Towards Fabrication of a Graphene MoS_2 Junction

William R. Cox, Roel L. Flores, and Ya-Qiong Xu

KEYWORDS. Graphene, MoS_2, nanotechnology

BRIEF. Single-layer graphene and MoS_2 were isolated in an attempt to fabricate a Schottky barrier.

ABSTRACT. Graphene is a recently discovered two-dimensional material that has proved to have an immense array of interesting physical and electrical properties. Molybdenum disulphide (MoS_2), a material potentially useful in nanotechnology when isolated to few layer and monolayer flakes, has interesting electrical properties distinct from graphene. An interface between these two materials is what we propose to fabricate, and it is expected to have characteristics of a Schottky barrier, namely current rectification. A PDMS (poly-dimethyl siloxane) stamping technique was used to deposit multi-layered flakes onto a Si/SiO_2 wafer with pre-patterned gold electrodes, and then a laser thinning process was carried out to cleave off successive layers of the flake. Then a standard micromechanical cleavage technique was carried out to deposit single layer graphene on a substrate, and finally a mechanical transfer method was applied to align the two separate pieces. This study also intended to take electrical and photocurrent measurements to test the design and efficiency of a Schottky junction device. This study aimed to fabricate a graphene-MoS_2 junction to determine if it is a viable Schottky barrier and could be applicable for future optoelectronics.

INTRODUCTION.

In recent years, nanotechnology has grown tremendously with applications in materials science, medicine, physics, and energy conversion. Many new innovations and novel materials have emerged from this growing field. Among them, graphene, a two-dimensional sheet of carbon atoms arranged in hexagonal rings (similar to the network one might find in a beehive) [1], has become one of the most promising materials for future photovoltaics due to its relatively easy synthesis and remarkable physical properties. Ultra-high electron mobility makes graphene an ideal candidate for single molecule detection systems and fast integrated circuits [1-4]. Although the existence of a pure free-standing 2-D material was first thought to be theoretical, Geim and Novoselov successfully isolated graphene from graphite on a SiO_2 supported substrate in 2004. [1] With their landmark paper detailing the first graphene device Geim and Novoselov brought about the era of graphene study, and the future of graphene based nanoelectronics. [1] In this paper, they show a way to easily synthesize graphene on a very small scale by placing highly ordered pyrolitic graphite on clear adhesive tape, and then repeatedly cleaving the material until there exists a dense covering of graphite "flakes" measuring only a few layers in thickness. With this simple method, many researchers in the field of physics and microengineering were able to study graphene and identify its utility in a variety of applications [2, 4, 5].

As mentioned previously, graphene has many unique properties that make it ideal in the field of nanoelectronics. These characteristics are extremely diverse, ranging from the distinct behavior of charge carriers in graphene, its mechanical strength and flexibility, and ability to be chemically functionalized. Graphene's unique electronic properties include the highest electron mobility (in certain conditions) of any material yet discovered, and the fractional quantum hall effect- the formation of quantized electrical charge in the presence of a magnetic field. [3, 6], All of these properties have given researchers the idea and motivation to further study graphene and implement it in various commercial electronic devices, replacing silicon as the channel material for specific applications, such as for touch screen capacitors or for devices requiring vary fast electrical transport [3].

Another unique material that possesses intriguing electrical properties is nanoscale molybdenum disulfide (MoS_2). Bulk MoS_2 has long been used in industry as a solid lubricant, because of its ability to ease friction between moving parts. MoS_2 has this ability because it is also composed of sheets of atoms stacked upon one another, with each sheet loosely bound to the next. Structurally, MoS_2 differs from graphene in that one unit of MoS_2 is composed of three sheets of atoms which are linked, a layer of molybdenum atoms, sandwiched by two layers of sulfur atoms. This different arrangement of atoms and bonding gives MoS_2 different properties than graphene. For example, while graphene is a zero band-gap material, limiting its use in switching electronics, single-layer MoS_2 has a natural band gap of about 1.29 eV, allowing for it to be used in active electronics more readily [7].

A common type of material junction in semiconductor electronics is called a Schottky junction or Schottky barrier. A Schottky junction is composed of a metal and semiconductor pair, which can form a diode useful to certain types of electronics, such as solar cells. Not all metal and semiconductor pairs form a Schottky barrier, as it depends on the difference between the two materials' minimum energy to excite a non-conducting electron (Work functions). A metal and a semiconductor paired together that don't create a Schottky junction create an Ohmic contact. The principal difference between an Ohmic contact and a Schottky junction is that an Ohmic contact does not have the rectifying capabilities that a Schottky barrier has, because of the properties of the materials which make up the two different junctions. This project proposes to fabricate the aforementioned Schottky junction from graphene and MoS_2, where graphene will act as a metal, because of its zero band-gap, and single-layer MoS_2 will play the role of the semiconductor, having a natural large direct band-gap. The differences in the work functions of these two substances should be enough to create a Schottky junction as opposed to an Ohmic contact. This junction could then be used in widely varied fields, and could help to potentially make electronics faster and smaller.

MATERIALS AND METHODS.

Micromechanical Exfoliation.

The method very similar to the one described by Geim *et al* was used for the micromechanical exfoliation of graphene and MoS_2. [1] Multiple pieces of graphite were placed onto a piece of ordinary adhesive tape. This tape was then folded over and pulled apart to cleave the bulk piece into two (or more) pieces of thinner bulk graphite. This process was repeated between 15-20 times depending upon the investigator's discretion. After sufficient cleavage, a less adhesive blue (Nitto) tape was used to pick up some of the thinned graphite. The above process for distributing layer across the piece of tape was used. This tape was used because it is less adhesive than clear tape and thus leaves far less residue. Finally, the tape was placed either on a silicon/silicon dioxide ($Si/300nm\ SiO_2$) wafer, or a glass slide coated with polymethyl-methacrylate (PMMA). The glass slide is spin-coated with A4 PMMA for a thickness ~ 100 nanometers, so that the optical contrast is enhanced for single-layer graphene. The substrate is then taken to a bright field optical microscope to identify candidates for transfer.

PDMS Stamping.

In order to isolate MoS_2, PDMS stamping was used instead of micromechanical exfoliation, due to the fact that the micromechanical exfoliation process tears apart the more brittle flakes of MoS_2, making it difficult to isolate a large-area, single-layer flake. A bulk flake of MoS_2 is first exfoliated on a piece of blue tape so that the flakes do not break apart as fast as they do on clear tape. The amount of MoS_2 on the tape is kept very dense, to allow for maximum deposition. A clean, prepared stamp of PDMS, roughly 2 x 2 cm is then placed on the tape, and pulled off quickly to grab the most pieces. This stamp is then positioned

over the Si/SiO_2 wafer, where it is pressed for roughly 30 seconds. Then the stamp is slowly removed so that many thick pieces will be taken off, but thinner ones will remain. This wafer is then taken to an optical microscope where pieces of MoS_2 that are good candidates for substrate transfer are identified. Good candidates for transfer are flakes that look to be large enough in area (>70 microns) to use in a prefabricated transistor device, but also thin enough for either laser-thinning or direct deposition.

Raman Spectroscopy and Laser Thinning.

A Thermo DXR Raman spectrometer was used to perform Raman shift measurements on both graphene and MoS_2 samples. A laser of 532 nm with a normal resolution grating of 900 lines/micron is used at a power of between 0.1 and 3 mW for Raman shift measurements, and a power of 10 mW for laser thinning. The laser thinning procedure described by Castellanos-Gomez *et al* was used as a building block for this technique, with some slight alterations. [8] The same Raman spectrometer mentioned above was used to perform the laser thinning, so that there could be *in situ* experimentation and characterization. The thinning was conducted by finding a flake of MoS_2 that looked to be less than 7-10 layers thick (characterized under the microscope visually by having a slight light-bluish tint). Then a Raman map was used so that there could be laser impaction at the smallest resolution of this instrument (1 micron). Therefore, a flake that was 10x10 microns would have a 100 point grid overlaid on it. At each point three exposures were taken, each lasting 0.5 seconds, with a maximum laser power of 10 mW. After the map was taken, a sample spectrum could be obtained to examine the effect of the thinning; the thinning could also be verified with optical means.

Mechanical Transfer.

Once laser-thinned MoS_2 has been successfully prepared and deposited on prefabricated gold electrodes, a single layer of graphene, which had been deposited on a glass slide covered in PMMA, was mechanically transferred on top of it. The glass slide was placed into a custom holder, and then the device was placed under it on a heated stage. The slide was aligned to the best of the experimenter's ability so that the graphene was positioned such that when it was transferred, it would be touching the MoS_2 and the gold electrode. Then the stage was heated up to approximately 160° C in order to be above the melting point of PMMA. Once the graphene was properly aligned, it was pressed onto the device, and held there. The slide was held long enough (~15-30 seconds) so that the PMMA would have the opportunity to melt and adhere to the substrate. Then the device was bound to the glass slide to transfer the flake of graphene onto the pre-patterned gold electrodes. To remove the glass slide, but leave the graphene on the electrodes, it is placed in an acetone bath, for anywhere from 12-48 hours, or until the device is removed.

Characterization Measurements.

To confirm the number of layers of flakes in question, and also corroborate the results given by Raman spectroscopy, AFM and SEM were performed. A Hitachi 2400 Scanning electron microscope was used to image flakes at magnification ranging from 10kx to 20kx. A Digital Instruments Nanoscope IIIa was used in tapping mode to evaluate the height differential between flake and substrate, therefore giving us total thickness.

RESULTS.

Micromechanical Exfoliation.

Using micromechanical exfoliation, a piece of single layer graphene can be isolated from bulk graphite. Graphite was first cleaved onto Si/SiO_2 wafers to perfect the exact technique. Graphite was then exfoliated onto a PMMA covered glass slide. Examples of graphite and single layer graphene are shown in Figure 1. As noted in the image, graphene is easier to visualize on a PMMA coated substrate as compared to a Si/SiO_2 substrate, but it loses its distinctive coloring, becoming lighter as the layers go down, instead of changing hue. The black arrow indicates single layer graphene while the white arrow indicates multilayered graphite.

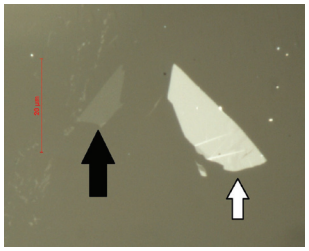

Figure 1. Graphite which has been cleaved onto a PMMA covered glass slide. The scale bar is 20 μm. The white arrow is pointing to a flake which is multilayered graphite, while the black arrow is pointing to a flake that composed of mainly single layer graphene, with some bi-layer on the edges.

PDMS Stamping.

A PDMS stamping technique was used to simultaneously thin and deposit MoS_2. A PDMS stamp, with MoS_2 deposited on it, was placed on a Si/SiO_2 wafer. As shown in Figure 2, thin layers of MoS_2 can be isolated using this technique. Figure 2A depicts a few multilayered flakes that are about 10-13 layers thick on a 300 nm Si/SiO_2 substrate. Figure 2B is more multilayered flakes of about the same thickness, but on a 285 nm Si/SiO_2 substrate. In both of these pictures, the crosshairs are alignment markers that are used to relocate samples after they have been identified. While this method is limited in the size of the area we can stamp, it can produce good candidates for our prospective device.

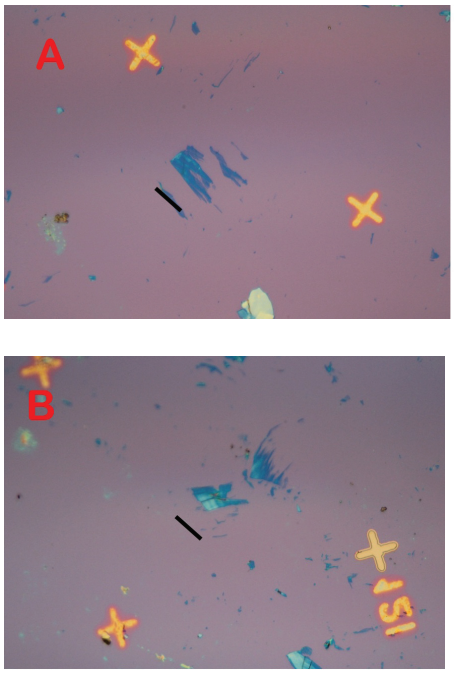

Figure 2. A) MoS_2 fabricated *via* PDMS stamping on a 300 nm Si/SiO_2 substrate. Scale bar is 20 μm in length. B) MoS_2 also fabricated *via* PDMS stamping, but on a 285 nm Si/SiO_2 substrate.

Raman Spectroscopy and Laser Thinning.

Raman spectroscopy has been used to determine the number of layers and existence of two-dimensional materials since their inception [9]. When looking at the output of a Raman spectrum, a few things must be considered, chiefly what the spectrum should look like in context. For graphene, the relative intensities of the G (~1580 cm-1) and G' (~2700 cm-1) peak are most important. The difference in intensities between these two peaks can roughly tell how many layers are being looked at. MoS_2 is not so simple; the relative intensities are of very little importance to the number of layers. The most telling characteristic of the Raman spectrum of MoS_2 is the difference between the two peaks of few-layer MoS_2. As the two peaks shift towards each other, a difference of around 20 cm-1 is ideal for single-layer MoS_2 . Figure 3 gives examples of the Raman spectrum of both graphene and MoS_2.

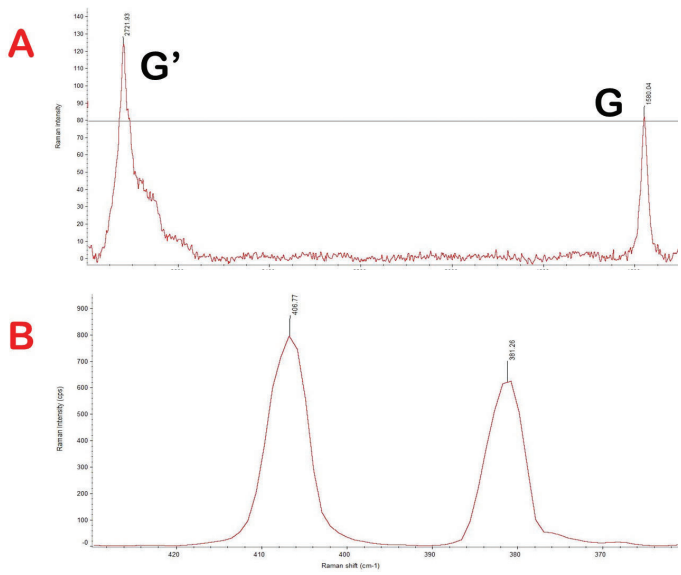

Figure 3. A) Raman spectrum of single-layer graphene, relative intensity of G' peak is larger than G peak, indicating one-layer thick graphene. B) Raman spectrum of MoS_2, a difference of around 20 is accepted as single to double layer MoS_2, here the difference is around 28, suggesting 3-5 layer MoS_2. Units on the vertical axis are counts, and units on the horizontal axis are cm-1

A thin flake of MoS_2, such as that shown in Figure 2, was then bombarded with a laser to etch away additional layers. A Raman spectrophotometer can be used to do this procedure, and also characterize it *in situ*. Raman spectra taken from the MoS_2 being laser-thinned were compared to quantify how much material is removed from the top of the target flake. The three Raman spectra in Supplemental Figure 1 represent the spectra taken before laser thinning, and after each treatment. It can be seen that as more treatments are applied to the sample, the two peaks near the right end of the spectrum shift toward each other, this is characteristic of few layer MoS_2, and can also help us in quantifying the change in number of layers between treatments.

DISCUSSION.

While graphene and other two-dimensional materials have been introduced as a potential replacement for silicon in traditional electronics, development protocols as well as characterization of these materials must be studied further. Principally, there exists a need for a simple way to fabricate pristine graphene on demand. We have shown, through the use of Raman spectroscopy and optical imaging that with traditional scotch tape method graphene can be produced with reasonable accuracy and ease. Given that there will still be many issues that have to be figured out before this process could even be thought of to be used in a large scale manufacturing process, the need for only a small amount of this material, due to its characteristics and natural scale, is advantageous for fundamental materials science studies.

MoS_2, another material recently found to have interesting electrical, mechanical, and optical properties at the nano-scale, is even more difficult to isolate *via* the scotch tape method, usually requiring dozens of man-hours until one piece suitable for use can be found. In this study, it was found that a PDMS stamping procedure greatly increases the yield for a similar number of hours worked. Although the PDMS stamping procedure does not create a large number of single-layer MoS_2, it does produce many more pieces of few-layer MoS_2, ranging from between 3-10 layers. With this improvement, the samples can then be processed using a laser to shave layers of MoS_2 off of the surface. We have shown that laser thinning works through optical means, *in situ* Raman spectroscopy, scanning electron microscopy, and also through atomic force microscopy. This combination of PDMS stamping and laser thinning produces single layer flakes of MoS_2 which can then be subsequently characterized and used in a wide variety of nanoelectronics. A junction between graphene and MoS_2 could create what is known as a Schottky junction, or Schottky Barrier. This barrier has interesting and useful electrical characteristics, such as the ability to rectify incoming current, and a lower voltage drop compared to a similar p-n junction. Using these two materials to fabricate a Schottky junction is a completely novel approach in researching electronics at the nanoscale. While these processes are not yet fit for large-scale manufacturing, this study lends to the first steps toward establishing a proof of principle. The use of these two materials in traditional electronics could indicate the advent of a new technological era. In the future, these two materials could be used to create a junction of this type, even though a successful operating device was not fabricated in this research. The procedures used in this article have shown to be successful on their own, but have given confounding results when attempted to be used in conjunction. More work will be done to continue to transfer flakes of MoS_2 onto flakes of graphene, thereby fabricating a Schottky barrier. Work is being done to perfect the transfer stage device, and to make to PDMS stamping method more accurate and more reliable. Finally, another avenue to pursue might be to use CVD (Chemical Vapor Deposition) grown graphene, but this might create problems in the area of quality of the junction.

ACKNOWLEDGMENTS. I would like to thank Nathan Fisher, Logan Sweet, Zina Jarrahi, Yunhao Cao, and Tu Hong for training and general assistance. I would also like to thank Dave Caudel and the Bolotin Group for use of their transfer stage. This work was supported by the National Science Foundation (ECCS-1055852 and CBET-1067213), SCEEE Research Initiation Grant and Vanderbilt Nicholas Hobbs Discovery Grant. The project described was supported by Award Number R25RR024261 from the National Center For Research Resources. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Center For Research Resources or the National Institutes of Health.

SUPPORTING INFORMATION.

Figure S1. Flakes of MoS_2 before and after laser treatment

REFERENCES.

1. K. S. Novoselov *et al.*, *Science*. 306, 666 (2004).
2. D. Cohen-Tanugi, J. C. Grossman, *Nano Letters.* (2012).
3. A. H. Castro Neto, F. Guinea, N. M. R. Peres, *et al.*, *Rev Mod Phys.* 81, 109 (2009).
4. Y.-M. Lin *et al.*, *Science.* 332, 1294 (2011).
5. T. Kurkina, K. Balasubramanian, *CMLS*. 69, 373 (2012).
6. K. S. Novoselov *et al.*, *Science.* 315, 1379 (2007).
7. B. Radisavljevic, a Radenovic, *et al.*, *Nature Nanotech*. 6, 147 (2011).
8. A. Castellanos-Gomez, M. Barkelid, A. M. Goossens, *et al.*, *Nano Lett*, 12, 1 (2012).
9. A.C. Ferrari *et al.*, *PRL*. 97, 18 (2006).

William R. Cox is a student at John Overton Comprehensive High School in Nashville, Tennessee, and enrolled in the School for Science and Math at Vanderbilt.