Nanomanipulation of Graphene Using Atomic Force Microscopy

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Abstract— **The numerous electrical and mechanical properties with which graphene possess has paved the way into a new era of research and exploration. With many companies researching synthesization and transportation techniques there is a demand for the research of tailoring techniques for the future mass industrial usage of graphene within electronic devices. As such, we explore the efficiency, speed, and quality of mechanical manipulation by way of Atomic Force Microscopy (AFM). In particular ideal force, speed, and length parameters were determined for cutting monolayer graphene (MO) on a SiO$_2$ substrate. The ideal force value was determined to be 2.5 µN and ideal length around 150 nm long, with resulting speed relationships producing significant evidence to claim that speed is not a factor in the cutting of MO as long as it remains below a certain threshold velocity, hypothesized to be a result of thermal drift of the AFM cantilever in the Z-axis direction. The overall mechanical manipulation of graphene was then confirmed and an electrode tailored using this technique with said parameters.**

I. INTRODUCTION

The rapid advancement of scientific breakthroughs has far exceeded even our wildest expectations. Ten year ago we never would have imagined where we would be today and the industry is still growing; but unfortunately this trend cannot last forever. Moore's law is already reaching its quantum limits and soon we will need to find new methods to satisfy our technological demand. Fortunately a possible solution is within our grasp. Graphene, a novel material discovered to be the building blocks of graphite, has been receiving positive reviews within the scientific community. Graphene in its pure form is a monolayer consisting of a single atom thick grid of hexagonal shaped carbon atoms all bonded together in a sp^2 hybridized arrangement. Just like its cousin's diamond, sp^3 hybridized carbon atoms, and CNTs, graphene rolled up into tube shaped structures, graphene possess some of the most desirable properties of any known substance. With strength of nearly 200 times that of steel, electrical conductivity adjustable to almost 6 times that of copper and innumerable optically desirable properties, graphene research is currently one of the leading areas of interest.

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Recently, many researchers have been astonished by the potential that this previously unknown substance has to offer, but since it first successful synthesization in 2004, graphene has continually frustrated scientists. Because of its small structure, difficult and costly production, and the lack of current knowledge available, scientist are finding it difficult to incorporate it into current technology. While many scientists believe that graphene may holds the solution to our future technological problems, there still remains a level of skepticism, as with all novel substances. Graphene's seemingly limitless potential is only matched by its nearly insurmountable difficulties. Graphene, for one, is anisotropic, meaning that its measurable properties vary by direction; particularly showing variations in friction, cutting force, and conductivity [1] along the armchair and zigzag orientations, contradicting what group theory [2] had originally believed about structure possessing six-fold rotational symmetry. But after taking into effect the atomic and quantum structure of carbon, a correct solution of the wave equation was identified predicting instead a two-fold rotational symmetry for graphene. This lead to a number of possible benefits, including direction sensitive cutting and adjustable friction or conductivity control, but at the same time introduces directional limitations when fabricating microchips or other devices which wish to incorporate graphene within their technology. That is why it is necessary to investigate and understand how these properties work.

For this reason we seek both a qualitative and quantitative understanding of graphene and its intrinsic physical properties. We are particularly interested in industrial manufacturing techniques for future production of graphene. For this, an in-depth analysis of graphene's mechanical properties was performed with an emphasis upon cutting and tailoring techniques which could be used in future industry. Nano machining techniques through the use of Atomic Force Microscopy (AFM) were utilized for the purpose of determining effective parameters and limitations for graphene manufacturing, including an analysis of efficiency, speed, and quality. The graphene sample experimented upon was obtained from NASA and was grown on a copper substrate through a process known as chemical vapor deposition, with nominal parameters of 850 °C and 250 W Plasma, with a flow rate of 70 sccm of H$_2$, 76 sccm of CH$_4$ for 1 hour. The graphene was then taken and transported onto a silicon dioxide substrate as in Figure 1.
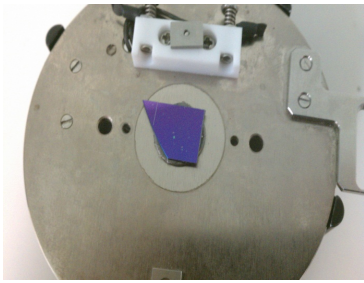
Figure 1. Graphene on silicon substrate attached onto AFM sample holder.

II. Experimental Setup

A. Graphene Synthesis

The primary obstacle with the mass applicability and experimentation of graphene has to do greatly with its fabrication process. Despite numerous methods of production, there are few which can be considered practical, and none without its own faults. But among them, epitaxial growth, particularly the process of chemical vapor deposition (CVD), has shown immense potential for future applicability. CVD, as the name suggest, is a technique by which gases (usually CH_4 and $H_{2)}$ are introduced at high temperatures and through complex mechanisms are able to react with and deposit the desired material on to the surface of a substrat. Normally in regards to graphene CVD, a copper or nickel substrate is chosen because of their unique mechanisms favorable for the graphene growth.

Though the process for producing graphene is quite similar for both nickel and copper, the result can vary greatly, owing primarily to the contrasting solubility levels of the two substrates [3]. This process works by heating the substrates to an extremely high temperature, in the range of 700 °C to 1000 °C [4], in order to promote surface interaction of the substrate and the gaseous carbon atoms. H_2 and CH_4 (usually ionized) are then introduced to the surface of the substrate, and as they transport over the substrate some of the carbon atoms (in methane) get attached and chemisorbed onto the surface. These methane molecules then dehydrogenate (dissociate their hydrogen atoms) onto adjacent surface sites and begin to diffuse into the surface. This happens much less intensively in Copper than in Nickel because of its lower solubility levels, and as such, most of the carbon atoms remain attached to the surface. This is why it is observed that Copper substrates independently produce primarily monolayer graphene, where Nickel relies heavily upon the following step to obtain uniform graphene layers. The substrate is then rapidly cooled which causes a resurfacing of the diffused atoms at the surface sites of the substrate. The H_2 gas then acts as a catalyst and removes the remaining hydrogen atoms form the surface, while the resurfacing carbons atoms, wanting to be in a lower energy state, bond together in a sp^2 hybridized state, effectively "growing" graphene [3].

This processes along with the increased interest in graphene transportation methods [5-7] has given us the capability to produce graphene sheets on the scale of 30 in^2 [8] using the roll-to-roll production techniques. But, despite the potential of this process as a mass production method of graphene, it is still limited by the considerable duration it takes to perform, upwards to three hours [9] to produce even small scale graphene samples. We find similar constraints such as with cost [10], size, and uniformity [11] found in other manufacturing techniques such as exfoliation [12-13] or Gaphite Oxide reduction [14], making graphene very difficult to produce. It is because of these constraints, that graphene still remains almost unused in current industry.

B. Tools

For this investigation into the mechanical properties that graphene possesses the use of two separate instruments were required. The first, a dry box (McDry MCU-201, Seika Machinery Inc., USA) was used to insure that the graphene sample remained pristine and was not affected by ambient condition. In order to guarantee that the water vapor and other particles in the air did not interact with the single atom thick substance and influence the results, it was necessary to store it inside a dry box, which could maintain a relative humidity of 1%, while tests weren't being performed.

The second instrument, and the primary focus of the researched, is an atom scale imaging device known as an Atomic Force Microscope (AFM). The particular AFM used to perform our experiments was Agilent SPM 5500 ILM. The company also supplied an operating program known as PicoView, which was the primary interface to the device, and supplied the images and data recorded by the sensors. The scans of Graphene were performed with the latest version, PicoView 12 and to ensure that the graphene layers weren't stressed or damaged during the tapping mode was utilized as a special precaution.

III. Experimental Results

A. Lattice Orientation Analysis of Graphene

Upon reception of our graphene sample tests were performed in order to verify the distribution of uniform monolayers of graphene. The confliction about the uniformity of the sample arouse due to the questionable surface characteristics. Particularly the presence of small green impurities distributed over the surface of the sample. It was undetermined whether or not these corresponding green impurities where monolayers, bilayers, or not graphene at all. We believed that the entire surface had graphene deposited over it, so in order to confirm this, numerous AFM scans were taken of both the neutral areas and the small green disturbances to identify firstly whether the green impurities were monolayer graphene and then whether or not the rest of the sample was monolayer graphene. The scans were performed using a TAP190ALG tip (Budgetsensors.com) under AC mode and the resulting images and height analysis can be seen in Fig. 2. As we can see by the image scan of one of the green flakes (Fig. 2 (a)), the overall height of the green flake (Fig. 2 (b)) is over 20 nm, which, compared to the nominal thickness of monolayer graphene 0.36 – 1 nm [15], couldn't be a monolayer of graphene. Then multiple images were taken of the neutral area as represented by Fig. 2 (c). The major issue that was encountered with such imaging of graphene is that as scan size decreases noise begins to become a factor in image quality. Noise free images were only able to be produced on the scale of 500 nm x 500 nm scans, and decent images could not be seen much lower than 100 nm x 100 nm scans making it difficult for identification

and classification of the overall surface structure of graphene, which needed scans as small as 1.5 nm x1.5 nm images to see the structure. So, in order to filter out the noise that was encountered a technique known as Fast Fourier Transformations (FFT).

FFT is a mathematical algorithm used for identifying and manipulating any function into a finite sum of sines and cosines. This is very beneficial when one wishes to analyze frequencies and other periodic phenomenon. As was theorized and later verified by Louis de Broglie, all forms of matter can be represented in a wave form as well as a physical form. In other words, all matter is made up of finite combinations of frequency, which can be represented as a finite combination of sines and cosines. What this means is that we can analyze almost all forms of matter by breaking them down into their corresponding frequency elements and analyze the data intrinsically. As for the purpose of the FFT transform, it is to take data, which would be otherwise useless, and remove it from the image. An example would be interference or noise brought about by both, outside factors such as: sound, vibrations, heat, etc. and internal factors such as: tip size and quality, electrical interference, systems errors, or thermal drift. The primary goal of this technique is taking and removing noise which could otherwise interfere with your image. The corresponding FFT images and the significant benefits of FFT transform can be seen in Fig. 2 (e) and as can be seen by Fig. 2 (f) showing the length of the drawn in lines on Fig. 2 (e), they are consistent with accepted bond length of carbon-carbon bonds of ~.143 nm.
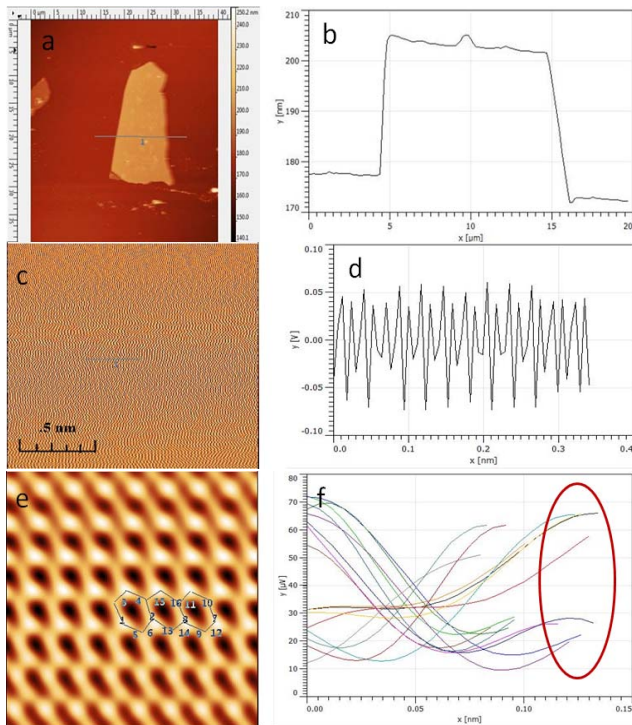

Figure 2: Data and results of sample structure measured over numerous locations. (a) Image scan of a single green flake on the sample surface and (b) the corresponding height data. Then (c) the amplitude image obtained from that scan with corresponding amplitude data (d). (e) The image obtained after performing FFT with lines drawn in the show the structure and corresponding line length data (f) of the drawn in lines on image (e).

B. AFM Based Nanolithography on Graphene

After calibration testing, a proper scan size and consistent cut length constrained, strength was eventually narrowed down to a range of force values between 6.2 µN to 2.5 µN as seen in Fig. 3 (a), by process of elimination of higher strength values. Unlike the previous force test though, these scratches produced very accurate depths ranging from ~1 nm to as low as 0.5 nm as seen by the height analysis data in Fig. 3 (b). These were very positive results, since they were both accurate to the thickness range of epitaxial monolayer graphene and demonstrated a significant depth change with little alteration in applied force, implying that the tip was no longer able to breach some threshold value (i.e. that of the SiO2) and thus not able to penetrate deep into the SiO2 substrate layer. This was just one more confirmation that we were indeed dealing with a monolayer surface of graphene. So with good results between 6.2 and 2.5 µN, lower valued forces were also tested, but no useful results were produced, which meant that ~2.5 µN was the threshold force for cutting into graphene. So, with this knowledge and the observed scratch image showing little to no debris surrounding the scratch surface, it was concluded that this value was the ideal force parameter for future testing as well as industrial graphene tailoring methods.
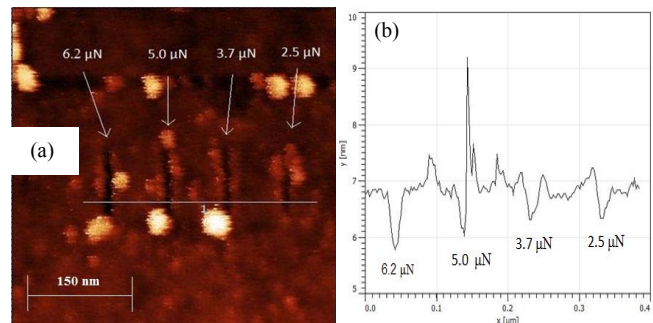

Figure 3. (a) AFM image of scratched graphene layer and (b) corresponding depths with different applied forces.

With favorable and accurate result for force analysis, testing could proceed for appropriate speed parameter. Parameter were kept the same as those mentioned in the previous section while keeping a constant force of 2.5 µN and varying the cutting speed values from 2.5 nm/s on the low end all the way up to 30 µm/s on the high end with resulting scratches and height analysis shown in Fig. 4.

As observed, all speeds ranging from 2.5 nm/s to 30 µm/s produce visible apparent results, but with so much data it was difficult to see any real pattern, so in order to derive an appropriate relationship between the cut depth and the speed of cutting these results were compiled together and the resulting data summed up in Fig. 5 (a). As might be interpreted by the results seen in Fig. 5 (a), there seems to be an inverse or logarithmic trend to the data, but the results were very irregular, producing a very low R^2 value of 0.6503. But upon further analysis of the data it was observed in Fig. 5 (b) that some of the scratch depths were below the nominal graphene thickness, which implied that the scratches weren't completely cutting the graphene, but instead just deforming the structure. So by removing these data point a much more uniform distribution of the data was observed in Fig. 5 (c) producing very consistent result with an average value of

0.622 nm and standard deviation of 0.094 nm. These results implied that cutting speed produced very little alteration in cut depth and as such, wasn't a major factor in the manipulation process for monolayer graphene as long as a threshold speed was breached.
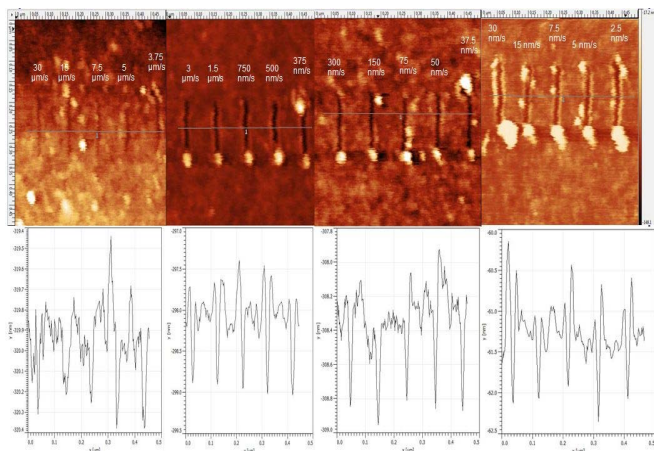

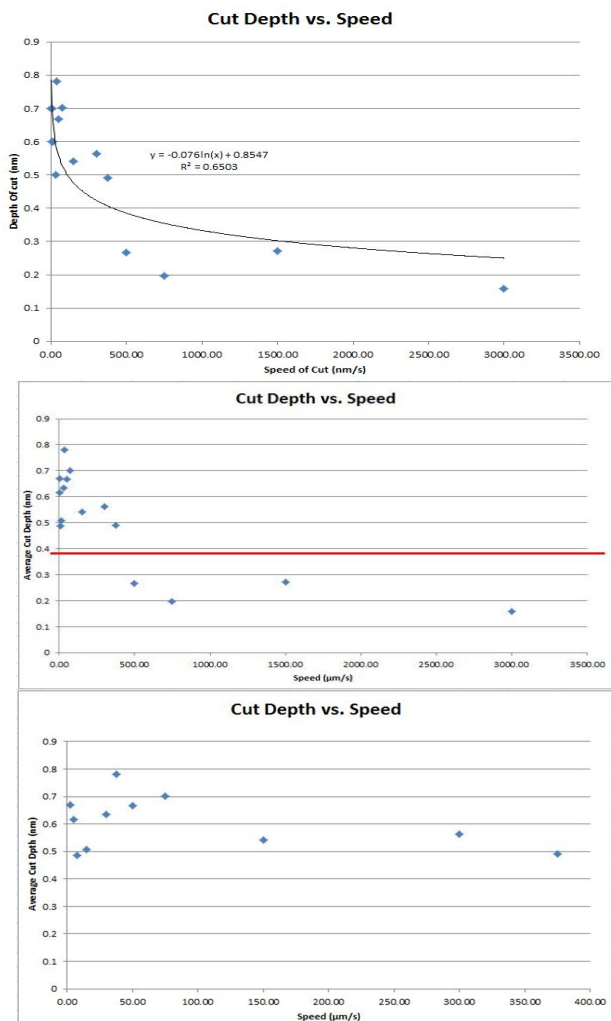Figure 4. Nanolithography speed testing from 2.5 nm/s to 30 μm/s.

Figure 5. Graphs of average depths vs. speed starting with (a) raw data with r^2 of 0.6503, then (b) incorporating the thickness of graphene and (c) removing data points below the value and finally a uniformly distributed graph with average value of 0.622nm and standard deviation of 0.094 nm.

IV. CONCLUSION

Upon beginning this research project, the goal was the mechanical manipulation of graphene through AFM, and to determine key parameters for strength, speed, and efficiency with respect to our given sample, for a mechanical cutting method which could be used in industry. Another promising area of research for the future would be to produce a bias voltage across the graphene sample and to observe how that affects the efficiency parameters of such a mechanical cutting process. Then other methods such as electron beam or electrical force cutting methods could be explored and compared in order to identify the overall most efficient method for the tailoring and manipulation of graphene monolayers.

REFERENCES

[1] L. G. Kreidik, G. P. Shpenkov, "Atomic Structure of Matter-Spcae,"Chapter: Anisotropy of Unstrained Pristine Graphene, Print. 1-4 (2001).
[2] L. Mihaly, M. C. Martin, "Solid State Physics Problems and Solutions," Print. State University of New York, John Wiley & Sons Inc. 72, 204-206 (1996).
[3] M. Losurdo, M. M. Giangregorio, P. Capezzuto, G. Bruno., "Graphen CVD growth on Copper and Nickel: Role of Hydrogen in Kinetics and Structure," *Phys. Chem. Chem. Phys.,* 2011,**13**, 20836-20843.
[4] Y. H. Kahng , S. Lee, *et. al*, "Thermal stability of multilayer graphene films synthesized by chemical vapor deposition and stained by metallic impurities," *Pub Med*. 1-5, Feb. 24 2012.
[5] A. Reina, H. Son, L. Jiao, B. Fan, S. Mildred, *et. al,* "Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates," *J. Phys. Chem. C*, 2008, 112 (46), pp 17741–17744, 1-3 (2008).
[6] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, R. S. Ruoff, "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates," *ACS Nano*, 2011, 5 (9), pp 6916–6924, 1-8 (2011).
[7] Y. Lee, S. Bae, H. Jang, S. Jang, S. Zhu, S. H. Sim, Y. Song, B. H. Hong, J. Ahn, "Wafer-Scale Synthesis and Transfer of Graphene Films", *Nano Lett.*, 2010, 10 (2), pp 490–493, 1-3 (2010).
[8] Sukang B., Hyeongkeun K., Youngbin L., Xiangfan X., Jae-Sung P., *et. al* "Roll-to-roll Production of 30-inch Graphene Films for Transparent Electrodes," *Nature Nanotech.,* 5, 574 (2010), 1-5.
[9] K. Hoe Joon, "Design and Fabrication of the Microcatilever heater for rapid chemical vapor graphene synthesis," *IDEALS,* 1-20, (2011).
[10] Sheng K, Sun Y, Li C, Yuan W, Shi G. "Ultrahigh-rate supercapacitors based on eletrochemically reduced graphene oxide for ac line-filtering." *Sci Rep.,* 2012 ;2:247. Epub 2012 Feb 3. (2012).
[11] S. Chen, W. Cai, R.D. Piner, *et. al,* "Synthesis and Characterization of Large-Area Graphene and Graphite Films on Commercial Cu-Ni Alloy Foils," *Nano Lett.*, 2011, 11 (9), pp 3519–3525, 1-6 (2011).
[12] Hui H., Yang X., Xinyong T., Jun D., Junwu F., Yongping G., Wenkui Z., "Highly efficient electrolytic exfoliation of graphite into graphene sheets based on Li ions intercalation–expansion–microexplosion mechanism," *J. Mater. Chem.,* 2012,**22**, 10452-10456, 1-4, (2012).
[13] Jianxin G., Byung-Seon K., Seung Bo Y., Hee-Tae J., "Preparation of graphene relying on porphyrin exfoliation of graphite," *Chem. Commun.,* 2010,**46**, 5091-5093, 1-3 (2010).
[14] S. Stankovich, D. A. Dikin, R.D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon*, **45** 1558–1565, 1-7 (2007).
[15] P. Nemes-Incze, Z. Osvath, K. Kamaras, L.P. Biro, "Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy," *Carbon,* **46**, 11, pp. 1435-1442, (2008).