

**Identification and Mapping of Mechanically Exfoliated
1H-MoS₂ Flakes for Field-Effect Transistors**

by Mariela Georgieva and Terrance O'Regan

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August 2014

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Sensors and Electronic Devices Directorate, ARL**

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14. ABSTRACT Following the discovery of graphene, there has been increased interest in materials that allow for the construction of two-dimensional (2D) devices. In this project we will focus on 1H-molybdenum disulfide (MoS₂), which, like graphene, is a monolayer; unlike graphene, however, it has a band gap. 1H-MoS₂ differs from silicon in that its band gap is direct and, like graphene, can be mechanically exfoliated (ME) to isolate it as a single molecular layer. We will lay the groundwork required for fabricating field-effect transistors and address the effects that the material microstructure has on transistor properties by comparing the quality of ME-MoS₂ to MoS₂ grown by chemical vapor deposition (CVD-MoS₂). The layer count and material quality will be analyzed using Raman spectroscopy, photoluminescence spectroscopy, and atomic force microscopy (AFM) mapping, after which the transistors will be built using e-beam lithography.					
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Student Bio

Mariela Georgieva is currently a junior at the University of Maryland, College Park, majoring in materials science and engineering in the Clark School of Engineering. Her past research experiences include gathering Earth sciences metrics and calibration data at NASA. Her future plans include going to graduate school to continue materials science studies.

1. Introduction/Background

Following the discovery of graphene, there has been increased interest in the use of materials that allow for the construction of two-dimensional (2D) devices. 2D materials both allow for more compact devices, as well as the potential to find a material to compete with, or at least compliment, silicon.¹ Graphene does not have a band gap, which means that there is no on/off switch, and, hence, does not lead one to consider graphene for logic applications. On the contrary, transition metal dichalcogenides (TMDs) do have band gaps, many of which are direct in nature. Consequently, this report will focus on 1H-molybdenum disulfide (MoS_2), which has a direct band gap and can be exfoliated to a single molecular layer. If the quality of the material can be maintained during processing, MoS_2 may prove to be a valuable resource for future technologies. This report aims to cover the process of finding useful molecular layer flakes on MoS_2 that was mechanically exfoliated (ME- MoS_2) by use of the Scotch Tape-method. The flakes will then be used to fabricate devices, and the material quality will be tracked throughout the device fabrication process. This tracking will allow for a comparison of material quality between naturally acquired ME- MoS_2 and MoS_2 grown in a lab by Chemical Vapor Deposition (CVD- MoS_2). The comparison is important with regard to the fact that ME- MoS_2 is of higher purity, but that CVD- MoS_2 is easier to fabricate, and both are at risk for displaying degraded material quality following processing. As a result, it is important to study and compare the final material quality received at the end of the fabrication process to determine which would be a more realistic path to generate 1H- MoS_2 to use for consistent device fabrication. In the future, the effects of each processing step will be qualified using non-invasive Raman spectroscopy, which is ideal for assessing material quality without actually making an impact on the material. Initially, when the (possibly multilayer) ME- MoS_2 flakes were being analyzed, the layer count and material quality were analyzed using Raman spectroscopy, photoluminescence (PL) spectroscopy, and atomic force microscopy (AFM) mapping. The transistors are currently being built using electron beam lithography, and Raman will be used to test for damage. The spectra will be measured in the backscattering configuration using a 100 $\times$ objective and either a 600 or 1800 grooves/mm grating. The spot size of the laser will be ~ 342 nm, resulting in an incident laser power density ~ 140 $\mu\text{W}/\text{m}^2$.⁴ The comparison of the effects of the fabrication process on ME- MoS_2 and CVD- MoS_2 will allow us to correlate material degradation to device performance and innovate new ways to maintain material quality during fabrication.

2. Experiment/Calculations

Molybdenum disulfide (MoS_2) is of interest due to its electronic, optical, and catalytic properties, and also for its use as a dry lubricant. As the latter suggests, it is held together through van der

Waals forces.² For this report, it is important to understand the difference between 1H-MoS₂ and 2H-MoS₂. There is a change in functional modes between 1H-MoS₂ and 2H-MoS₂, as shown in Fig. 1. 1H-MoS₂ is 2D and has a direct band gap, while 2H-MoS₂ is three-dimensional (3D) and has an indirect band gap, which occurs as a result of stacking, shown in Fig. 2. 1H-MoS₂ is also what is referred to as a single sheet, because it contains exactly 1 Mo and 2 S, while 2H-MoS₂ is a monolayer made by stacking two layers of 1H-MoS₂. Any greater number of layers is stacked 2H-MoS₂, which can be used to construct bulk MoS₂.¹²

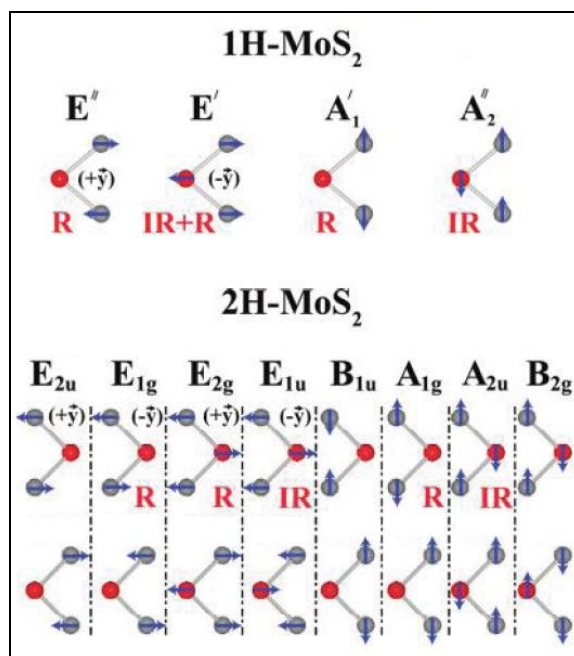


Fig. 1 A comparison of the functional modes of 1H-MoS₂ and 2H-MoS₂, adapted from Ataca et al.¹²

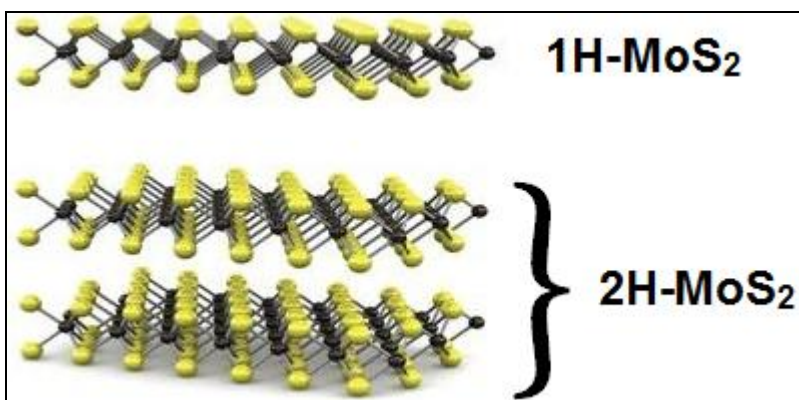


Fig. 2 Example of 1H- and 2H-MoS₂. The thickness of 1H-MoS₂ is usually 0.7 nm, and the thickness of 2H-MoS₂ is usually 1.4 nm.¹⁴ Adapted from Radisavjevic et al.¹³

1H-MoS₂ on SiO₂ substrate is about 0.8–1.0 nm in height. The molecular layer, itself, is about 0.5–0.7 nm, which is in accordance with the theoretical value of 6.15 Å. The increased thickness is due to adsorbents on the surface of the substrate, which contribute to it.² It is possible that glue from the exfoliation process has become caught beneath the molecular layer, making it appear to be greater in height. 1H-MoS₂ is also the first atomically thin material that is an effective emitter of light. It has a strong PL because of slower electronic relaxation arising from unique electronic structure.² Its strong PL makes it possible for use in photostable markers and sensors that can be adapted to probe nanoscale dimensions. The controllability of the band gap may be used to optimize the material's use for photovoltaic applications.³ It is also promising for use in logic circuits and optoelectronic devices, along with flexible and transparent substrates.⁴

MoS₂ molecular layers are visible on Si as a result of the effect of MoS₂ on the reflected light. Light reflects differently off the surface of the sample based on whether MoS₂ is present, or if there is only Si. This is the same reason that graphene is visible under an optical microscope, or even to the naked eye.⁶ The presence of even a small amount of graphene causes optical interference, so the reflected light is of a different intensity and there is enough contrast to see the graphene. It is important that the graphene be slightly opaque for this to occur, or there will not be enough interference to allow it to be visible; molecular layer graphene and 1H-MoS₂ are both sufficiently opaque to be viewed by the human eye. The amount of contrast also differs based on the wavelength of light used to illuminate the sample and the thickness of the SiO₂ layer. Using this, optimal contrast can be achieved by matching the thickness of the SiO₂ layer with a color filter.

Contrast between the MoS₂ flakes and the Si substrate was the initial technique for identifying 1H-MoS₂ flakes. An optical microscope was used to visually scan the chip using a 100× objective, with a grid created at MIT used to record the coordinates of the flakes to make them possible to relocate in the future for device fabrication. A 100× objective had to be used because most flakes were only a few microns in size, and the increased magnification also made it easier

to distinguish between the color of molecular layer flakes and substrate. However, using this magnification on a 1 cm^2 chip meant that it took about 100 sweeps back and forth across the chip to cover the whole area. Because contrast increased with increased layer count, flakes with minimal contrast to the substrate were marked as potentially being molecular layers. Flakes needed to be at least $3 \times 3\text{ }\mu\text{m}$ to be suitable for device fabrication. Smaller flakes were also noted for the possibility that the shape allowed for a device to fit (most flakes are irregularly shaped, not a perfect $3 \times 3\text{ }\mu\text{m}$ square) or for potential imaging or laser power tests to be done in the future. Imaging and the effects of high laser powers on molecular layers are also interesting topics to study, though they were not the subject of this report. An example of a flake with a combination of 1H-MoS₂ and 2H-MoS₂ is shown in Fig. 3, showing the extent of contrast between flakes used for the experiment and substrate, as well as an average size for most flakes studied.

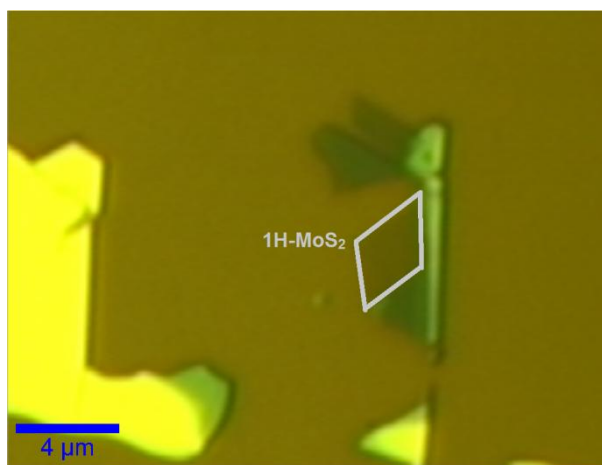


Fig. 3. MoS₂ flakes surrounded by a Si substrate. Under the green filter, the 1H-MoS₂ flakes are the grey-green pieces. MoS₂ becomes more yellow in color as the amount of layers increases. The dark green flakes are bilayer, the green are multilayer, and the yellow are bulk.

Layer counts were confirmed with Raman spectroscopy, atomic force microscopy, and photoluminescence spectroscopy. AFM scans were initially conducted to check if what appeared to be 1H-MoS₂ through the optical microscope was the appropriate thickness. Results from the AFM alone were not completely conclusive, due to the previously mentioned possibility of substrate effects, and it was necessary to perform additional scans to be certain that a flake was 1H-MoS₂. After AFM scans, PL was used to approximate layer counts. A higher intensity PL peak indicates a lower layer count. As the number of layers increased, the intensity of the photoluminescence decreased. This is due to the transition from indirect to direct band gap that occurs as the layers are stripped down to a single molecular layer.¹¹ Raman scans provided the last check to verify that the flakes were molecular layers. Figure 4 provides examples of the

difference in PL and Raman values for 1H-MoS₂ and 2H-MoS₂, clearly showing the difference in the transition from direct to indirect band gap, as well as the change in functional modes.

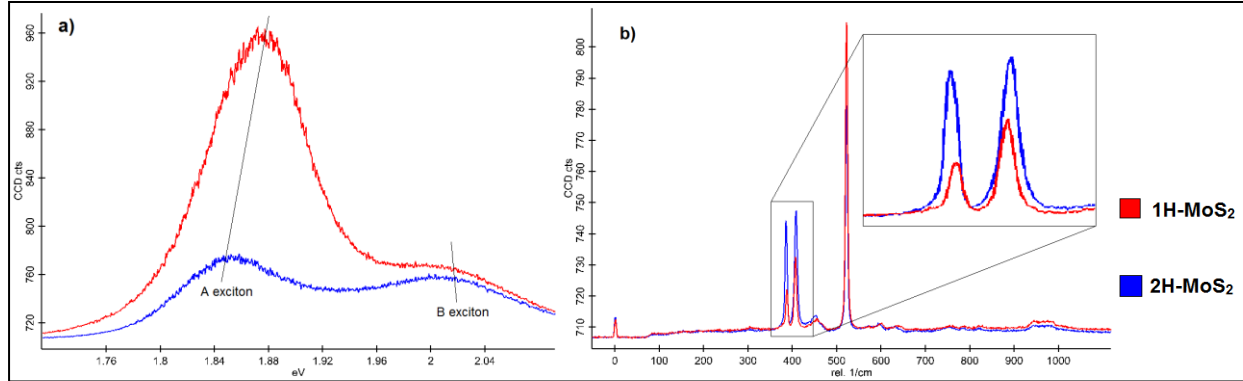


Fig. 4 a) Image of a PL plot for 1H-MoS₂ and 2H-MoS₂ flakes, showing the peak intensities of each. As layer count increases, the PL plot tends to flatten, with no discernible peak intensity for either the A or B exciton.³ b) Image of a Raman plot for the same flakes, showing the silicon and functional mode peaks (zoomed in to show the difference between the functional mode peaks for the 1H and 2H), as well as a fourth peak where some of the laser leaks through the filter. For bulk MoS₂, there is no silicon peak visible and no difference between in-plane and out-of-plane frequency because the silicon is covered by the MoS₂ and molecular motion is equally restricted in all directions, as opposed to 1H-MoS₂ where molecular motion is easier out of the plane because there is nothing restricting the atoms from moving.⁹

Checking the layer count with Raman involved determining the peak positions of the E' and A'₁ functional modes. The frequency of in-plane E' mode decreases with thickness, while the out-of-plane A'₁ mode increases with thickness.^{7,8} Using these modes, the thickness can be determined on the atomic level using Raman. Raman spectroscopy is non-invasive and does not cause any damage to the material while taking measurements, unlike other techniques, such as AFM, which may scrape the surface of the material.⁹ Figure 5 provides a reference of the images produced by the different scans, as well as what they mean in terms of distinction between 1H-MoS₂ and 2H-MoS₂.

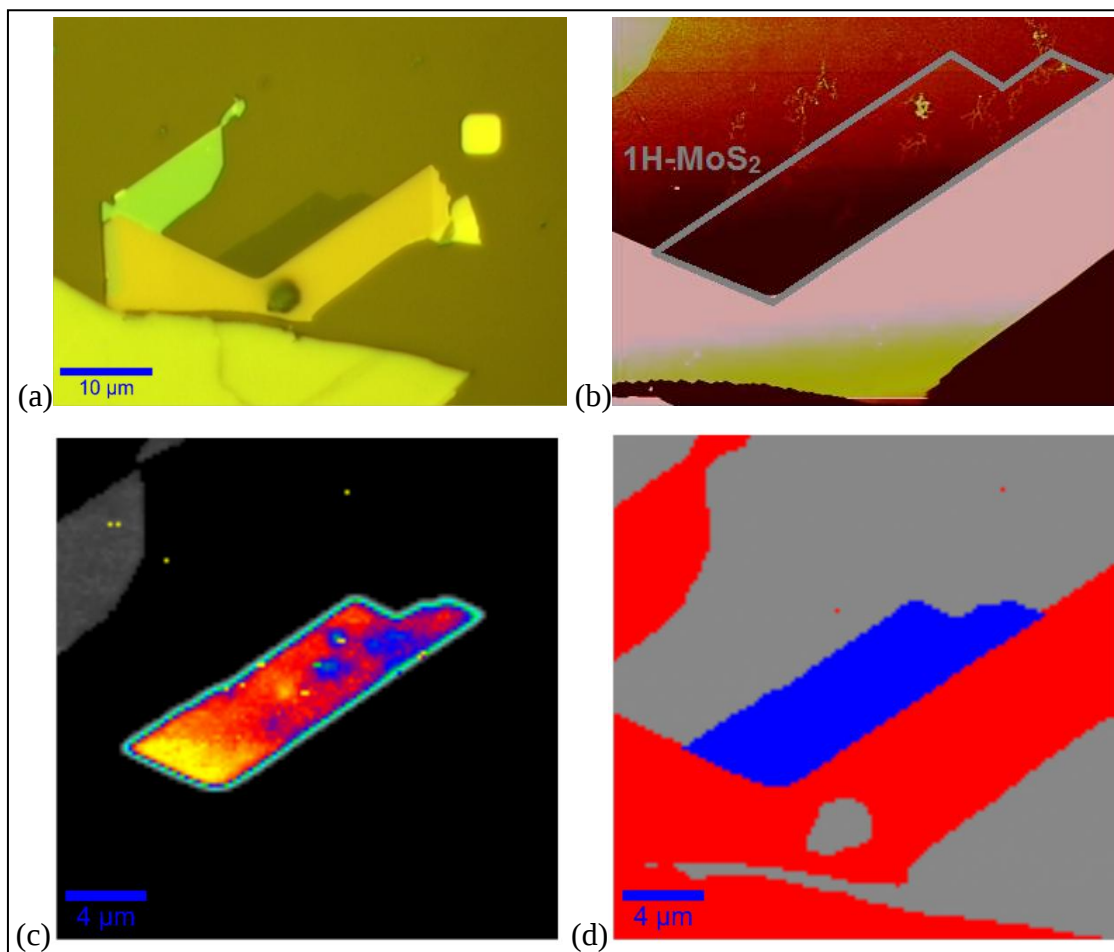


Fig. 5 Various scans used to analyze Flake 66. a) Optical microscope image of the flake, where the 1H-MoS₂ area of interest is the green/grey rectangle in the center. b) AFM image of the flake. The slightly lighter area is the 1H-MoS₂ flake, showing the faint difference between the height of the molecular layer and that of the substrate. AFM images usually show a greater contrast between molecular layer and substrate, though in this case the bulk surrounding the molecular layer diminished the effect of the height difference between the molecular layer and the substrate. c) PL image of the flake, showing increased intensity with red and yellow coloring where the 1H-MoS₂ flake is located. d) Raman image of the flake, where the 1H-MoS₂ is shown as blue and bulk is red.

Electron-beam lithography (EBL) will be used to fabricate variable channel length field-effect transistors (FETs) and Hall bar structures directly onto 1H- and 2H-MoS₂. A methyl methacrylate (MMA) and polymethyl methacrylate (PMMA) bilayer resist process will be used for all steps. The MoS₂ layer will be patterned using a low-power inductively coupled plasma reactive ion etch (ICP-RIE) in a CH₄/O₂ plasma, and source and drain contacts will be deposited using e-beam evaporated Ti/Au (15/85 nm). In order to analyze any damage or variation in the MoS₂ structural chemistry during processing, high-resolution Raman and PL imaging will be performed on the active device area after each processing step.⁴ Figure 6 provides examples of devices built on MoS₂ samples, and Raman and PL scans done regarding electrical performance.

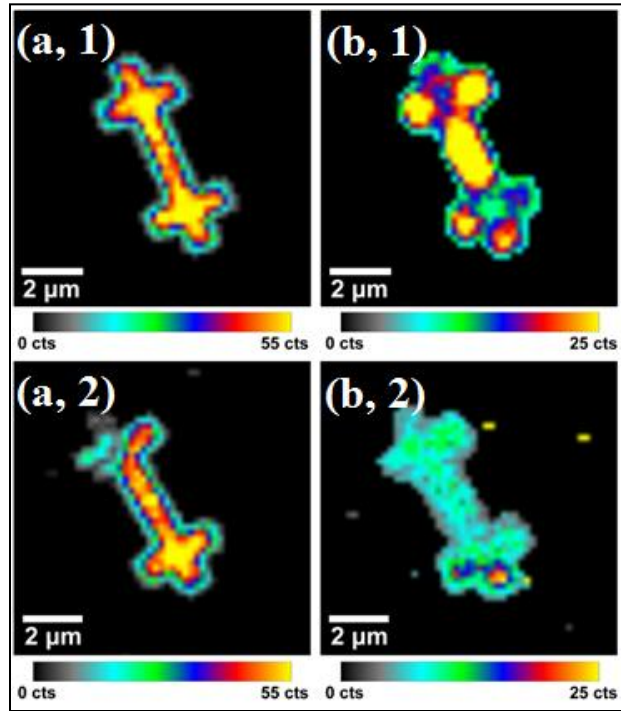


Fig. 6 Examples of Raman and PL scans of devices built on MoS₂. a, 1) The Raman intensity of the in-plane mode. a, 2) The PL intensity of the in-plane mode. b, 1) The Raman intensity of the A exciton. b, 2) The PL intensity of the A exciton.¹⁰

3. Results and Discussion

The chip sample studied was $\sim 1 \text{ cm}^2$ in size and revealed 70 MoS₂ flakes of interest, with six potential 1H-MoS₂ flakes of a reasonable size for processing devices. There were also high numbers of bilayer, multilayer, and bulk flakes that could be used to build devices, as well as a number of nanoscrolls that could prove promising to study. Nanoscrolls could be either 1H-MoS₂ or 2H-MoS₂, depending on how they formed. Though the main focus of this study was the effects of processing on 1H-MoS₂, flakes with varying amounts of layers were also worth testing because of their potential to be useful and the fact that they are more abundant than the 1H-MoS₂ flakes.

Fabrication is currently in process. Plans are to continue fabricating devices on all the eligible 1H-MoS₂ flakes, and then to test for basic transistor characteristics. Post-fabrication plans include measuring transistor performance, and obtaining the carrier mobility of ME-MoS₂ molecular layers and comparing this to the value for CVD-MoS₂.

4. Conclusions

The experiment focused on analyzing the differences between the material characterization of CVD-MoS₂ and ME-MoS₂, using the same processes to build and analyze devices. At this point, potentially useful 1H-MoS₂ flakes have been identified on ME-MoS₂ using a variety of tools, including an optical microscope, Raman spectroscopy, photoluminescence spectroscopy, and atomic force microscopy mapping. Device fabrication is currently in processing, with plans for its conclusion before the end of the fiscal year.

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List of Symbols, Abbreviations, and Acronyms

2D	two-dimensional
3D	three-dimensional
AFM	atomic force microscopy
CVD-MoS ₂	MoS ₂ grown by Chemical Vapor Deposition
EBL	Electron-beam lithography
FETs	field-effect transistors
ICP-RIE	inductively coupled plasma reactive ion etch
ME-MoS ₂	mechanically exfoliated
MMA	methyl methacrylate
MoS ₂	1H-molybdenum disulfide
PL	photoluminescence
PMMA	polymethyl methacrylate
TMDs	transition metal dichalcogenides

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