Transfer Process with 2D Transitional metal Dichalcogenides Materials

William Huang
BS/MS Microelectronics Engineering, Materials Science and Engineering
Rochester Institute of Technology
Rochester, NY
Email: txh9958@rit.edu

***Abstract*— The goal of this project is to expand RIT's knowledge on non-traditional 2D materials and to develop a tape-transfer process for single to double atomic layers of Molybdenum Disulfide from a substrate containing bulk MoS_2 to a blank substrate. The exfoliated materials will be inspected and characterized through both optical microscope and Raman Spectroscopy. The ultimate goal is to build it into devices to conduct electrical testing for its material and electrical properties. Material and electrical properties of the exfoliated materials will further be investigated and compared to MedeA simulation results.**

I. Introduction / Theory

Transitional Metal Dichalcogenides, also known as TMD, is formed by a covalent bond between a transitional metal atom from either group 4, 5, 6, or 7, and two chalcogen atoms from group 16. The general chemical formula for TMD is MX_2. It has the benefit of graphene as well as the characteristic of a very promising semiconducting material. By interchanging the transitional metal atom, one can formulate his/her desired device property. In this research experiment, molybdenum disulfide (MoS_2) is the main research focus.

Whenever the term '2-Dimensional materials' is introduced, people normally think of graphene. Graphene is also a 2-dimentional material that has a very high mobility resulting in supreme electrical conductivity. However, its performance as a semiconductor device is relatively poor due to the nonexistence of a bandgap. This results in an inability to switch between the on and off states.

When TMD materials are in monolayer form, they exhibit a direct bandgap. Once the layer stacks up to become a bilayer or multi-layers, it becomes an indirect semiconductor. **Figure 1a** and **Figure 1b** illustrates the bandgap simulation for monolayer and bilayer MoS_2 respectively. The direct bandgap property has a superior property that benefits the device by conserving the energy of the electrons since the electrons only have to move directly upwards from ground state to excited state. On the other hand, indirect bandgap characteristics may not be so desirable in this case since most of the devices are for photo or luminating sensitive devices. Different from direct bandgap, indirect bandgap requires the electron to travel upward and shift in order to reach the excited state from the ground state and that will reduce the initial photo activity. Therefore, a direct bandgap semiconductor device will result in a larger interaction with the incident light as compared to the same device incorporating a semiconductor material with an indirect bandgap.

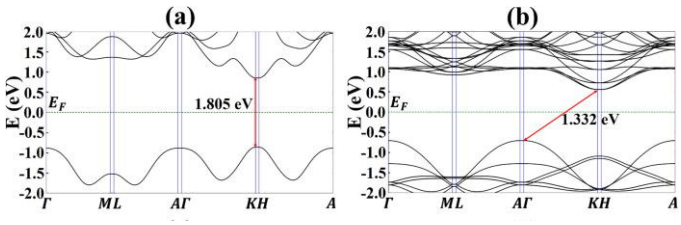


Figure 1: **(a)**This figure demonstrates the bandgap for monolayer MoS_2 **(b)**This figure demonstrates the bandgap for bilayer. MoS_2

II. Theory and Simulation Fundamentals

Vienna Ab-initio Simulation Package (VASP) was used to simulate all band structures. It is one of the most adapted simulation packages for research and educational uses. It has a database of potentials for each material as well as the bond lengths between different atoms. Moreover, the software package uses Density Function Theory (DFT) to compute quantum problems for materials. On the other hand, the most significant drawback on this simulation package is that it may be very time consuming depending on how computationally intense the simulation itself is.

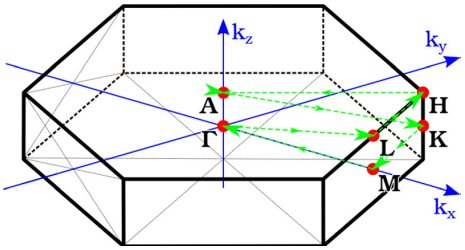


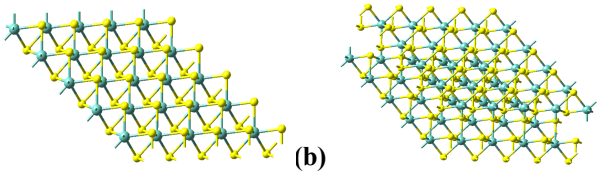
Figure 2: This figure demonstrates the k points in Brillouin zone

As illustrated in **Figure 2**, it represents the k-points in the Brillouin zone, which demonstrates the zone boundaries. Each letter shown represents different points in the crystal structure.

With a close comparison between **Figure 3(a)** and **Figure 3(b)**, one may observe that **Figure 3(b)** is the result of stacking two sets of the supercells illustrated in **Figure 3(a)**. The bottom

William Huang is a student at Rochester Institute of Technology in the Department of Electrical and Microelectronic Engineering.

layer is bonded to the top layer with van der Waals force. This is how the multilayer structures are formed.



(a) **(b)**

Figure 3: **(a)** This figure demonstrates the monolayer MoS_2 5 by 5 supercell **(b)** This figure demonstrates the bilayer MoS_2 5 by 5 supercell

Illustrated in **Figure 4** and **Figure 5** are the bandgap energy plot simulated through MedeA VASP for single cell monolayer and bilayer MoS_2, respectively. The simulated bandgap was with spin orbit coupling. Supercell simulation is still yet to be conducted due to the extra splitting bands that may result due to all of the extra cells presented, but the result may still be very close to the single cell simulation. Comparison of the monolayer to the bilayer are similar other than the direct versus indirect bandgap at the k space. A similar splitting can be observed that is due to the extra energy states. The Brillouin Zone was sampled with 12x12x1 k point spacing, with 12 units in the positive k_x direction, 12 units in the positive k_y direction, and 1 unit in the positive k_z direction, as shown in Figure 2. The different spacing between M, Γ, and K is a result of the location of three points in Brillouin Zone shown again in **Figure 2**. A right triangle property makes their distance between each other different.

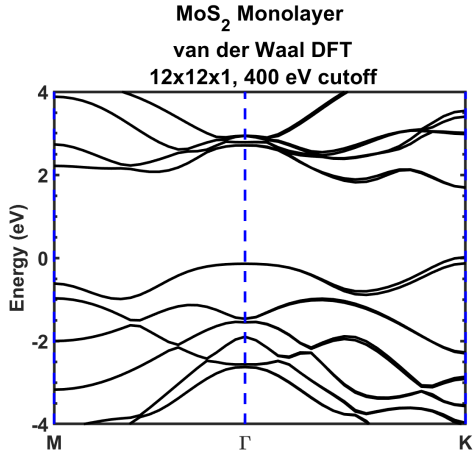


Figure 4: This figure demonstrates the MedeA VASP simulated bandgap for monolayer MoS_2

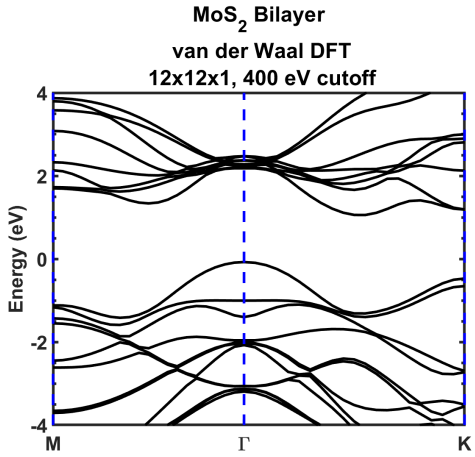


Figure 5: This figure demonstrates the MedeA VASP simulated bandgap for bilayer MoS_2

III. Experiment Procedures

A host substrate with 3000Å wet oxide on top was prepared for optimum bonding force and the ability to visualize the monolayer materials. The next step is to do contact cut and aluminum deposition and patterning.

Various sizes of square grids were initially direct written onto the transfer substrate to understand the approximated size of the exfoliated material. The sizes are 50μm, 100μm and 200μm in both length and width direction as illustrated in **Figure 6**. Four large squares set a clear indication of the four corners of the grid followed with several 4μm by 4μm squares outlining the perimeters. The grids were etched into the silicon wafer serving as both the level 0 alignment mark for future lithography processes as well as to locate the transferred material under the Raman Spectrometer microscope after visual inspection on an optical microscope. It was discovered that the 200μm size grids fits the best for the tape transfer process as all of the flakes do lay within the square grid with several laying on top of the perimeter lining. Grid sizing matters because the grid patterns were etched into silicon causing a difference in step height even after 3000Å of wet oxide were grown on top of the substrate. The step height will cause the exfoliated material to warp and affect with both the physical integrity, therefore affecting the electrical properties, as well.

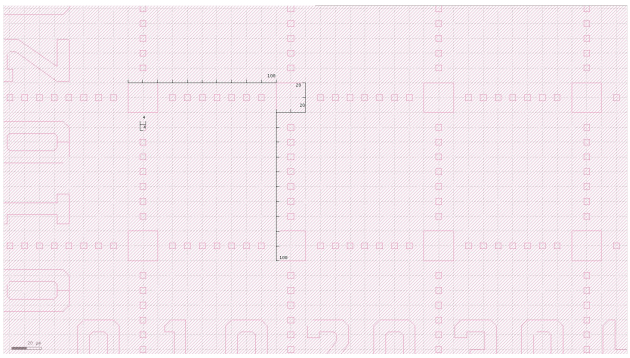
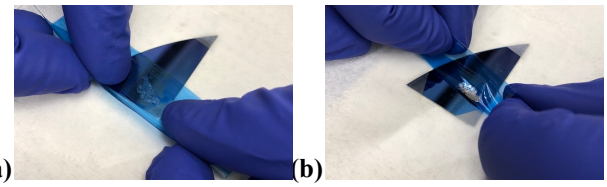


Figure 6: This figure demonstrates one of the many grid designs

Following in **Figure 7** and **Figure 8** illustrate the tape transfer process to achieve a monolayer TMD material. **Figure 7(a)** shows the material received from the material supplier where it looks like folded and cramped foil wrap. A small piece of the MoS_2 chunk was then separated and securely fixed onto a glass slide, where a blue cleanroom tape laid on top to peel off some layers of MoS_2 as illustrated in **Figure 7(b)** and **Figure 8(a)** respectively. After the cleanroom tape was placed onto the transfer substrate, the region where the MoS_2 was adhered was pressed firmly and then the tape was gently peeled off, as shown in **Figure 8(b)**.

(a) **(b)**

Figure 7: **(a)** MoS_2 chunk from SPI Supply **(b)** Bulk MoS_2 flake on double sided kapton tape waiting to be exfoliated



(a) **(b)**

Figure 8: Both **Figure (a)** and **(b)** demonstrates the exfoliation process for transferring TMD materials

Exfoliated material can then be inspected under a high-resolution and high-magnification optical microscope. The sample shown in **Figure 9** was viewed under 100X magnification. Under this magnification, different layers can be identified through different color shading of the material. The bluer the shading is, atomic layering there is in that region. This is due to the fact that the oxide layer underneath has a blue color characteristic. Take a closer look at **Figure 9**. One can observe that on the top left corner of the sample, where a loss of focus can be noticed. That occurred because when the tape peeled off the transfer substrate, the flake did not fully adhere to the substrate and was curled up. That region is typically where the monolayer would be discovered.

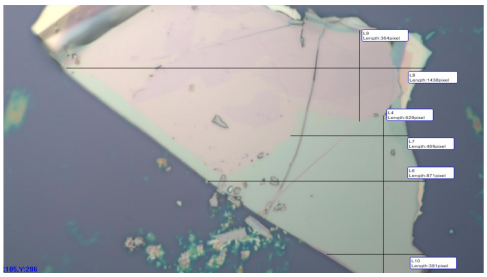


Figure 9: This figure demonstrates a visual inspection after a successful tape transfer of MoS_2

IV. Results and Discussion

Raman spectroscopy is a tool that utilizes the information of small vibration, rotation, and other low frequency by shining a laser beam on the sample for a structural fingerprint result. This tool is widely used in the research laboratories to be able to identify the molecule by the unique fingerprint results. That being said, each molecule has its own unique fingerprint and the difference in the number of atomic layers of the material will also reflect on that.

Raman spectrum of any atomic layer of MoS_2 has two bold peaks that illustrates the in-plane mode and out of plane mode. The in-plane mode shows that the opposite direction where Sulphur atoms and Molybdenum atoms vibrate; and the out of plane mode is just the Sulphur atoms vibrating. This brings back to the fundamental of TMD materials, where the material is constructed with only one transitional metal atom and two chalcogen atoms forming the general MX_2 chemical formula or MoS_2 for Molybdenum Disulfide in this study.

Figure 10 shows the difference of peak difference in Raman Shift (cm^{-1}), supplied from the tool manufacturer, Horiba Scientific, from different atomic layers of MoS_2 starting from monolayer on the bottom to penta-layer on the top. A "V" shape characteristic can be observed that the peak difference evolves with thickness. The difference in peak increases as the layer adds onto the material.

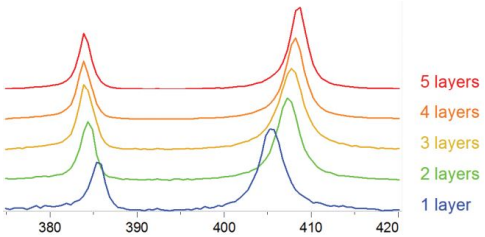


Figure 10: This figure demonstrates the peak difference in regard with the difference in atomic layer for MoS_2

Figure 11 demonstrates a various spot and sample across a various number of atomic layers of exfoliated MoS_2. A slight "V" shape characteristic can be observed in the data plotted through OriginLab. The color is just an indication of different data sets, from green, red, blue to black shows the increasing of atomic layer from bilayer (green) to a bulk material (black). As mentioned before, the spot size of the laser is considered to be slightly too large for the purpose of this study where the spot size diameter is approximated to be around 30μm. This will be over reaching most of the transferred material and most of the times the laser will be overlapping with other different atomic layer MoS_2 and even the tape residue around the exfoliated samples, as shown in the bottom left of **Figure 9**. Some small peaks can be observed in both **Figure 11** and **Figure 12** where there are believed to be some "hiding" monolayer to bilayer samples that their vibration had been overpowered by the bulk materials around as well as caused by the potential overlapping of the laser beam.

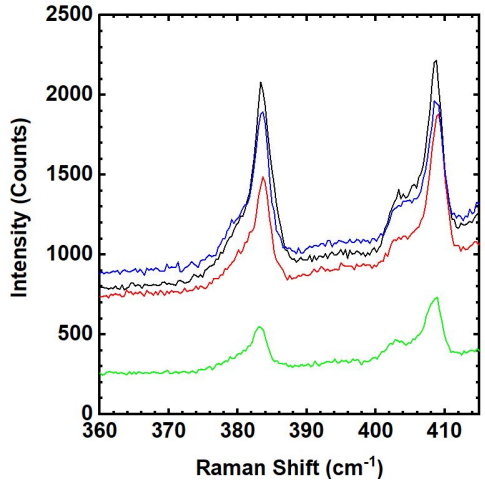


Figure 11: This figure demonstrates a various of sample measurements for various number of atomic layers

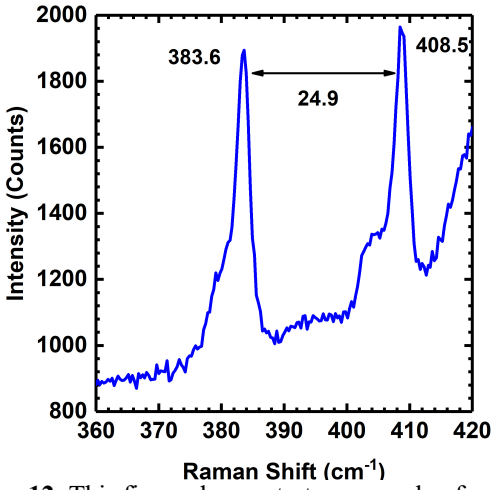


Figure 12: This figure demonstrates a sample of a clean measurement that estimates in a range of bilayer to quad-layer

V. Conclusion

Simulation results shown in **Figure 1(a)** demonstrates the direct bandgap characteristic for monolayer TMD materials and **Figure 1(b)** demonstrates the indirect bandgap for anything thicker than a bilayer TMD materials. The simulated results agree with the theoretical assumptions on the behavior of TMD materials. Raman spectrometry inspection results shown in **Figure 11** indicate a positive match on tri-layer exfoliated MoS_2, and a monolayer transfer can only be based on assumption by optical inspection. Large laser spot size may interact with substrate and cause the laser to detect over different atomic layers of material and tape residues. The next step of the research process will be finding a way to identify a monolayer region and further fabricate it into either a resistor or transistor for electrical testing.

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William Huang, BS/MS Microelectronics Engineering and Materials Science and Engineering is from Taipei, Taiwan. Previously, he co-oped with Element Six Technologies, a De Beers Group Company, as a CVD Diamond Research Intern in Santa Clara California and AdarzaBio as an Engineering Intern in Rochester New York. He will be working under Dr. Puchades over the summer to conduct research into Carbon Nanotube Thin Film Transistors and return to campus next semester to continue some aspect of this project as well as to complete his master's degree in Materials Science and Engineering.