

5-24-2024

Relationship Between the Height of Graphene and Its Adhesion Value

Tyler Larson
Linfield University

Follow this and additional works at: https://digitalcommons.linfield.edu/physstud_theses



Part of the [Physics Commons](#)

Recommended Citation

Larson, Tyler, "Relationship Between the Height of Graphene and Its Adhesion Value" (2024). *Senior Theses*. 53.

https://digitalcommons.linfield.edu/physstud_theses/53

This Thesis (Open Access) is protected by copyright and/or related rights. It is brought to you for free via open access, courtesy of DigitalCommons@Linfield, with permission from the rights-holder(s). Your use of this Thesis (Open Access) must comply with the [Terms of Use](#) for material posted in DigitalCommons@Linfield, or with other stated terms (such as a Creative Commons license) indicated in the record and/or on the work itself. For more information, or if you have questions about permitted uses, please contact digitalcommons@linfield.edu.

Relationship Between the Height of Graphene and its Adhesion Value

Tyler Larson

A THESIS

Submitted to the Department of Physics
LINFIELD UNIVERSITY
McMinnville, Oregon

In partial fulfillment of the requirements
For the degree of

BACHELOR OF SCIENCE

May 2024

Thesis Acceptance

Linfield University

Thesis Title: Relationship Between the Height of Graphene and its Adhesion Value

Submitted by: Tyler Larson

Date Submitted: May 2024

Thesis Advisor: _____

Dr. Michael Crosser

Physics Department: _____

Dr. Joelle Murray

Physics Department: _____

Dr. Tianbao Xie

ABSTRACT

Two-dimensional materials, such as graphene, have remarkable properties. As one of the thinnest, strongest, and most conductive materials known to humanity, graphene holds promise for revolutionizing numerous technological applications. These applications all require different numbers of layers of graphene. However, with graphene being so thin it is difficult to quickly determine how many layers there are. By using an adhesion value and a height value of graphene one may be able to identify the number of layers more accurately.

Contents

1 Introduction	6
1.1 Graphene	6
1.2 Production of Graphene	7
2 Methods	10
2.1 Mechanical Exfoliation	10
2.2 Graphene Research Now	12
2.3 Atomic Force Microscope	13
2.4 Tapping Mode	15
2.5 Peak Force Tapping Mode	16
2.6 Single Point Spectroscopy	16
3 Theory	17
3.1 Experimental Expectation	17
3.2 Adhesion	18
3.3 Plotting a Relationship	19
4 Results and Analysis	21
4.1 Graphene Scans	21
4.2 Height / Adhesion Relationship	23
5 Conclusion	24
REFERENCES	25

List of Figures

1.1 Hexagonal structure of carbon atoms in graphene	6
1.2 Common methods used for the growth and production of graphene	8
2.1 Obtaining graphite and set up	11
2.2 Scotch tape method and transfer method	11
2.3 SiO_2 chips used in this experiment with mechanical exfoliated graphene stuck on them	12
2.4 Bruker dimension edge atomic force microscope with ScanAsyst	14
2.2 Inner workings of an AFM.	15
3.1 Force / deflection example plot	18
3.2 SiO_2 force / deflection plot	19
3.2 Graphene height and peak force setpoint relationship	20
4.1 Graphene scan and step height scan	21
4.2 Adhesion plots for scan	22
4.3 Height / adhesion relationship	23

Introduction

1.1: Graphene

Graphene, a two-dimensional sheet of carbon atoms arranged in a hexagonal lattice nanostructure [1], has captured the imagination of scientists and engineers since its discovery in 2004. Graphite naturally forms sheets of this lattice stacked on top of each other (see Fig 1.1). Graphite that has fewer than 10 layers is generally referred to as graphene. The discovery of graphene by Andre Geim and Konstantin Novoselov [2] earned them a Nobel Prize in Physics in 2010 [3], which cemented graphene's status as a transformative material.

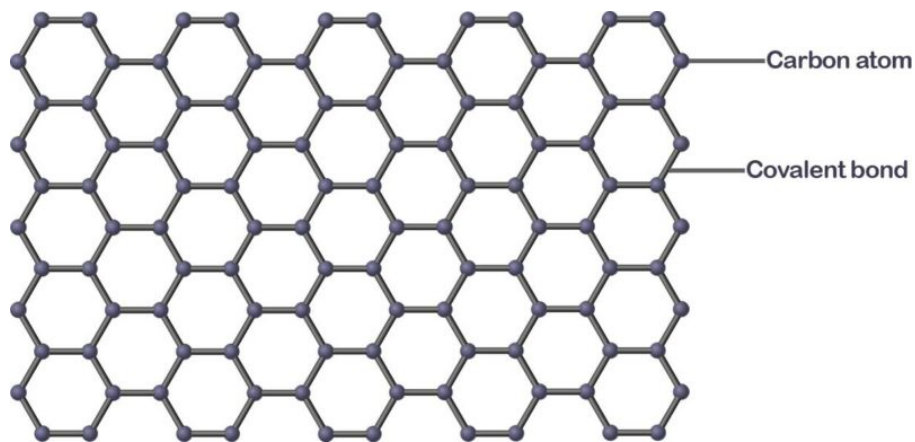


Figure 1.1: Hexagonal structure of carbon atoms in graphene. These shapes are stacked on top of each other to then make graphite (more than ten layers). A covalent bond holds together all the carbon atoms [1].

Since graphene is two-dimensional it is difficult to manipulate. There are techniques for growing it and techniques for making it. Both have their own pros and cons, from how much can

be made and how easy it is to make it, to how much it costs to make. The next section goes over some of these techniques and the pros and cons.

1.2 Production of Graphene

Common ways to make or grow graphene are SiC, liquid-phase exfoliation, CVD, and mechanical exfoliation. Figure 1.2, reproduced from [4], relates the quality of the final graphene to the expense to manufacture it.

The SiC method involves epitaxial growth of graphene on a SiC substrate [4]. Since the graphene is grown directly on the SiC there is no transfer process leading to no residues being left on the device. However, this method sometimes fails to work due to the epitaxial method being restricted to certain substrates that have lattice-matched properties.

A liquid-phase exfoliation has been developed based off the mechanical exfoliation method (mentioned later). This method was developed to generate a solution-processible graphene [5]. Most exfoliation methods use a strong acid or base as the oxidation and reduction agents. This process can be destructive, causing the samples to not be uniform, which then makes the size and layer number of graphene hard to control [6].

Another popular graphene growth method is chemical vapor deposition (CVD). CVD has been said to be the most effective way to advance the industrial development of graphene [4].

The CVD method has been well established in the growth in layered materials of carbon thin film [7]. CVD systems usually have the same several components, which include a heating furnace, gas introduction system, and a reaction chamber [8]. In CVD the carbon source will decompose into a carbon cluster on a metal catalyst substrate. These clusters are then diffused to form the graphene [4]. This method is great for mass production but lacks the quality wanted for accurate measurements needed in this experiment.

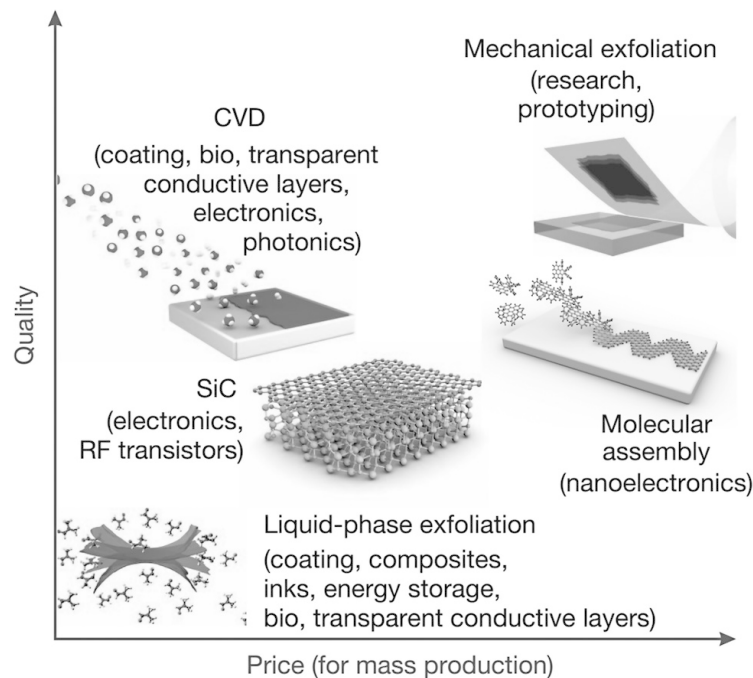


Figure 1.2: Common methods used for the growth and production of graphene. These are used for specific applications based on the price and quality of graphene desired [4].

Mechanical exfoliation, also known as the scotch tape method, created by Geim and Novoselov [2], remains the best method for studying the mechanical properties of graphene [4]. It remains the best method because the graphene is taken from bulk graphite, which has fewer

defects than if graphene is grown. However, this method is not viable to produce uniform graphene in large amounts due to the poor reproducibility of this method [9]. This method was used for this research and is explained step by step in the methods section.

Methods:

2.1 Mechanical Exfoliation

The following steps were taken to create graphene using the process of mechanical exfoliation. The first step involves sterilizing tweezers with acetone to get rid of any bacteria or junk, followed by isopropyl alcohol to remove the left-over acetone, and lastly blow drying the tweezers with a clean air source. These tweezers are used to grab small amounts of graphite; therefore, it is important that the tweezers are very clean so that only graphene will end up on the final chip. Scotch tape is laid sticky side up and layered with a small amount of graphite. Then, the process involves sticking the tape together to pull apart layer by layer of the graphite. After about seven or eight repetitions, part of the graphite starts to become transparent, which indicates it is ready to be transferred to a silicon (Si) chip with silicon dioxide (SiO_2) grown on top. This final layer that is transferred to the SiO_2 chip separates the graphite in a small fraction so that some graphene will be deposited. When this transfer is completed there will be some spots of graphene and others with graphite. Figure 2.3 shows several chips used with graphene on them. A microscope is used to find where the true graphene is. The entire mechanical exfoliation process is depicted in Figures 2.1 and 2.2.

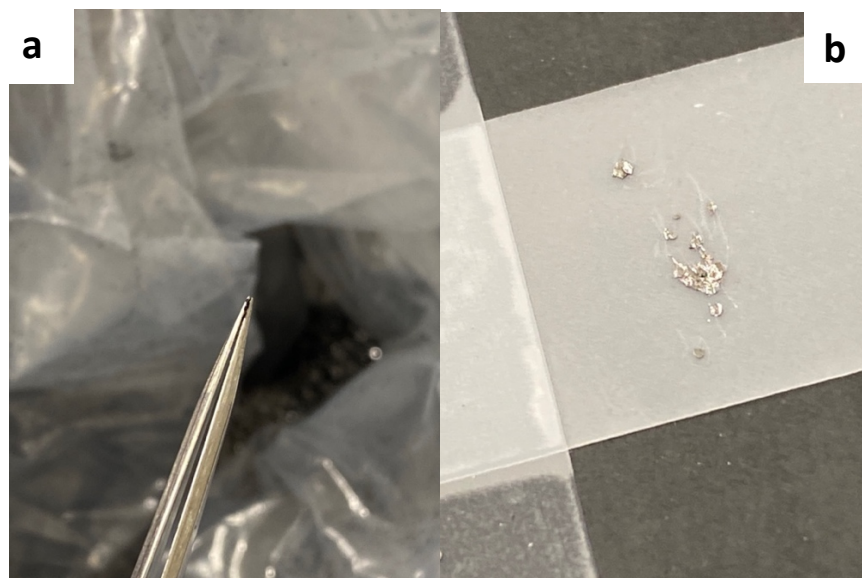


Figure 2.1: a) shows obtaining a small amount of graphite with tweezers. b) shows the graphite being firmly placed on a piece of scotch tape.

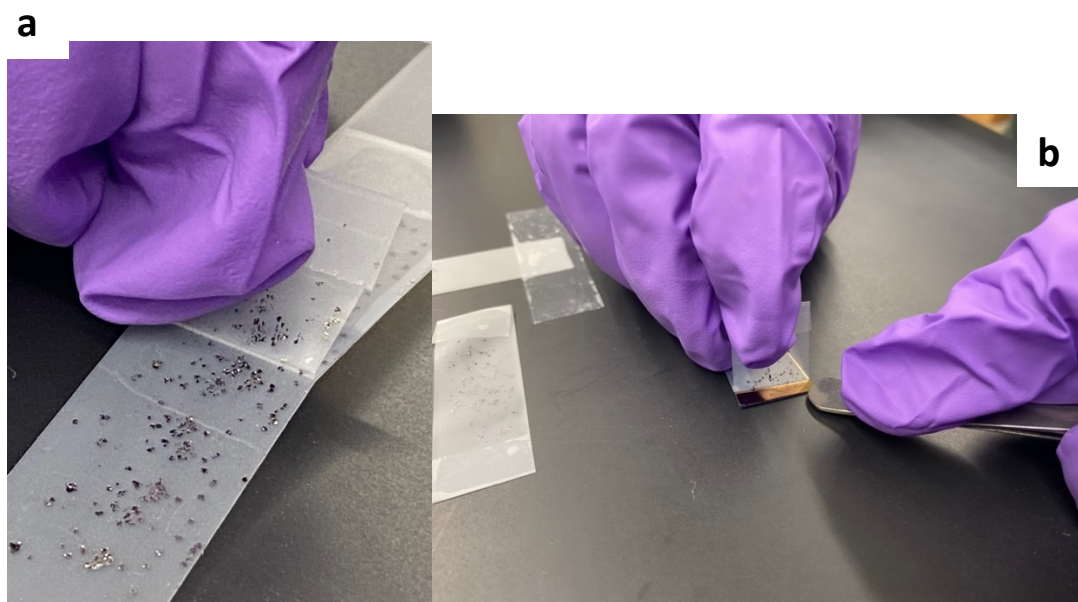


Figure 2.2: a) shows the peeling process of the graphite on the scotch tape. b) shows the final transfer process to a SiO_2 chip that will then be used to study the graphene.

2.2 Graphene Research Now

As the uses of graphene continue to grow it will be important to understand exactly how much graphene you have on a sample. AFM studies have reported graphene to have a thickness of somewhere between 0.4 nm to 1.7 nm [10]. This range can be caused by numerous things, including the buffer layer of condensed water under the graphene and on top of the SiO_2 , which is not consistent in every sample. The SiO_2 plays a crucial role in holding the graphene samples for transportation and research.

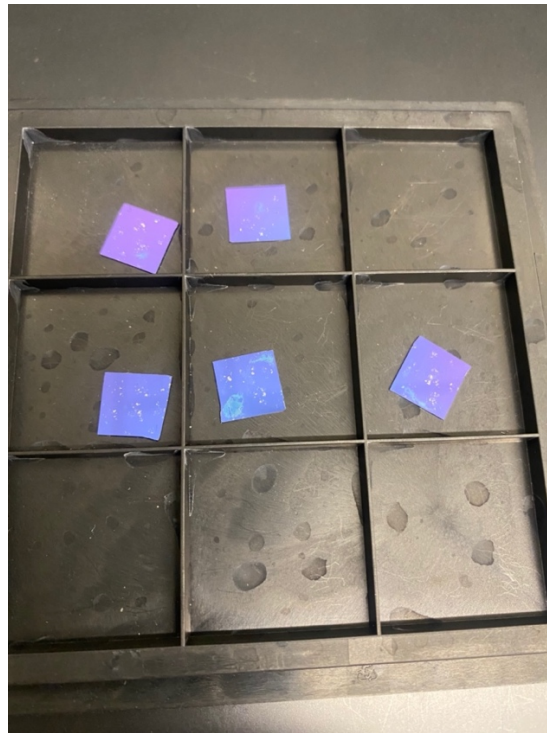


Figure 2.3: SiO_2 chips used in this experiment with mechanically exfoliated graphene transferred on them.

When looking under a microscope it can be difficult to find the small clumps of single layer graphene due to mechanical exfoliations randomness in the transfer process. Once graphene is spotted on the microscope, we use an Atomic Force Microscope (AFM) to complete scans of an area believed to be thin graphene. An AFM is a technique that uses a sharp tip to scan the surface of the material and maps out the contours to record images on the atomic scale. For the purposes of this experiment, the AFM is preferred to other methods such as Raman Spectroscopy. Raman Spectroscopy is a chemical analysis technique that provides information about the chemical structure of the sample based on the light interaction with the chemical bonds of the material [11]. Although this is the best technique to determine how thick graphene is, it is not spatially specific and not appropriate for scanning a chip to find graphene amongst graphite.

Since the thickness of a single layer of graphene has a large range, it can be difficult to tell exactly how many layers the sample has. Knowing the exact number of layers a particular graphene sample has becomes more important as the usefulness of this material grows. Scientists and engineers need to know how many layers they need and how to tell how many layers they have quickly. We propose a relationship between the thickness of the graphene and the graphene's force / deflection curve (adhesion) needs to be found.

2.3 Atomic Force Microscope

An AFM was used to accurately study the graphene samples. The Bruker AFM system (see Fig. 2.4) is equipped with a high-resolution scanner, which allows for imaging with sub-

nanometer resolution. The AFM does this by having three subsystems that all perform separately. These subsystems are sensing, detecting, and positioning [12]. The sensor is called a cantilever that has a small sharp tip shown in Figure 2.5. A laser shines on the cantilever and reflects into split photodiode. When the tip gets close enough to the sample that you want to scan it is affected by Van der Waals forces. These forces deflect the tip, which causes the whole cantilever to bend. As the cantilever is bending, the deflection of the laser is obtained by the photodetector. Lastly, there is positioning hardware called piezo actuators used to change the position between the cantilever and the sample in three dimensions [12].



Figure 2.4: Bruker dimension edge Atomic Force Microscope with ScanAsyst used in this experiment. a) shows the AFM with its lid on and b) shows the exposed interior parts of the AFM.

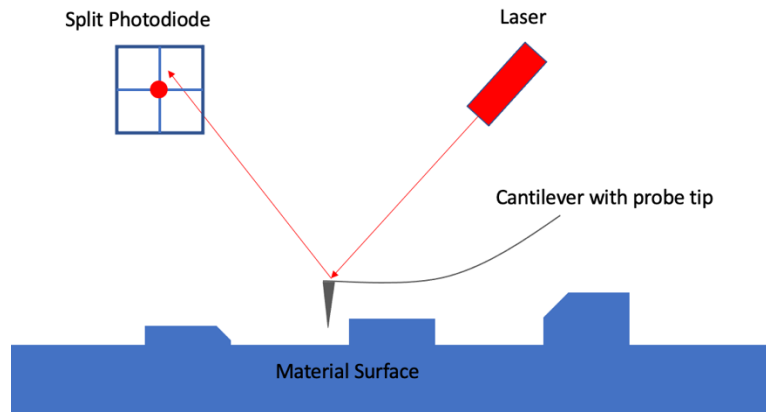


Figure 2.5: Inner workings of an AFM including the material surface, cantilever and probe tip, laser, and the split photodiode.

2.4 Tapping Mode

Tapping mode is one of the most used operating modes in the AFM. In this mode, the cantilever is forced to oscillate near its resonance frequency. When the cantilever interacts with the surface, the amplitude decreases. As the tip scans across the surface, the interactions are with the individual atoms on the surface of the sample. The amplitude of this oscillation is kept constant by a feedback loop. The feedback loop then adjusts the height of the tip above the sample surface to maintain the constant amplitude. This then generates a topographic image of the scan area on the sample [12].

2.5 Peak Force Tapping Mode

This leads to the peak force tapping mode (PFT). This mode is similar to the tapping mode as it uses a tip to scan the sample surface to create a topographic image. However, it is not at a resonance frequency like in tapping mode, instead it is oscillated at its own mechanical resonance. Because of this, the peak force tapping's piconewton force sensitivity combines with its highest resolution AFM imaging to make clear scans for accurate analysis [13]. When the tip touches the surface, it does so with a force control. This allows the oscillation to be modulated and the force between the tip and the sample is kept constant by adjusting the peak force during each cycle of the oscillation. This then reduces the risk of damaging the sample and provides more gentle imaging conditions, which then provides improved imaging. This was the main mode used in this experiment because the scan could be done in this mode and then point spectroscopy could be done with the same tip.

2.6 Single Point Spectroscopy

Force spectroscopy is another valuable tool that the AFM provides. It is also known as single point spectroscopy (SPS) since the measurement this mode takes is at a single point on the sample. The plot that this measurement gives is known as a force or deflection curve relative to the distance between the probe and the surface of the sample. The AFM is usually known for its high-resolution imaging capabilities, but this powerful tool is also used for sensitive force measurements [14]. This allows one to generate a force / deflection curve for a single point on layered graphene.

Theory:

3.1 Experimental Expectation

Using either the peak force tapping or regular tapping mode on the AFM, the specific height of the graphene samples can be acquired. In the images of the graphene (located in the results section), you can clearly see that there are different layers from different shades of blue. The blue color comes from the light refraction on the SiO_2 . Next, using single point spectroscopy, a force / deflection curve can be found for each section of graphene with different layers. The important part of the curve is the adhesion data shown in Figure 3.1. This data is different depending on how many layers of graphene there are in the sample. With these two points of data, the height and adhesion value, there can be a relationship found to easily tell how many layers are in a sample.

3.2 Adhesion

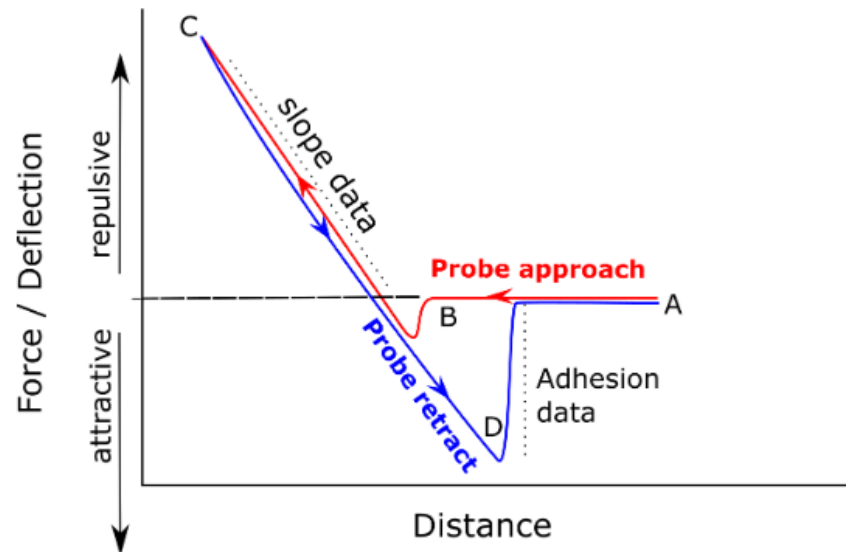


Figure 3.1: A) the probe approaches the graphene. B) the graphene and probe experience attractive Van der Waals forces prior to touching. C) the probe presses into the graphene until a given deflection setpoint. D) Adhesion is the lowest deflection value when the probe is removed [15].

Following the path in Figure 3.1, as the probe is approaching there is a small dip when the probe touches the sample. The small dip is there because the material has a slight attraction to the probe from Van der Waals forces. The slope data is taken until the probe reaches its set trigger point, which means it will start pulling away from the sample. Adhesion data can be explained by how much attraction the graphene has to the probe when it is pulling away. The adhesion will be visibly more or less when there are more layers or less layers. The adhesion is calculated as shown in Figure 3.2.

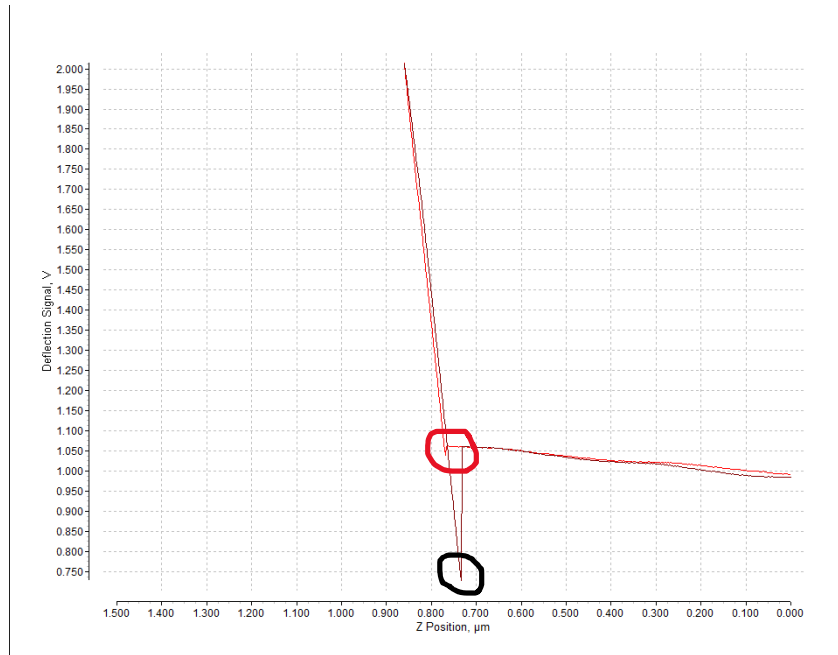


Figure 3.2: Force / deflection plot showing adhesion for bare SiO_2 on the same chip as graphene.

The adhesion is calculated by taking the force / deflection value circled in red in Figure 3.2 and subtracting the force / deflection value circled in black in Figure 3.2. For the SiO_2 the adhesion is about 0.325 V. This is the same calculation used in the force / deflection plots when the adhesion data was taken for the graphene samples (see Fig. 4.2).

3.3 Plotting a Relationship

When all the height and adhesion data has been collected for the graphene, there should be a relationship that can be made into a plot similar to the one shown below in Figure 3.3. The plot below [10] shows the relationship found between the graphene's height in nm and the peak force setpoint in nN. This was done by first scanning what was found to be a single

layer of graphene using PFT. Next, peak force setpoint was manually changed, which determines how hard the probe presses on the graphene. Because the height changes based on how hard the probe is pressed onto the graphene, it can be said that the water buffer layer between the graphene and SiO_2 plays a critical role in the measured heights of graphene. This may be why the data in the results section is spread out (see Fig. 4.3).

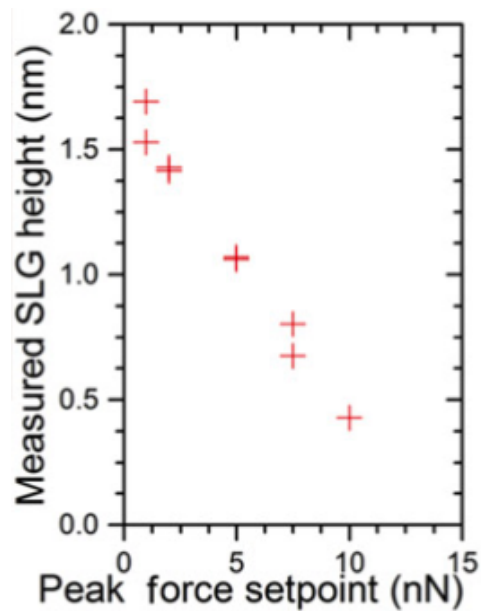


Figure 3.3: Plot showing the relationship between graphene's height and peak force setpoint [10].

Results:

4.1 Graphene Scans

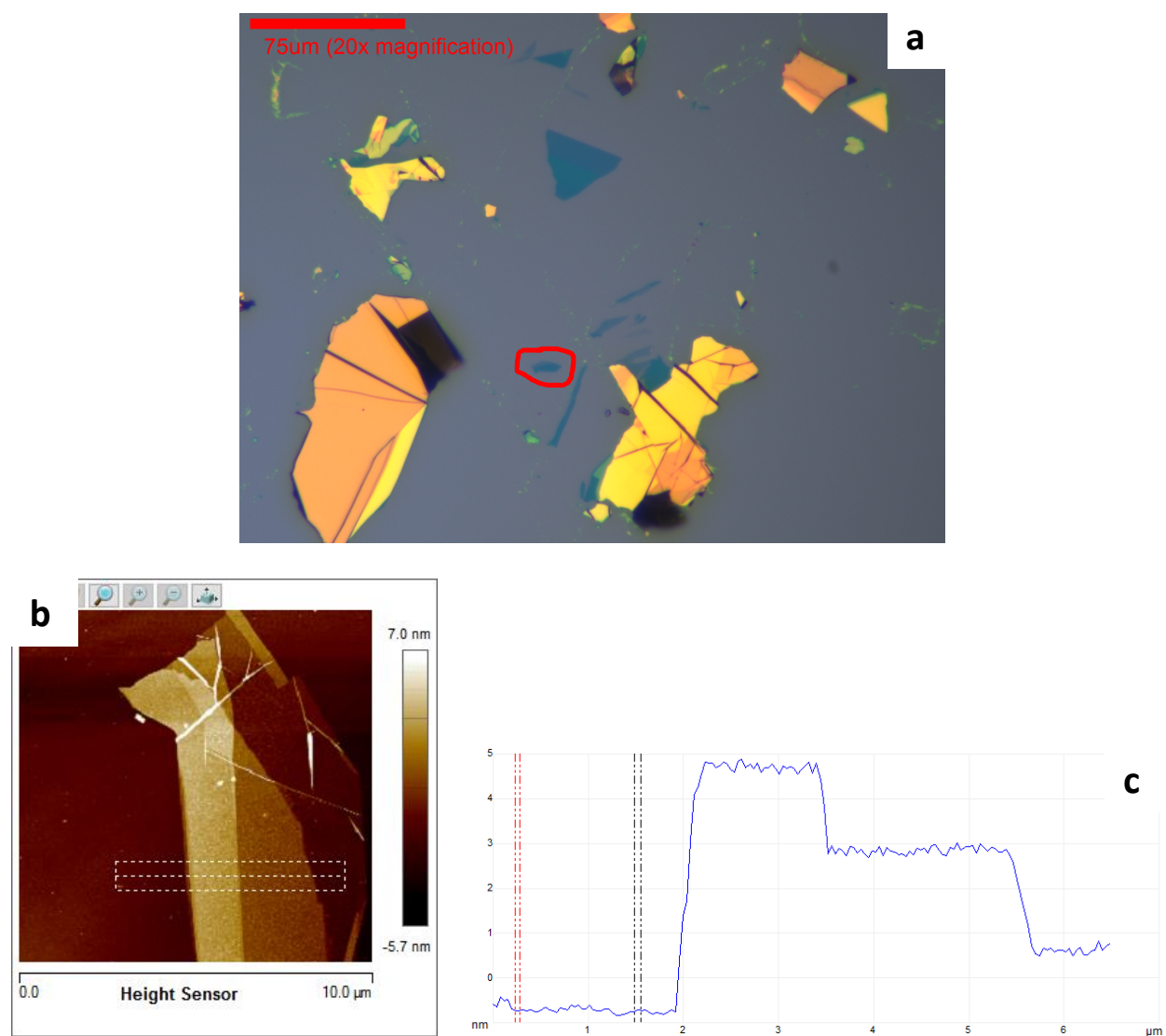


Figure 4.1: a) shows a 20x magnification of a section of one of the chips used in this experiment (see Fig. 2.3). Circled in red is where the actual scan was taken. b) AFM image of graphene. Dotted line shows location of where a line scan was taken. c) shows the heights of each layer of graphene taken from the dotted box in (b).

The scan in the section circled red (see Fig. 4.1) was done using the AFM with the PFT mode. The plot was obtained by using a step height tool. The left side at about -0.5 nm in the plot is the SiO_2 . The plot shows that there are three different layers of graphene in this scan. The heights were recorded as 5.5 nm, 3.5 nm, and 1.25 nm from left to right. At each height SPS was done to determine the adhesion values (see Fig. 4.2).

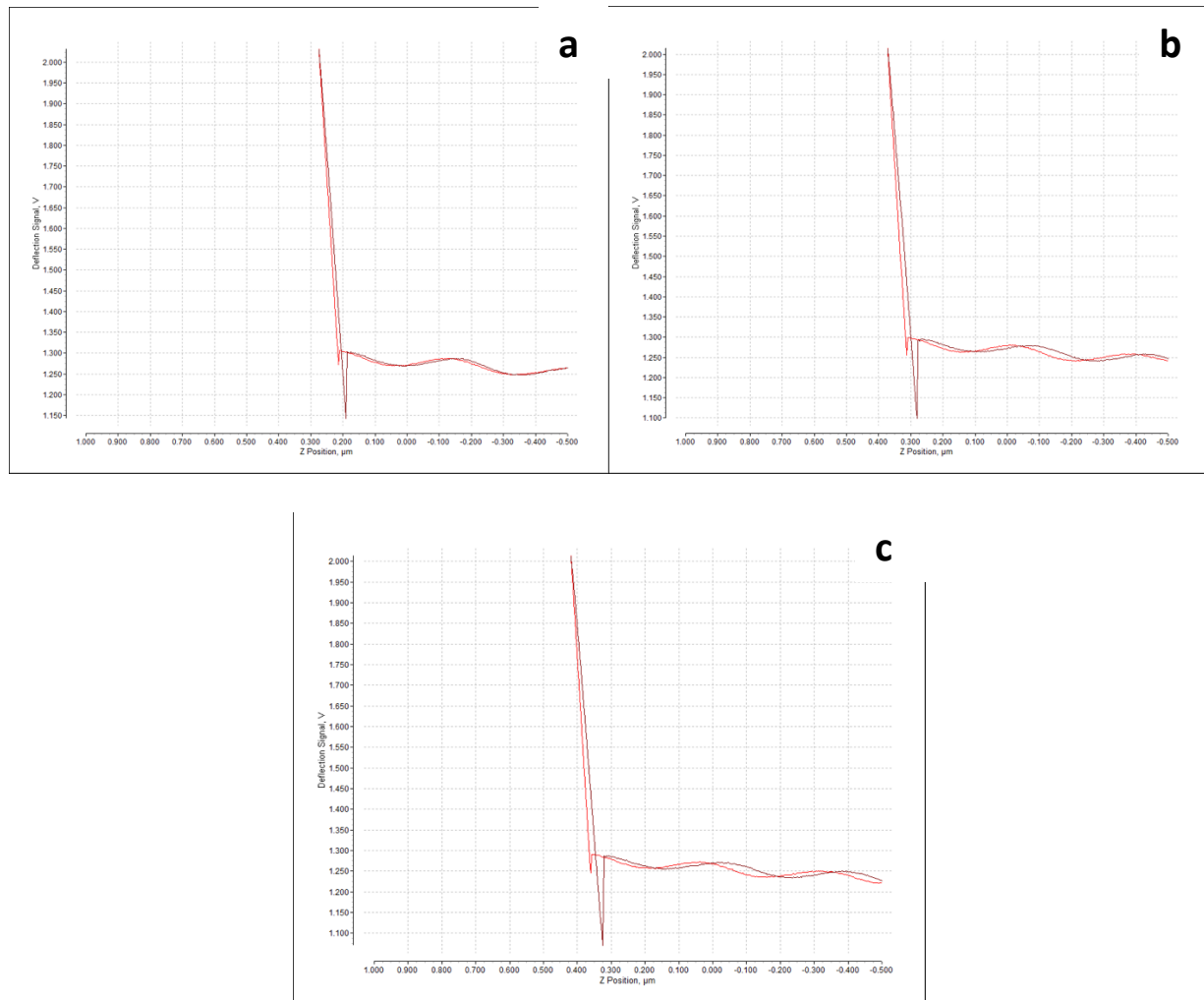


Figure 4.2: Adhesion data for the clump in Figure 4.1. a) shows the adhesion data for the 5.5 nm thickness. b) shows the adhesion data for the 3.5 nm thickness. c) shows the adhesion data for the 1.25 nm thickness.

Using SPS the 5.5 nm thickness recorded an adhesion of 0.15V, the 3.5 nm thickness recorded an adhesion of 0.2 V, and the 1.25 nm thickness of 0.25 V. This is outlined in Figures 4.1 and 4.2. These adhesion calculations were done the same way as shown in Figure 3.2. These steps were repeated for multiple clumps with multiple heights of graphene on multiple SiO_2 chips.

4.2 Height / Adhesion Relationship

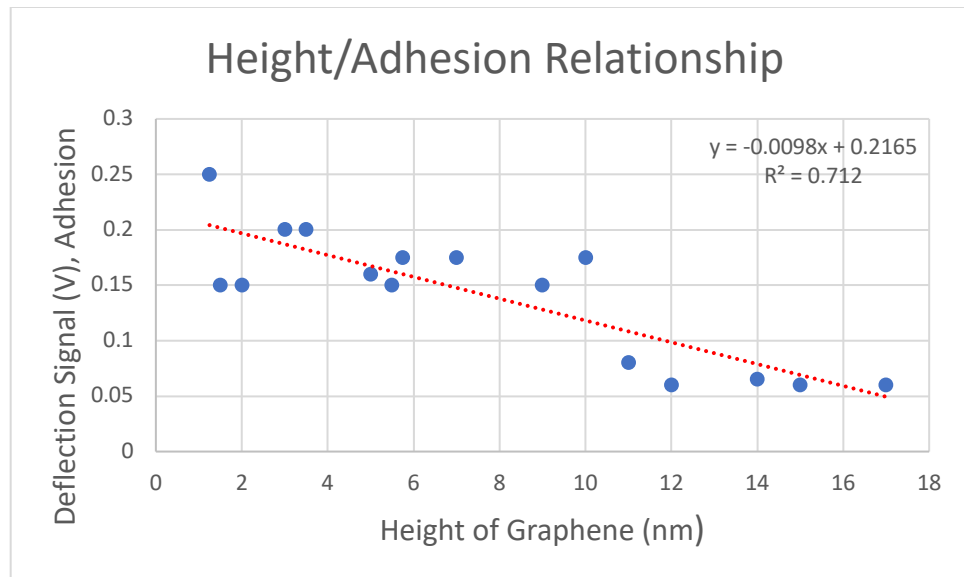


Figure 4.3: Plotting a relationship between the heights of the graphene scanned and the adhesion data gathered from single point spectroscopy.

The plot shows a slightly negative slope indicating that adhesion will decrease with more layers. However, the R^2 value is 0.712, which indicates that the data is too spread out, and not precise enough to signify a causal relationship. This means that there is no true relationship between the heights of graphene and their adhesion values.

Conclusion

Overall, this experiment has proved there is a slight difference in adhesion values based on the height of graphene. However, Figure 4.3 shows that the data is still spread out, so even though there is a negative slope, indicating some relationship, there is no causal relationship between the number of layers and the adhesion value. This means there is no one adhesion value to describe a given thickness of graphene; there is only a small downward trend in the relationship.

To further this thesis experiment, the sample size and range of the study should be increased to determine whether the negative trend between graphene's number of layers and adhesion value continues.

References:

- 1 Admin. (2022, December 8). *What is Graphene and What is Graphene Used For?* Graphene Uses. <https://www.grapheneuses.org/what-is-graphene/>
- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* 306, 666 (2004).
- 3 Chodos, Alan. *October 22, 2004: Discovery of graphene*. (n.d.). <https://www.aps.org/publications/apsnews/200910/physicshistory.cfm>
- 4 Geng, D., & Loh, K. P. (2017). Controlled growth of graphene crystals by chemical vapor deposition: from solid metals to liquid metals. In *Cambridge University Press eBooks* (pp. 238–256). <https://doi.org/10.1017/9781316681619.014>
- 5 Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., and Ruoff, R. S., Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45 (2007), 1558–1565.
- 6 Paton, K.R., Varrla, E., Backes, C., Smith, R.J., Khan, U., Neill, A.O., Boland, C., Lotya, M., Istrate, O.M., King, P., Higgins, T., Barwich, S., May, P., Puczkarski, P., Ahmed, I., Moebius, M., Pettersson, H., Long, E., Coelho, J., O'Brien, S. E., McGuire, E. K., Sanchez, B. M., Duesberg, G. S., McEvoy, N., Pennycook, T. J., Downing, C., Crossley, A., Nicolosi, V., and Coleman, J. N., "Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids," *Nature Materials*, vol. 13, pp. 624–630, 2014.
- 7 Lau, K. K. S., Caulfield, J. A., and Gleason, K. K., Structure and morphology of fluorocarbon films grown by hot filament chemical vapor deposition. *Chem. Mater.* 12 (2000), 3032–3037.
- 8 Dobkin, D. and Zuraw, M. K., *Principles of Chemical Vapor Deposition* (Kluwer, 2003).
- 9 Si, Y. C. and Samulski, E. T., Exfoliated graphene separated by platinum nanoparticles. *Chem. Mater.* 20 (2008), 6792–6797.
- 10 Shearer, C. J., Slattery, A., Stapleton, A. J., Shapter, J. G., & Gibson, C. T. (2016). Accurate thickness measurement of graphene. *Nanotechnology*, 27(12), 125704. <https://doi.org/10.1088/0957-4484/27/12/125704>
- 11 *What is Raman Spectroscopy? – HORIBA*. (n.d.). <https://www.horiba.com/int/scientific/technologies/raman-imaging-and-spectroscopy/ramanspectroscopy/#:~:text=Raman%20Spectroscopy%20is%20a%20non,chemical%20bonds%20within%20a%20material>.
- 12 Oxford. *Atomic Force Microscopy - An Overview from Asylum Research*. (n.d.). Oxford Instruments. <https://afm.oxinst.com/outreach/atomic-force-microscopy>
- 13 Bruker. *Bruker Peak Force Tapping - How AFM Should be - Coherent Scientific*. (n.d.). <https://www.coherent.com.au/products/atomic-force-microscopes/atomic-force-microscopes/bruker-peakforce-tapping-how-afm-should-be-1377.html>
- 14 Bruker. *Free PDF: A Practical Guide to AFM Force Spectroscopy and Data Analysis*. (n.d.). Bruker. <https://www.bruker.com/en/products-and-solutions/microscopes/bioafm/resource-library/a-practical-guide-to-afm-force-spectroscopy-and-data-analysis.html>
- 15 User, S. (2022, August 31). *Measuring and Analyzing Force-Distance Curves with AFM*. <https://www.afmworkshop.com/newsletter/measuring-and-analyzing-force-distance-curves-with-atomic-force-microscopy>