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UC Merced Undergraduate Research Journal

Title

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Journal

UC Merced Undergraduate Research Journal, 12(2)

Author

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Publication Date

2020

DOI

10.5070/M4122048145

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Undergraduate

The Methods to Unlock Molybdenum Disulfide

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Abstract

In today's world, we've invented many new technologies that have allowed us to map out the earth's surface but just as we can map out surfaces on a large scale, we can also map out surfaces on a very small scale such as in nanometers. Thus, giving us opportunities to study & discover various materials such as molybdenum disulfide (MoS_2) crystalline flakes. MoS_2 is a material that has a similar yet different structure to graphene, low friction when compared to SiO_2 (a low friction material as is), and provides many potential applications that can be implemented into aerospace as a solid lubricant. But like any fellow researcher studying a material, each has their methods/techniques that they use to obtain results. In our proposal, we will cover the research that has taken place to provide a consensus of MoS_2 's potential application as a solid lubricant in aerospace to its low frictional properties in the nanometer scale. And the technologies we'll be looking into to access for our methods/techniques for researching will be Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-Ray Photoelectric Spectroscopy (XPS), X-Ray Diffraction (XRD), and Tribometers at the University of California, Merced (UC Merced).

Introduction

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Discovered in 2004 through mechanical exfoliation or in simpler terms, the scotch tape method, graphene has been a leading material due to its lightweight, thin, and strength capabilities that come from its unique one-layer structure [2,4]. But like any discovery, another one comes along showing much potential, in this case, a new 2D material which is MoS₂. Similar in structure and 2D appearance, MoS₂ has become widely known for its wide use in applications, a major one being as a solid lubricant in space [1,5,10]. MoS₂ has a complex atomic structure in which the atoms are orientated in multiple hexagonal planes, **Figure 1b & 5**. These planes stack upon each other and have a strong covalent bond that exists between the molybdenum and sulfur atoms. Although graphene's properties have been identified and documented before [4], there is still much to be learned about MoS₂ with ongoing experiments that can bring new light into properties we've yet to observe any potential applications it may be implemented to such as in aerospace.

In today's aerospace technology, there are many commonly used lubricants in the application. Properly understanding these lubricants is extremely important. Should a lubricant ever malfunction in a space system, this could lead to serious damage to the system, which typically has no backup or substitutable system [1,4]. The main use in satellites and other aerospace technology is the lubricant used in sliding mechanism pistons, rotators, and moving components. Perfluoropolyether, and multiply alkylated cyclopentane are some examples of the lubricants currently used most in

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aerospace technology. Despite these various available materials for lubricants, there is

still a demand for lubricants that can operate in high and low-temperature environments. Lubricants are often thought of as a liquid substance, such as the greases and oils used in most terrestrial mechanical systems. Though typically effective, these forms of lubricants are sometimes unsuitable for use and a solid lubricant is required for full effectiveness. Often liquid lubricants for Low Earth Orbit (LEO) are vaporized at high temperatures and vacuum pressure. Because of this, it would make sense why this form of lubrication would be unsuitable for use in aerospace mechanics. These machineries are often exposed to and undergo extremely high temperatures, making solid lubricants more preferable [1]. Close study and observation of MoS_2 will allow confirmation on whether or not this material is a suitable lubricant for aerospace aircraft. MoS_2 is a material that is already in use in LEO satellites [1,5,10]. The material is thin-layered, containing low frictional properties and high durability. The image below, **Figure 1a**, contains a sample of MoS_2 , illustrating the characteristics and features.

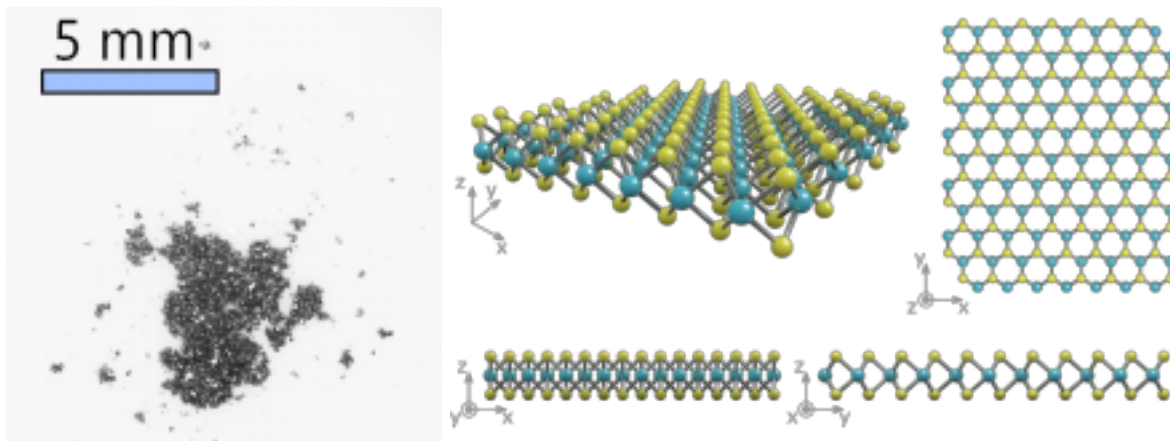


Figure 1 (a) Powdered sample of molybdenum disulfide (MoS_2) **(b)** MoS_2 structure model, molybdenum atoms (Blue) & Sulfur atoms (Yellow). Adapted from *Ossila*, Retrieved April 26, 2020, from <https://www.ossila.com/pages/molybdenum-disulfide-mos2> & <https://www.ossila.com/products/molybdenum-disulfide-powder?variant=8789263253621>. Copyright © 2020 by Ossila.

As illustrated in **Figure 1a**, the material (MoS_2) exists in a thin powdered form. MoS_2 has several advantages that promote its use as a lubricant. This material is effective for lubrication in part to its lamellar state and atomically-thin plates that easily slide against each other due to weak Van der Waals forces between them [9]. Molybdenum disulfide (MoS_2), though effective by itself for lubrication, can also be used in addition to liquid lubricants. This combination of solid and liquid lubricants is beneficial because it ensures that the material is effectively and safely lubricated. MoS_2 also reduces the weight of systems compared to liquid lubricants. Aside from the physical beneficial factors of solid lubricants over liquid lubricants, there are also economic benefits to using MoS_2 over liquid lubricants. This material, along with other solid lubricants in some cases is less expensive to use and maintain than oil and grease lubricants [5,6]. Though these factors cause MoS_2 to seem suitable for lubricant in aerospace mechanics,

For this material to be a suitable fit for the application, there are qualifications it must meet in a space environment. For MoS_2 to be an effective aerospace lubricant, the

material must maintain its properties under atomic oxygen exposure [4-7]; thus being able to withstand the bombardment of oxygen atoms coming rapidly from LEO since objects travel/ orbit the earth a lot faster than down on the surface. For example, it is a fact that MoS₂ can operate effectively in various ranges of temperatures from far below freezing, to hundreds of degrees Celsius. More research is needed on this material to determine and understand how to improve its lubricating properties. In this proposal, we will go through the different methods/techniques that can be tested on MoS₂, compare each technique's results to one another to find a correlation, and distinguish from those results how MoS₂ can be applied as a low friction material & solid lubricant.

Procedures

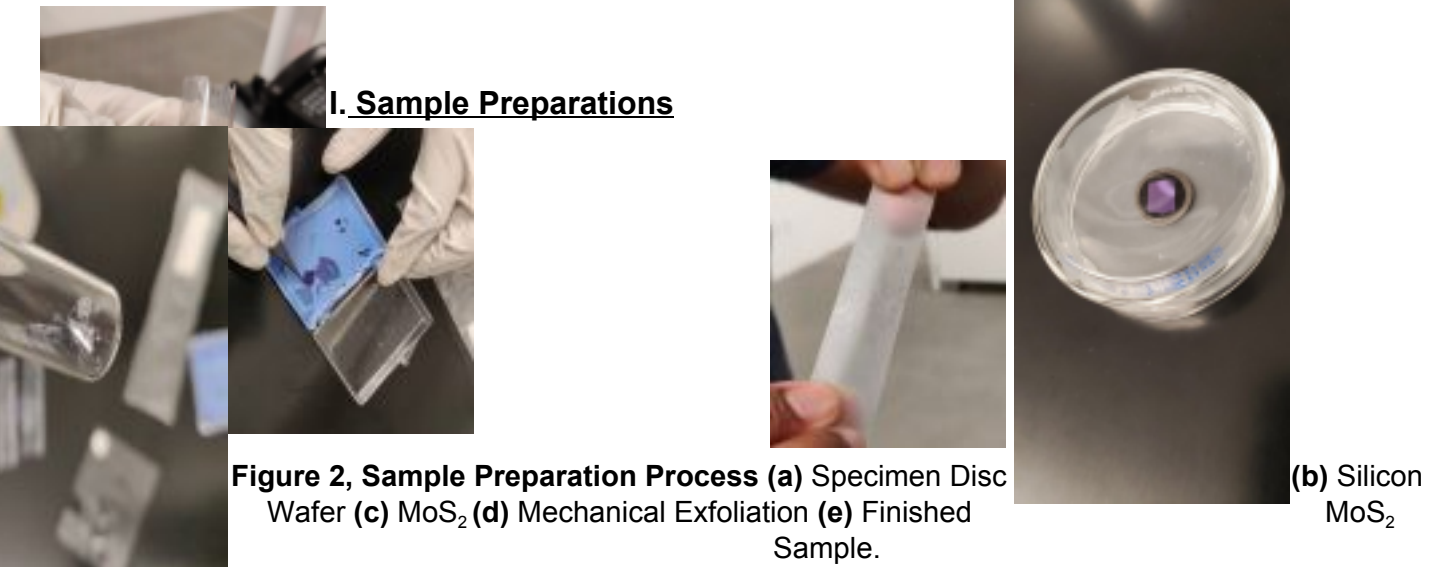
Overview:

The usage of different characterization methods will be the backbone of the research on MoS₂. Before even thinking about using methods for experimentation we need to prepare the samples in a fashion that has the flakes in a single atom layer to get the best results. The sample may or may not be placed in a silicon wafer depending on the methods that will be used. A machine that can help get a better understanding of MoS₂ is the AFM

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machine because it will be able to measure the frictional and adhesional forces in MoS₂, and height/depth of the material for later analysis of lubricant type properties. Another method we can use for analysis is the Scanning Electron Microscopy which can be used to look at the surface of the flakes for confirmation on the height and surface topography of MoS₂. The SEM will give a high-resolution image that can be compared to the AFM;

whereas the AFM will be able to better record more accurate readings. For the research, we will want to use XRD and XPS. XRD will be used to study the spacing and crystal structures while XPS will give element analysis. The two techniques will help in identifying the unit cell structure and composition of the MoS₂ which will then allow us to anticipate how it will be affected differently in space and different parts of the atmosphere. Lastly, we will be doing tribology tests using a micro tribometer to directly measure the Coefficient of Friction (COF) of the MoS₂ as a coating to record its lubricant-like properties, applying certain amounts of load

I. Sample Preparations



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For sample preparation we will embed the MoS₂ flakes onto a small silicon wafer which will also be used as a reference material for friction measurements, **Fig. 2b**, glued, or (double-sided) taped to a portable surface, **Fig. 2a**. To obtain the MoS₂ flakes onto the silicon wafer, we would need to use mechanical exfoliation/"scotch tape method," **Fig. 2d**, with a very small amount of the MoS₂ crystals kept in a small tube, **Fig. 2c**, obtained from a NASA collaborator and commonly grown by a chemical vapor transport technique using iodine as a transporting agent [16]. After we are done with the

sample, we will place the sample onto a 5mm conductive specimen disc, **Fig. 2a**, attached by a double-sided carbon tape. Then we will keep it in an isolated container to keep dust/dirt particles from contaminating the sample between data collecting, **Fig. 2e**, which would introduce artifacts into our data/results. We will make sure that the sample is produced in a humidity-controlled room to ensure that the wafer samples will provide consistent data. Note not all sample preparations will have the MoS₂ flakes placed in the silicon wafer especially for methods like tribology testing and XRD. XRD will not have silicon wafers because the silicon will interfere with the data.

II. Atomic Force Microscopy (AFM)

AFMs are commonly known to measure friction (lateral average) and topography (Height). How this is all possible is due to a small but sensitive cantilever that contains a very small but very sharp tip at the very end. As

the tip approaches the surface, it scans the sample given, and with a laser aligned to the cantilever, the laser beam then deflects onto a photodetector that records the movements as the tip encounters sudden drops or jumps in the surface height, **Figure 3a**. It continues this motion from Left-to-Right (Trace) then returns from Right-to-Left (Retrace); afterward shifting up ever so slightly and repeating the process until the desired dimensions are reached “[X, Y]” with a result that is much like in **Figure 3b**.

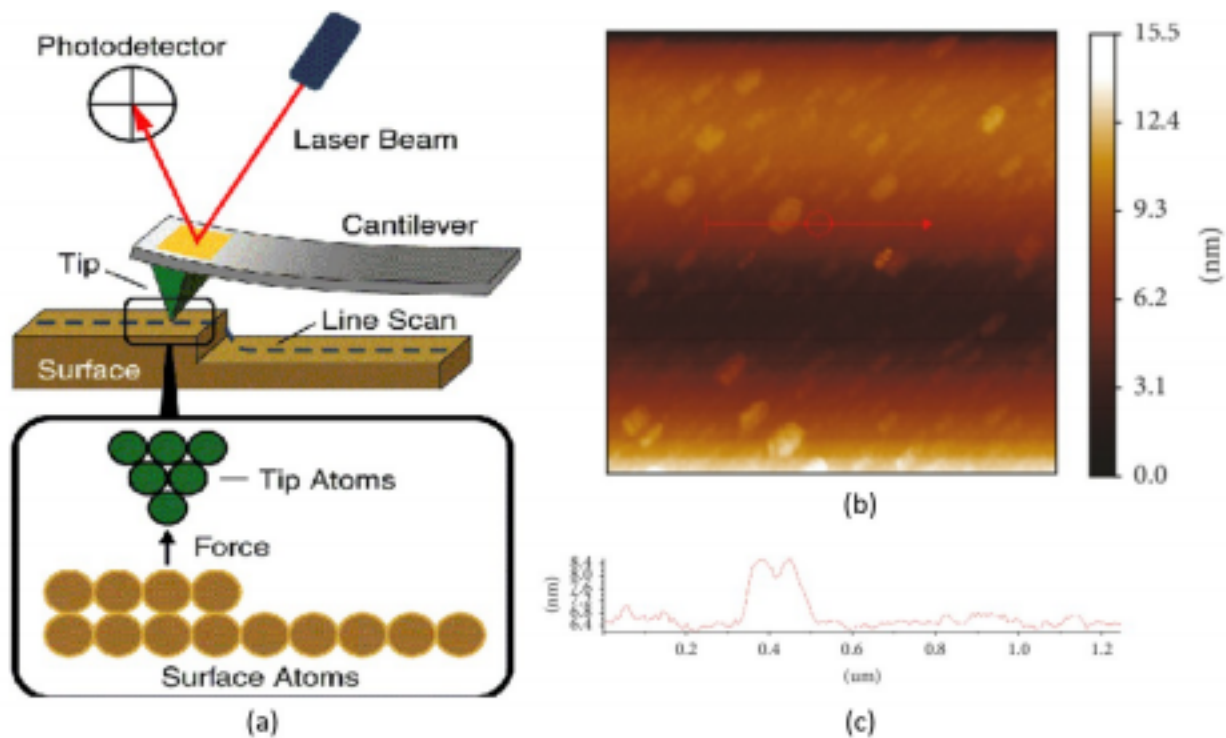


Figure 3 (a) Process to obtain AFM image maps via Cantilever tip scanning the surface of a material. (b) AFM image map of liquid exfoliated MoS₂ with dimensions of [0.293μm, 0.293μm] along with the Right-hand scale portraying the Z-axis measurements. (c) A plot of the height from a 3~5 layer MoS₂ flake obtained from liquid exfoliation, the plot is referenced from the red line in Fig.5(b) [4].

In Khan's article, the research presented used an AFM to record "the average lateral dimension," which in other words is the Friction of MoS₂ that resulted in 0.5~1 microns(μ) and the height of a 3~5 layer MoS₂ flake,

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Figure 3c [4]. From the result, it confirms the exfoliated state of the MoS₂ where we may move on confirming with an SEM. All at the same time looking at the conditions in which the experiments take place like the environment's humidity to obtain consistent results such as results from a linear load-dependency test & contact angle measurements obtained with a SiO₂ substrate for the work of adhesion [11].

Yet, as much as an AFM can be used experimentally, it can also be used for

theoretical purposes that can then be further applied in “simulations.” Something we will be interested in looking into. From those simulations, an author concludes that the AFM can also greatly enhance the reactivity of the MoS₂ through its defects, and from the research, he states how the AFM can be used to modify the electronic environment of monolayer MoS₂ [14]. Therefore, leaving us curious to see if we may find a similar simulation relating to friction and/or work of adhesion of MoS₂ to further reinforce our results.

III. Scanning Electron Microscopy (SEM)

The SEM is also one of the most used methods aside from the AFM to study MoS₂, not only because of its superior high-resolution images where one can't get anywhere else (besides a Transmission Electron Microscope, TEM, which requires higher standards for sample preparation) but for obtaining the surface height and composition of MoS₂. Hence, confirming our Height values

gathered via AFM from the MoS₂ Sample in an article [4], **Figure 3** (AFM) & **4** (SEM). 9

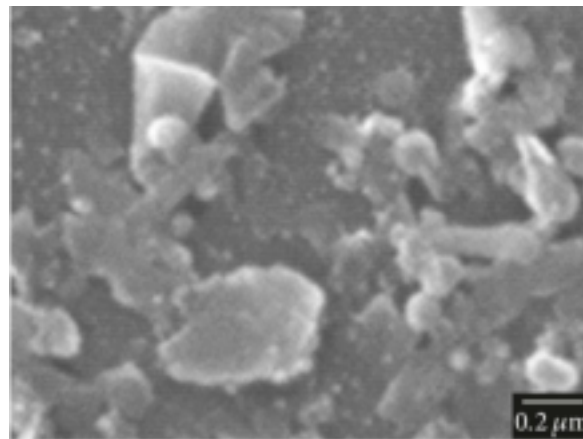


Figure 4 An SEM image of exfoliated MoS₂ from the sample used in Figure 3(a) [4].

To further elaborate on how an SEM works is by having a conductive sample

(MoS₂) put into the SEM chamber with vacuum conditions and after a few minutes of letting the chamber calibrate/initialize. The SEM will then shoot a beam of electrons from its heated tungsten filament onto certain areas of the sample which retrace back Backscattered Electrons (BSE) and Secondary Electron (SE), to its detectors from within the chamber and thus giving us an accurate image of the surface of materials such as MoS₂.

IV. X-Ray Photoelectron Spectroscopy (XPS) and Diffraction (XRD)

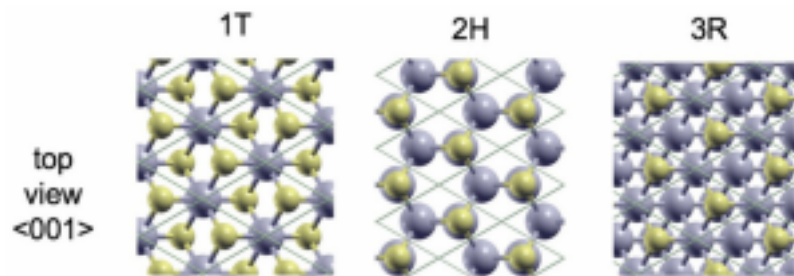


Figure 5 Lattice Structure of MoS₂, molybdenum atoms (Grey) & Sulfur atoms (Yellow), from a <001> top view. The 1T representing the “trigonal” structure of a

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single sheet, AA stacking. The 2H constituting the “hexagonal” structure with 2 sheets per cell in AB stacking. And lastly, the 3R depicting the “rhombohedral” structure which has 3 sheets per cell in ABC stacking [2].

The fourth technique/method which analyzes the surface of a material, XPS and XRD, both can indicate what elements the material is made of. But their differences are that XPS examines the elemental composition such as in **Figure 1b**, all while XRD examines the crystallinity. In Tagawa’s article [5], XPS was used to inspect the surface of MoS₂ after the effects of atomic oxygen exposure which revealed that molybdenum (Mo) served as a protective layer; thus, simulating experimentally what would happen to MoS₂ against atomic oxygen attacks at Low Earth Orbit (LEO) for Space Missions. XRD, on the other hand, identifies the crystal structure of MoS₂ which is $[002]$ or the same as

[001] which then allows us to determine the material's behavior [4]. XRD can be used to find a structure like [001] and their behaviors of having a low energy surface which can be used to understand if MoS₂ has a low friction surface. Structures that can be studied would be like structures in **Figure 5**. The XRD method will be used to retrieve a structure of [001] or others and from this, we can conclude that MoS₂ has a degree of reinforcement that can then be applied to filtration, gas barrier properties (similar to atomic oxygen exposure [5]) and an uncommon property that MoS₂ is not known for as of yet, dielectric spectroscopy measurements [4]. To further support this potential application of MoS₂, the crystal structure of MoS₂ via the XPS method has shown the

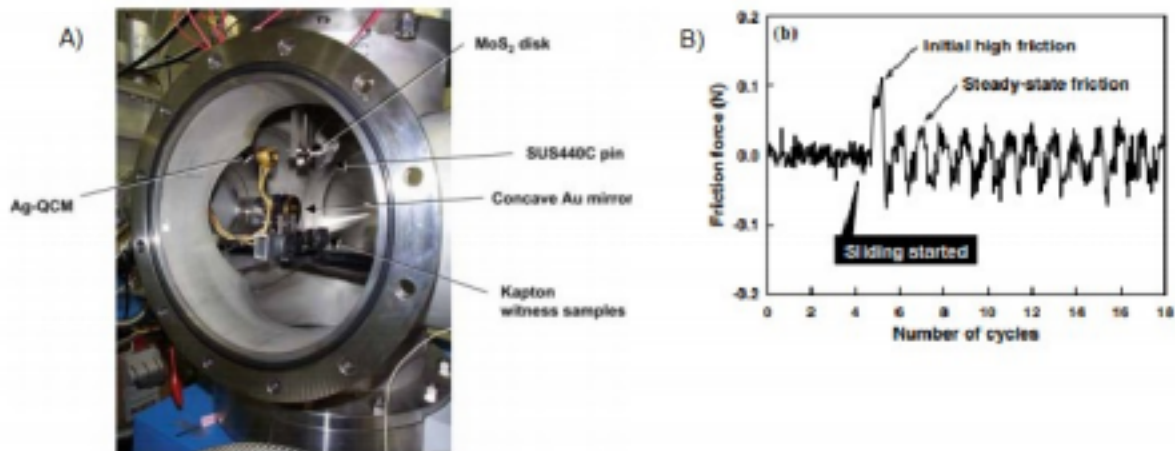


Figure 6 These are the systems and machines that will be used for tribology testing. (a) Is an image of the tribometer that is inside of an isolating chamber where oxygen is inputted into the system. MoS₂ disk and the pin is the tribometer and is where the sample is placed. The rest in the system is the device that measures the amount of oxygen and other particles in the

system.[1]. **(b)** This is an image of the data of a tribometer. It shows initial high friction which may be higher or lower from oxygen or other particle exposure. On the data set, there is an oscillating which is from the repetitive cycle of the tribometer across the flack's surface.

The last technique that will be used to investigate the flakes will be using tribological testing. This technique will report the MoS₂'s friction and wear-life for its tribological properties [1,5,10,12,13]. The tribological machine will not only test the friction for aerospace lubricants, but it will also be testing with atomic oxygen effects in case of low orbits [1] and space systems for MoS₂'s effectiveness in different vacuum conditions and humid air exposure [12,13]. In **Fig. 6** a lab uses a tribometer to test the friction in an isolated rig to input or remove atomic oxygen from

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testing [15]. With the tribological testing, there will be testing of the MoS₂ flake and those flakes will be compared to silicon wafers for reference. Another reason for tribological testing is that MoS₂ can be tested for its wear life which is important for aerospace applications since it is hard to fix equipment like satellites or unmanned systems in space. **Fig. 6b** shows initial and steady states of friction which will be helpful because initial friction can be a big variable in determining if MoS₂ is a viable lubricant. Results reported can also be compared to already existing research that is available, such as the number of cycles MoS₂ can handle on gears and surfaces under different loads [12,13].

Conclusion

Although many methods can be used in this Research Proposal to analyze MoS₂, through careful observation a correlation can be constructed in which certain methods such as AFMs share a common result in MoS₂ in which there is low friction and confirming the number of layers of MoS₂ used in the experiments by its

topography/height. As well as having SEM share similar MoS₂ flakes (the height) through the high-resolution images taken. However, as much as these methods share similar outcomes, Tagawa [5] points out, "...such research results are often contradictory. Discrepancies may come from the difference in experimental conditions such as atomic (or ionic) oxygen beam energy (thermal or keV), fluence (10¹² – 10²⁴ atoms/cm²), sample preparation and/or tribological test conditions." Therefore, telling us that no matter how much we've obtained a value

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corresponding within a similar value range from another test, each test will have its conditions and those conditions can manipulate the result. In simpler terms, it's very difficult to replicate an experiment to produce the same desired values. But that's the thing with research, there's never going to be an end to what we may discover and the challenges that lie ahead.

Additionally, through all the research that has been conducted on MoS₂, MoS₂ has played a big role in aerospace application thus far; an example being through space lubrication from MoS₂'s low frictional properties & wear [2], and coating from atomic oxygen exposure on the surface [5,10]. Yet, going past the fact that most articles mentioned MoS₂ role in aerospace[10,8,5,4,2,1], in some articles they've mentioned MoS₂ potential in electronics or more specifically, Nanoelectronics[14,3]. But unfortunately, the potential in Nanoelectronics has not been further pursued through experimentation; the most that some researchers have done is pursue this potential application of MoS₂ from a theoretical view [14].

This Research Proposal shows how the leading material, MoS₂, has shown many

potential applications that can be implemented, such as in aerospace as a solid lubricant. All of which were obtained through a diagnosis of methods. The method did not only show a correlation in AFMs but with many others like the SEM. More possible doorways of benefits may lie

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waiting to be opened for MoS₂ from other key methods/techniques that may have not been used as of yet.

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