ flakes using best parameters

Although there are still some thick areas on the flakes, there some which appear to be uniformly thin, indicated by the arrows in the figure.

### 4.2. Characterisation of thin WS$_2$ flakes

The WS$_2$ flakes synthesized by CVD were then studied using various techniques as mentioned in the Methodology Section earlier. The main focus was the thin WS$_2$ flakes.
4.2.1. Raman Spectroscopy

Raman Spectroscopy was used mainly for identification of objects rather than the study of the vibrational modes in the WS\textsubscript{2} flake. The Raman Spectroscopy results for thin WS\textsubscript{2} flakes on both sapphire and SiO\textsubscript{2}/Si substrates are shown in the graphs below.

![Raman Spectrum of WS\textsubscript{2} on Sapphire](image)

**Fig 30**: Raman Spectrum of WS\textsubscript{2} flake on sapphire substrate

![Raman Spectrum of WS\textsubscript{2} on SiO\textsubscript{2}/Si](image)

**Fig 31**: Raman Spectrum of WS\textsubscript{2} flake on SiO\textsubscript{2}/Si substrate

It can be seen that the peaks obtained for both Raman spectrums are the same, except that the spectrum taken on SiO\textsubscript{2}/Si substrate has an extra peak at 520cm\textsuperscript{-1}. According to Peimyoo et al.\textsuperscript{10}, this 520cm\textsuperscript{-1} peak corresponds to a vibrational mode in the Silicon present in the
substrate. For WS\textsubscript{2}, the 296cm\textsuperscript{-1}, 320cm\textsuperscript{-1} and 417cm\textsuperscript{-1} peaks correspond to the combination mode of 2LA-2E\textsubscript{2g}, combination mode of 2LA-E\textsubscript{2g} and out-of-plane A\textsubscript{1g} mode respectively. The 350cm\textsuperscript{-1} peak consists of 3 peaks corresponding to the in-plane vibrational E\textsubscript{1g} (M) mode, the second-order mode of longitudinal acoustic phonon 2LA (M) and the in-plane vibrational E\textsubscript{1g} (Γ) mode.\textsuperscript{10}

The position of peaks I obtained for WS\textsubscript{2} flakes all have very low percentage discrepancies, the highest being 1.82%. This information is especially useful identifying whether unknown objects observed on the substrate are WS\textsubscript{2}.

4.2.2. Photoluminescence Spectroscopy

PL is used mainly to determine the bandgap of thin WS\textsubscript{2} flakes. Below is the PL Spectroscopy results obtained for a thin WS\textsubscript{2} flake on SiO\textsubscript{2}/Si substrate.

![PL Spectrum of WS\textsubscript{2} flake](image)

The wavelength of the PL peak obtained ranges between 620-625nm. This wavelength corresponds to red light, which agrees with the results obtained in the Fluorescence Microscopy I performed. The energy of a photon of wavelength 625nm is 1.98eV. This agrees with Zhu et al.’s\textsuperscript{15} A exciton emission of 1.98eV at room temperature. This shows that the bandgap present in thin WS\textsubscript{2} flakes is 1.98eV, assuming it has a perfectly direct bandgap.
4.2.3. Atomic Force Microscopy (AFM)

The AFM machine used had relatively high noise level during the measurements. This can be seen in the amplitude of fluctuations in height relative to the step height corresponding to the transition from the WS$_2$ flake to the substrate, especially for the WS$_2$ flake on SiO$_2$/Si. The steps are identified by a steep decrease in height which corresponds to the position of the edge of the flake along the line of measurement. Using tapping mode AFM for thin WS$_2$ flakes, I obtained the following results shown below.

Fig 33: AFM results for WS$_2$ flake on a) sapphire and b) SiO$_2$/Si
The morphology along the 2 lines is shown in the graphs below.

For each of the graphs, the height values are split into 2 groups, namely the values before the step and after the step. Each step is labelled in the graphs. The values that are within the steps are excluded from calculations. For each group of height values, the average is calculated. The difference between the 2 averages is calculated to be the thickness of the WS$_2$ flake. The 2 thicknesses of the WS$_2$ flake on sapphire are calculated to be 1.30nm for the blue line and
1.13nm for the red line. The 2 thicknesses for the WS$_2$ flake on SiO$_2$/Si are calculated to be 1.72nm for the blue line and 1.43nm for the red line.

The thickness of 1 layer of WS$_2$ is approximately 0.7nm.$^{10}$ With this knowledge, the WS$_2$ flake on sapphire is 1-2 layers and the flake on SiO$_2$/Si is 2-3 layers.

**4.2.4. Fluorescence Microscopy**

Fluorescence microscopy was performed using white, blue and green light. The images obtained are shown below.

![Fluorescence Microscopy images](image)

Fig 36: Fluorescence Microscopy results for WS$_2$ flake on Sapphire

From the results of PL spectroscopy, we found that the PL exhibited corresponded with red light. This agrees with the fluorescence seen from the WS$_2$ flake on sapphire. It was evident that when using green excitation light, the fluorescence exhibited was stronger in intensity compared to that of blue excitation light, despite the fact that blue light has a higher energy
photon than green light. This shows that green light is closer to the excitation maximum than blue light.

It can be seen that the fluorescence exhibited on the flake has a certain pattern. It is suspected that this pattern reveals the grain boundaries present in the WS$_2$ flake, which is not visible under white light.

![Fluorescence Microscopy results for WS$_2$ flake on SiO$_2$/Si](image)

**Fig 37: Fluorescence Microscopy results for WS$_2$ flake on SiO$_2$/Si**

The fluorescence present on the WS$_2$ flake on SiO$_2$/Si substrate differs very much from that on sapphire. It is clearly seen that the edges exhibit a lot more fluorescence compared to the rest of the flake area. There are a few possible reasons for this.

One possibility is that the Sulphur precursor was not separately heated at a lower temperature. Heating the Sulphur precursor in the tube furnace gives rise to a relatively unstable supply of Sulphur in the chamber, resulting in non-uniform growth and PL,\textsuperscript{10} where the PL is exhibited more at the edges. This is very similar to the CVD carried out for SiO$_2$/Si in my project. For the CVD using SiO$_2$/Si, the Sulphur precursor was placed in the tube
furnace, whereas for the CVD using sapphire, the Sulphur precursor was heated at a constant
temperature outside the tube furnace.

Another possibility is that the edges of the WS$_2$ flake on SiO$_2$/Si are thinner than the rest of
the flake. Fluorescence microscopy was done on another region of the SiO$_2$/Si substrate and
the images are shown below.

![Fluorescence Microscopy of WS$_2$ flakes on SiO$_2$/Si substrate](image)

Although the position of the substrate was moved a bit between photos, it can be seen that
only the edges of thin areas of the WS$_2$ flakes exhibited fluorescence. This agrees with
Peimyoo et al. which states that intensity of PL decreases with increasing thickness of WS$_2$
flakes, indicating the transformation from direct to indirect bandgap. With this knowledge, it
could be the case that for the thin flakes, only the edges are thin enough to exhibit
fluorescence.

Attempts to use the AFM to analyse the height profile and determine whether there was
indeed a thickness difference at the edge of the flake, but the noise level present made it
difficult to do so.

### 4.3. Optoelectronic Device

Using the CVD method, other TMDs flakes such as WSe$_2$ monolayers was also synthesized.
According to Fang et al.\textsuperscript{16}, single layered WSe$_2$ has an ambipolar behavior, meaning that it
can behave as either a p-type or n-type semiconductor, depending on the material used for the
electrode. If the electrode used is Palladium (Pd), WSe$_2$ will behave as a p-type
semiconductor. According to Allen et al.\textsuperscript{17}, CdS can be used as an n-type semiconductor.
According to Dong et al.\textsuperscript{18}, CdSe can also be used as an n-type semiconductor. According to Baglio et al.\textsuperscript{19}, WS\textsubscript{2} could be used as either p-type or n-type semiconductor. With this knowledge, I wanted to construct a \textit{p-n} junction using WSe\textsubscript{2} and CdS\textsubscript{0.8}Se\textsubscript{0.2}.

Synthesizing WSe\textsubscript{2} flakes on sapphire substrate uses the same CVD technique as that of WS\textsubscript{2} flakes on sapphire. A heating plate was used to separately heat the Selenium precursor outside the tube furnace. According to Liu et al.\textsuperscript{20}, the bandgap for monolayer WSe\textsubscript{2} is approximately 1.6eV, which corresponds to photons of 775nm wavelength, which is in the infra-red spectrum.

An optoelectronic device was fabricated using a sapphire substrate with WSe\textsubscript{2} flakes grown on it and a CdS\textsubscript{0.8}Se\textsubscript{0.2} nanowire. This optoelectronic device helps us to incorporate the WSe\textsubscript{2} flake and CdS\textsubscript{0.8}Se\textsubscript{0.2} nanowire into a circuit through the use of electrodes, while keeping the WSe\textsubscript{2} flake and CdS\textsubscript{0.8}Se\textsubscript{0.2} nanowire exposed so that lasers can be incident onto it. This helps in the study of the optoelectronic properties of the heterostructure junction between WSe\textsubscript{2} and CdS\textsubscript{0.8}Se\textsubscript{0.2}. This optoelectronic device is fabricated through the Electron Beam Lithography (EBL) method.

For the measurements of IV graphs and Ivst graphs, different lasers of wavelengths 543nm (green), 405nm (blue), and 660nm (red) were used separately. The power for all 3 lasers used was 1.00mW with a spot size of approximately 2mm\textsuperscript{2}.

\textbf{4.3.1. IV graphs}

The IV graphs were measured for dark current (with no laser incident upon it) and with lasers of different wavelengths.
The IV graphs are shown below.

![IV Graphs](image)

Fig 39: IV Graphs

The shape of these IV graphs show that this heterostructure junction behaves as a \( \textit{p-n} \) junction. The order of IV graphs obtained were initial dark current first, followed by green, then blue then red laser. It can be seen that the initial dark current is higher than the current using blue and red lasers. I found this strange and went ahead to obtain another dark current IV graph after the above IV graphs were taken. This is labelled as Final Dark Current.

It can be seen that after the IV measurements using lasers, the dark current has significantly decreased. This degradation in conductivity could be caused by the incident lasers or exposure to air. This makes it difficult to determine the additional current when a laser is incident upon the junction. This additional current is called the photocurrent.

### 4.3.2. Current against time (\( \text{Ivst} \)) graphs

To overcome this problem, another technique is used. Instead of measuring current against voltage, a measurement of current against time is made while keeping the potential difference constant at 2V. During the measurement, the laser is allowed to incident upon the device for 5
seconds, followed by blocking the laser for another 5 seconds. These “ON” and “OFF” states are repeated approximately 5 times. These I-v-t graphs are shown below.

Fig 40: Current against time graph using Green laser

Fig 41: Current against time graph using Blue laser
It can be clearly seen that there is a photocurrent present for all 3 lasers. All the current values in the “ON” state were averaged to give the current under illumination, $I_{\text{illum}}$. All the current values in the “OFF” state were averaged to give the dark current, $I_{\text{dark}}$. The difference between these 2 averages would be the calculated photocurrent. All current values that were ambiguous to whether they were during the “ON” or “OFF” periods were excluded from calculation. This was done for all 3 graphs of different lasers.

Following this, the Photoresponsivity ($R_{\text{res}}$), External Quantum Efficiency (EQE) and Photodetectivity ($D^*$) was calculated for the different lasers.

### 4.3.2.1. Photoresponsivity

Photoresponsivity is a measure of the amount of photocurrent generated in response to the amount of power incidence upon the device from the excitation laser.

$$R_{\text{res}} = \frac{I_{\text{pho}}}{P_{\text{opt}}} = \frac{I_{\text{illum}} - I_{\text{dark}}}{(P_{\text{inc}})S}$$

Where $I_{\text{pho}}$ is the photocurrent, $P_{\text{opt}}$ is the light power. $S$ is the effective area of the optoelectronic device, which consists of the WS$_2$ flake and the section of the CdS$_{0.8}$Se$_{0.2}$ nanowire which carries the current. $P_{\text{inc}}$ is the power density of the illumination. $S$ is calculated to be approximately $5.0 \times 10^{-11} \text{m}^2$ and $P_{\text{inc}}$ is approximately $500 \text{W/m}^2$. Using this
information, $R_{res}$ was calculated to be $0.161AW^{-1}$ for green laser, $0.150AW^{-1}$ for blue laser and $0.0442AW^{-1}$ for red laser.

A similar experiment was carried out by a senior student in NUS, where the electrodes were placed on a single WSe$_2$ flake on her device. A laser of wavelength 532nm was used for global irradiation with a power of 2.8mW and a spot size of ~2mm$^2$. The photoresponsivity calculated was $25mAW^{-1}$. It can be seen that by adding a CdS$_{0.8}$Se$_{0.2}$ nanowire, the heterostructure has enhanced the overall photoresponsivity compared to if just WSe$_2$ was used. These results are currently in the process of being published.

According to Kang et al.$^{22}$, the photoresponsivity of WSe$_2$ was calculated to be approximately $4.5mAW^{-1}$ when using a excitation wavelength of 785nm and power of 1mW. Although the excitation wavelength used is not the same as the ones used in my project, this photoresponsivity value supports that the use of heterostructure is probably better than non-heterostructure.

### 4.3.2.2. External Quantum Efficiency

External Quantum Efficiency (EQE) shows the number of additional charge carriers generated per photon that incidence upon the device. EQE is calculated using the equation below.

$$EQE = \frac{hcR_{res}}{e\lambda}$$

Using the photoresponsivity, $R_{res}$, the EQE can be calculated. $h$ is Planck’s constant, $c$ is the speed of light, $e$ is the charge of an electron and $\lambda$ is the excitation wavelength.$^{23}$ The EQE calculated is 0.492 for green laser, 0.458 for blue laser and 0.135 for red laser.

The EQE calculated from using a single WSe$_2$ flake was 0.0583.

### 4.3.2.3. Photodetectivity

Photodetectivity is a measure of the performance of a photon sensitive device. Photodetectivity is calculated using the equation below.$^{22}$
\[ D^* = \frac{R_{res}}{(2eI_{dark})^{\frac{1}{2}}} \]

The photodetectivity calculated to be $9.90 \times 10^6$ Jones for green laser, $9.98 \times 10^6$ Jones for blue laser and $3.46 \times 10^6$ Jones for red laser.

From the photoresponsivity, EQE and photodetectivity calculated, it can be seen that the green laser of 543nm yields the best results compared to the other 2 wavelengths. This is interesting because even though blue photons possess a higher energy per photon, the green laser exhibits better results. This show that wavelength 543nm is closer to the excitation maximum peak than 405nm for either the WSe$_2$ or CdS$_{0.8}$Se$_{0.2}$ or both. I did not identify the extent of the individual contributions from the different components of the device. This will be discussed further in the later section 5.2. of “future work”.
5. Conclusion

5.1. Summary of project

In my project, I managed to synthesize thin WS$_2$ flakes on sapphire and SiO$_2$/Si substrates. This was done by optimising the parameters for the Chemical Vapour Deposition process. The parameters that were varied for the parameter search were the position of the substrate, position and amount of precursor, temperature settings, gas supply rate, pressure and a few others. The parameters used on SiO$_2$/Si could also be used for Si$_3$N$_4$ substrate.

Next, the characteristics of the WS$_2$ flakes were studied using different techniques. Raman Spectroscopy was used for identification of WS$_2$. Photoluminescence Spectroscopy was used for determining the bandgap of WS$_2$, which is approximately 1.98eV, corresponding to a wavelength of 625nm. Atomic Force Microscopy was used to measure the morphology and thickness of the WS$_2$ flakes, where it was found that the WS$_2$ flakes grown on sapphire substrate were between 1-2 layers and the flakes on SiO$_2$/Si substrate were between 2-3 layers. Fluorescence Microscopy is used to observe which areas on the WS$_2$ flake exhibit fluorescence. It was observed that WS$_2$ flakes on sapphire substrate generally exhibited fluorescence throughout its whole area, whereas the thin WS$_2$ flake on SiO$_2$/Si exhibited fluorescence only at the edges.

Finally, with the use of a heterostructure optoelectronic device using a WSe$_2$ flake and CdS$_{0.8}$Se$_{0.2}$ nanowire, the current against voltage (IV) graphs and current against time (Ivst) graphs were obtained using lasers of 3 different wavelengths. The Ivst measurements were done for “ON” and “OFF” states where the laser was unblocked and blocked respectively. Photoresponsivity, External Quantum Efficiency (EQE) and Photodetectivity were calculated for each of the lasers. It can be seen that the excitation wavelength of 543nm was the closest to the excitation maximum compared to 405nm and 660nm wavelengths for either WSe$_2$ or CdS$_{0.8}$Se$_{0.2}$. Cross referencing the Photoresponsivity of WSe$_2$ flakes, the heterostructure junction shows promising improvements in optoelectronics.

5.2. Possible Future Work

Due to time constrains, there are a few more things related to my project that can be explored and studied in the future.
Instead of synthesizing the 2 materials of the heterostructure separately and then manually stacking them, another suggestion is that a 2 step CVD process can be used synthesize the heterostructure. This means that after synthesizing a TMD flake for example, the substrate can be used for the synthesis of the next TMD, where the second TMD can possibly grow on top of the first TMD. This might give rise to different or enhanced optoelectronic properties.

It was observed that only the edges of the thin WS\textsubscript{2} flakes grown on SiO\textsubscript{2}/Si substrate exhibited fluorescence whereas the other areas exhibited much less. More research can be done on this. A more accurate AFM with less noise can be used to measure a very detailed height profile at the edge of the flake to see if indeed the edge is thinner than the rest of the flake.

It was found that the heterostructure junction exhibits photocurrent when exposed to lasers. However, global irradiation was used, which means that the extent of photocurrent contributions from the different components on the device is unknown. Instead of using a broad beam laser, a focused laser can be used to irradiate only specific components on the optoelectronic device. This way, the contributions photocurrent from each component can be determined.

To expand on my findings, another identical optoelectronic device can be constructed, except that instead of having heterostructure junction of WSe\textsubscript{2} and CdS\textsubscript{0.8}Se\textsubscript{0.2}, only WSe\textsubscript{2} is used. This way, a direct comparison can be done between using a single material and a heterostructure junction, performing the exact measurements on each device.

Different combinations of heterostructures can be used too. There are other TMDs available such as MoS\textsubscript{2} and MoSe\textsubscript{2}. CdS and CdSe can also be used instead of CdS\textsubscript{x}Se\textsubscript{1-x}. 
References:


