Probing Interfaces between Two-dimensional Van Der Waals Materials with Scanning Probe Microscopy

Andrew Tompkins

August 12, 2022

1 Introduction

Van der Waal materials are the atomically thinnest materials in the world, with some being one atom thick, and have superb conductivity, allowing them to potentially revolutionize electronics [2] . Stacking these 2D plane-like materials (2-3 layers) alter the electrostatic properties, creating a new avenue for quantum materials. Twisting the top or bottom layer creates Moiré lattices, a phenomena occurring from the mismatch of lattices structures that transforms coupling in the layers. If the Moiré patterns can be better understood, so could the coupling.

Graphene is the most interesting material due to its zero bandgap structure, allowing for free-flowing in-plane electrons. Rotating the stacked graphene layers causes defects that have different electrostatic properties to appear within the layers [1]. Like the Moiré patterns, studying these defects is key to understanding graphene.

2 Methods

Van der Waal materials are the thinnest materials in the world, therefore human interaction is not possible. Atomic Force Microscopy (AFM) and Electrostatic Force Microscopy (EFM) are used to collect data from the stacked Van der Waal materials.

AFM uses a tip and cantilever that oscillates on the sample's surface to map the topography of the surface. EFM uses the same tip to induce a voltage that scans across the surface at a fixed height, probing electrostatic properties.

3 AFM and EFM Measurements

The AFM tip acts as a Driven Harmonic Oscillator, however, the tip and sample induce an electric field that creates a force gradient that shifts the resonance frequency of the cantilever by some degrees and must be taken into account during calculations.

$$\Sigma F = -kx + \beta\dot{x} + F_0 e^{-i\omega t} + (f_s x + f_0) = m\ddot{x}$$

where $-kx$ is Hooke's Law, $\beta\dot{x}$ is the damping force, $F_0 e^{-i\omega t}$ is the driving force, $f_s x$ is the tip-sample force gradient, f_0 is the constant force, and $m\ddot{x}$ is Newton's second law. Separate like-values.

$$= m\ddot{x} + \beta\dot{x} + x(k + f_s) = F_0 e^{-i\omega t} + f_0$$

The trial solution for this differentiable equation will be $x = A_1 e^{-i\omega t} + A_0$, therefore $\dot{x} = -i\omega A_1 e^{-i\omega t}$ and $\ddot{x} = -\omega^2 A_1 e^{-i\omega t}$.

$$= -\omega^2 m A_1 e^{-i\omega t} - i\omega\beta A_1 e^{-i\omega t} + (A_1 e^{-1\omega t} + A_0)(k - f_s) = F_0 e^{-i\omega t} + f_0$$

Separate based on e factor and reduce

$$= A_1(-\omega^2 m + i\beta\omega + k - f_s) = F_0$$
$$= A_0(k - f_s) = f_0$$

Therefore,

$$A_1 = \frac{F_0}{(k - f_s - \omega^2 m) + (i\beta\omega)}$$
$$A_0 = \frac{f_0}{k - f_s}$$

A_1 is a complex number, therefore it can be rewritten as $A_1 = |A_1|e^{i\rho}$ and the complex conjugate can be utilized, denoted A_1^*.

Since $A_1 A_1^* = (|A_1|e^{i\rho})(|A_1|e^{i\rho}) = |A_1|^2$

$|A_1| = \sqrt{A_1 A_1^*}$

$$A_1 A_1^* = \frac{F_0^2}{(k - \omega^2 m)^2 + (\omega\beta)^2}$$

$$\sqrt{A_1 A_1^*} = \sqrt{\frac{F_0^2}{[(k - \omega^2 m)^2 + (\omega\beta)]^2}}$$

$$|A_1| = \frac{F_0}{\sqrt{(k - \omega^2 m)^2 + (\omega\beta)^2}}$$

The force gradient will also have an effect on the phase shift.

The relation between the phase angle is

$$tan(\phi) = \frac{A_i}{A_r}$$

where A_i is the imaginary portion of the magnitude, and A_r is the real portion of the magnitude. To find A_{1i} and A_{1r}, we can multiply $|A_1|$ to find the form $A_{1r} + A_{1i}$.

$$A_{1r} + A_{1i} = \frac{F_0}{(k - f_s - \omega^2 m) - (i\omega\beta)} * \frac{k - f_s - \omega^2 m + i\omega\beta}{k - f_s - \omega^2 m + i\omega\beta}$$

$$= \frac{F_0[k - f_s - \omega^2 m + i\omega\beta]}{(k - \omega^2 m)^2 - (\omega\beta)^2}$$

This can be separated into the real and imaginary magnitude.

$$A_{1r} = \frac{F_0(k - \omega^2 m)}{(k - \omega^2 m)^2 + (\omega\beta)^2}$$

$$A_{1i} = \frac{F_0(-i\omega\beta)}{(k - \omega^2 m)^2 + (\omega\beta)^2}$$

Substituting these values into the relation gives

$$tan(\phi) = \frac{\omega\beta}{k - f_s - \omega^2 m}$$

There are multiple phase shift when working with the AFM, more specifically the phase shifts between the sample and ground plane. Taking the difference between these two shifts gives

$$\phi_s - \phi_b \approx \frac{f_s' - f_b'}{k\beta}$$

When the tip is induced with a voltage, the tip-sample interaction acts as a parallel-plate capacitor. Using the fundamental equation of capacitance, the force gradient from the sample acting on the plates gives

$$f_s' = \frac{1}{2}C''(\Delta V)^2$$

where f_s' is the force gradient from the sample, C'' is the second derivative of capacitance with respect to distance between the tip and sample surface and ΔV is the applied voltage. A connection between the above equation and the difference phase shifts is present, giving.

$$\phi_s - \phi_b \approx \frac{(\Delta V)^2}{2k\beta}(C_s'' - C_b'')$$

This is the main method to find the phase shift while using EFM. The higher the phase shift, the more electrostatic attractive the sample is.

4 Creating Heterostructures

Now that the AFM and EFM measurement theory is explained, the samples can be analyzed, more specifically heterostructures. Heterostructures are mechanically bonded Van der Waal materials that lay horizontally ontop each other. AFM allows the surface of the formed heterostructure to be analyzed and its surface potentials, capacitance, and charge coupling to be measured via EFM. For this experiment, a tri-layer heterostructure consisting of boron nitride (hBN) as the top and bottom layers and gold (Au) as the middle layer will be synthesized.

4.1 Materials

Listed will be all the materials needed to create a heterostructure: scotch tape, microscope, glass microscope slides, adhesive tape, tweezers, razor blade, silicon dioxide (SiO_2) wafers, boron nitride, and gold pellets, poly-carbonate .

4.2 Van der Waal Transferring

Cut off a piece of scotch tape and place boron nitride onto it. Fold the tape in half onto itself. This spreads the material around the tape, allowing thin layers

to be placed on the wafer. After the compound is thinned onto the tape, place the tape on the wafer and apply enough pressure to ensure the hBN flakes are transferred to the SiO_2's surface. This process needs to be repeated for addition silicon wafers. At least two wafers with hBN need to be used.

After all the wafers have been coated with hBN, gold needs to be added to a select amount of wafers. The E-Beam is used to evaporate the gold onto the surface of the wafer. A tray of SiO_2 wafers coated with hBN are placed upside down on the circular tray at the top inside the instrument. The gold pellets is then placed at the bottom inside the instrument and evaporated onto the surface of the wafers. This process takes an entire day to complete.

4.3 Creating Polydimethylsiloxane Stamps

Stamps are used to capture the the flake of interest, making it the top layer of the heterostructure. This process can be done by using Polydimethylsiloxane (PDMS). This is a silicon-based organic polymer that is heated to capture the flake of interest, as well as the flakes surrounding it, then cooled to ensure the flakes stay stuck on the surface of the polymer.

To create a stamp, two glass slides and Polycarbonate (PC) are needed to begin the process. Lay the glass slides side-by-side and place one drop of PC on one slide then lay the clean slide on top the PC slide. Apply a small amount of pressure to the slides then pull them apart. The PC layer will be dried on both slides and will be used later. Next, grab a new slide and one strip of orange tape. Place the orange tape vertically on the vertical glass microscope slide. Apply pressure via tweezers to ensure the adhesion between the glass and tape is secure. Use the tweezers to peel the plastic off the tape, leaving the adhesion substance exposed on the glass slide. Next, a small piece of polymer is placed near the top of the glass slide. Next, a three-inch piece of scotch tape is cut off and a small square section is cut from the tape. Take the piece of tape and place it over top the PC glass slide. The tape picks up the PC on the glass slide and under the square the thin PC layer can be seen. Now place the square cutout on the PC tape vertically over-top the polymer. Lastly, cut of any excess tape using a razor blade, completing the stamp.

4.4 Finding Flakes of Interest and Stamping

After the above preparations have been complete, all SiO_2 wafers and PDMS stamps can be taken to the microscope to create the hBN-AU-hBN heterostructure. The hBN wafer will be the first under the microscope since it is the top layer. Once at the microscope station, a vacuum tube and heating pad are used in coordination with the wafer to create a seal to stabilize the wafer. The wafer is placed over-top the suction area with the ceramic heating pad under the wafer. Once complete, focus the lens on the surface of the wafer. If done correctly, boron nitride flakes are seen with many having an orange or yellow color. Thin flakes need to be found. They are very feint and have a blue tint to

them. After a thin flake is found and pictures of the flake are taken, the stamp is mounted to the aligner instrument and arranged with the light shining through the polymer and onto the sample. The microscope is refocused and the stamp is lowered on the silicon wafer's surface. Once the stamp is lowered on the silicon wafer's surface, the ceramic heater is set to 150 degrees Celsius. After it has reached approximately 150 degrees Celsius, the stamp is lifted upward and the heater is disabled, cooling the polymer, encasing the flake of interest and the surrounding flakes inside the PDMS.

Now that the soon-to-be top layer of the heterostructure is captured in polymer, the Au-hBN wafer can be inspected. The wafer-heater-suction coordination, lens focus, and finding a thin flake are all repeated. When looking for a flake of interest on this sample, the flake must be thin and have gold on its surface. When the flake is found, the stamp is lowered on the surface of the sample with the top layer aligned on the newfound flake. Once aligned, the heating pad is heated to 170 degrees Celsius and lowered onto the wafer's surface. Once contact is made, the stamp is lifted and the heater is turned off to cool. The top layer of the stamp transferred to the wafer's surface.

The new wafer should look similar to this image:

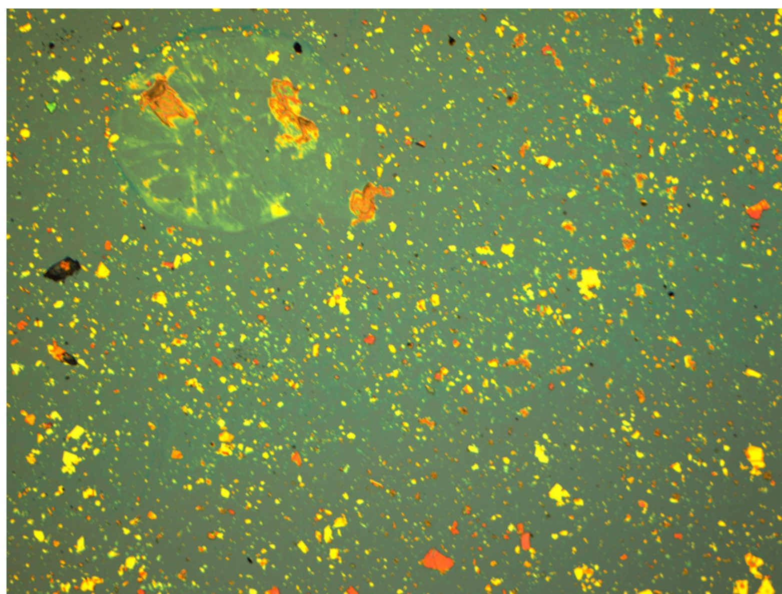

Figure 1: hBn-Au-hBn End Result

To ensure the creation of the heterostructure, focus the microscope on the surface and identify the two flakes of interest have intersected each other. Once confirmed, the wafer sits in chloroform over night to remove the PC layer. Once

removed, it is taken to the Atomic Force Microscopy instrument for further evaluation.

4.5 Probing Heterostructure

The hood of the AFM instrument is opened and the top, metallic head is removed. Under the head houses the cantilever and tip. Replace the tip if needed. Place the wafer on the sample board and place the head over-top the wafer, fitting in the three notches. Open the AFM software and configure the settings. The head emits a laser which needs to be aligned with the tip on the cantilever. If done correctly, the deflection should be close to zero. Zoom in on the wafer and adjust the focus until the flakes are visible. The area of interest contains the heterostructure. Adjust the X and Y plane until the heterostructure is located. Once located, fit the area of interest over the heterostructure and begin probing. This process takes approximately thirteen minutes to complete.

Once the topographic image is complete, the heterostructure's surface potentials, capacitance, and charge coupling are measured. The tip is induced with several different voltages, making this process several hours long. These voltages include: 250mV, 500mV, 750mV, 1.00V, 1.50 V, 2.00V, and each of their respective negative values. Once the data from each source is collected, it can be analyzed.

5 Analyzing and Visualizing hBN-Au-Hbn

To analyze the collected data, the deviation at the beginning of the paper

$$\phi_s - \phi_b \approx \frac{(\Delta V)^2}{2k\beta}(C''_s - C''_b) \tag{1}$$

must be used. Phase shifts of heterostructures are the most important data points when collecting EFM measurements. Surface potentials, capacitance, and charge coupling are all measured based on phase shifts. The phase shift, represented by ϕ, is already calculated through the software, however the phase shifts from the sample and background, denoted ϕ_S and ϕ_B respectively, need to be subtracted from each other to insure correct data.

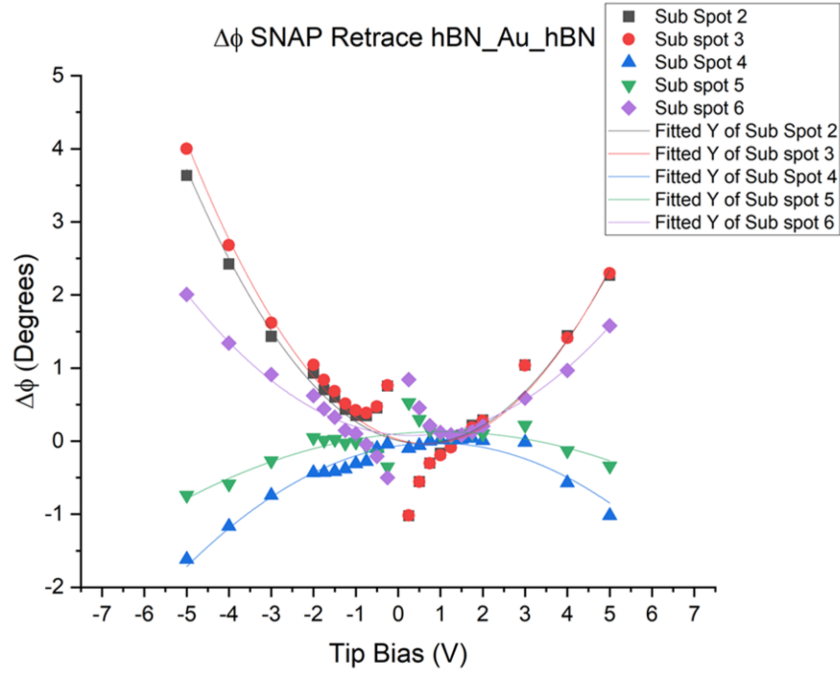

Figure 2: $\Delta\phi$ SNAP Retrace hBN-Au-hBN

The resulting data should form a positive or negative parabola depending on the materials being used, however, the resulting graph from this heterostructure is reciprocal. At this moment, what is causing this disruption in data is unclear. A leading idea is the numerator and denominator need to flipped, causing the function to be cotangent in the phase shift.

6 Graphene Scans

The following pictures are AFM and EFM scans of Few Layer Graphene. The goal was to find the defects mentioned in the introduction of this paper.

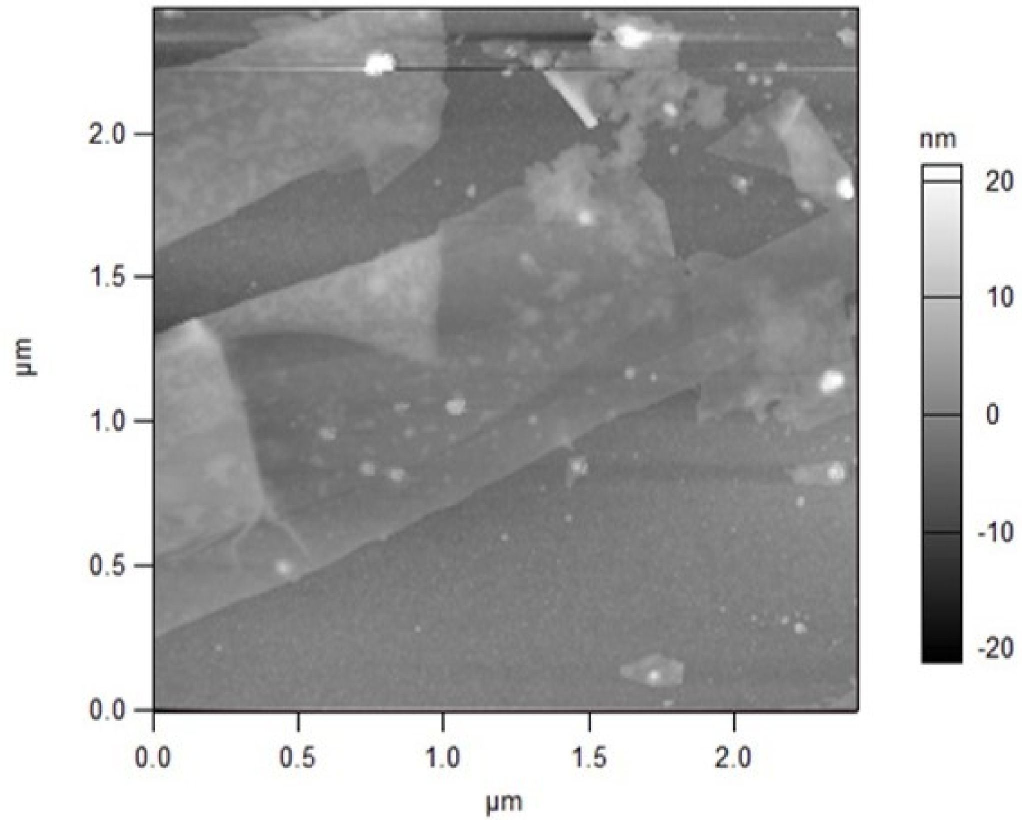

Figure 3: Graphene AFM Scan

The image is an AFM scan of few layer graphene. The lighter the contrast, the thicker the sample is however, the white specs are artifacts. Understanding the sample's surface is a priority before gauging the electrostatic potentials with EFM. Since there are folded layers within this sample, using EFM would prove useful.

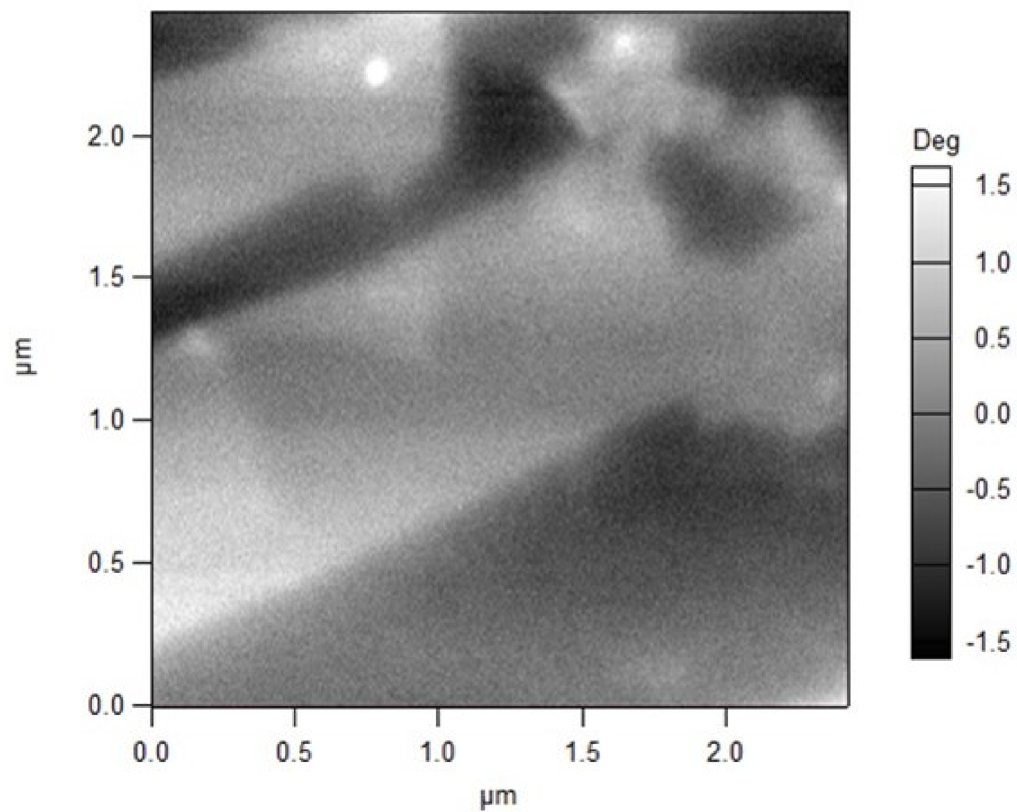

Figure 4: Graphene EFM Scan

The picture is the respective EFM scan. The tip and sample induces an electric field that creates a force gradient that shifts the resonance frequency of the cantilever by some degrees. The higher the shift, the more attractive the force is.

7 Future Goals

No defects were found in the EFM scans. More samples of Few Layer Graphene or Bilayer Graphene will be scanned to find defects. When found, Transmission electron microscopy will be used to further investigate the defects and Moiré patterns.

Acknowledgements

This is work is funded in part by the National Science Foundation under grant PHY-1950795. The University of Kentucky, Department of Physics and Astronomy, Graham lab, Department of Chemistry, Dr. Doug Strachan, Dr. Beth Guiton Kathryn Pitton and the NSF made this work possible.

References

[1] Douglas R. Strachan Datta Sujit S., E. J. Mele, and A. T. Charlie Johnson. “”Surface Potentials and Layer Charge Distributions in Few-Layer Graphene Films.””. In: *Nano Letters* 9.1 (2009), pp. 7–11. DOI: https://doi.org/10.1021/nl8009044.

[2] Kaustav Banerjee Pulickel Ajayan Phillip Kim. “Two-dimensional van der Waals materials”. In: *Physics Today* 69 (Sept. 2016).