

The Automation of Mechanical Exfoliation for the Synthesis of Graphene

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Abstract

Graphene is a two dimensional allotrope of carbon, that has displayed many outstanding qualities and characteristics that show promise for use in many modern applications. These applications range from super-efficient solar panels to highly sensitive sensors. The largest problem that has prevented the commercialization and/or research of graphene is the inability to consistently create the highest quality samples that graphene has to offer. Attempts to solve this problem have mostly consisted of finding alternate processes to synthesize the material. This study presents a possible solution to the problem through the refinement of the mechanical exfoliation process by reducing the effect of several variables with an automated roller system. With the use of the roller it was expected that we will see an effect on the amount and size of the graphite piece created when compared to the manual process. The results showed there was a significant increase in the amount of flakes, but also a significant decrease in their size.

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Introduction

The first computers of around 70 years ago were very much different from what we use today. One of the first systems that could be classified as a computer, the Electronic Numerical Integrator And Computer (ENIAC), relied on vacuum tubes to store data barely even comparable to the amount of data storage we have in inexpensive handheld calculators (History: Preceding Technologies, 2015). This system in total would cover around 167 square meters of space. A few years later, in 1948, the Manchester Small-Scale Experimental Machine showed rapid advancement in technology, displaying a system more similar to computers today which run software to perform different tasks (*SSEM* computer of Frederic Williams and Tom Kilburn, 2015). This system had around the equivalent of 128 bytes of memory. To compare to today's values, a hard drive with 16 Terabytes (17592186044416 bytes) of storage has recently been created. The amount of physical space required for computers has progressively decreased and the computational power has increased. This phenomenon was predicted by Gordon Moore in 1965 (50 Years of Moore's Law, 2015). Called Moore's Law, this trend describes how the computer's power, directly linked to the number of processors, has steadily increased over the past few decades. He predicted that the number of transistors in integrated circuits would double approximately every two years. Now however, we are reaching the point where the rate of development of new technology is starting to decrease. This decline in the rate of development is caused by the limitations of the materials used in microprocessors. As of now, silicon is the main material used for integrated circuits and many other components of computers. This is mainly attributed to silicon's accessibility. We must look for a new way to keep advancing our technology. One field where a solution may be found lies in the ever increasingly popular field of nanotechnology.

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Nanotechnology is technology on the nanoscale, and is often created by manipulating matter at the atomic and molecular scale. This is a rapidly growing field with applications not limited to computers, but to almost every field of science. Some notable examples aside from computers are sustainable energy, environmental remediation, and an assortment of health and medical applications. With nanotechnology becoming an increasingly appealing field of science to find solutions for many different problems, why is it taking so long for it to be fully applied? The main question that all research in nanotechnology must answer first is; what materials are best suited for a certain application and how best to create these materials? There are many different types of nanoparticles of various materials and shapes that have been found to have the potential for many different applications. A two-dimensional material is a type of nanomaterial that show promise as a replacement for silicon in integrated circuits.

Two-dimensional (2D) materials are not truly two-dimensional, but they are close, having a third dimension that is only one to a few atoms thick. Two-dimensional materials are allotropes, or a type of formation of atoms of a particular element. For example, graphene is a 2D allotrope of carbon, and phosphorene is a 2D allotrope of phosphorus. One important overall characteristic of two dimensional materials is that as the number of layers in the bulk material decreases, the properties of the material change. At times, they become more defined, while others become less like their bulk counterparts. One of the first two dimensional materials developed was graphene (Novoselov et. al., 2005). The popularity two dimensional materials have now can be attributed to the initial findings pertaining to graphene's incredible properties.

Graphene and other two dimensional materials were initially thought to be impossible to produce. Scientists originally believed that single layered materials would be thermodynamically unstable and if ever isolated would just curl due to the instability. In 2004, Konstantin Novoselov

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and Andre Geim were the first to produce a 2D material, when they isolated graphene from the bulk material, graphite (Novoselov, 2004). These scientists used the simple method of mechanical exfoliation in order to isolate a single layer of graphite. The properties graphene has displayed have led many to believe it to be the material that will bring the world to a new level of technology. Its two most significant characteristics are its immense strength and incredibly high electrical conductivity. Studies have shown it to achieve breaking strengths of up to 42 Nm^{-1} and an intrinsic strength of 130 gigapascals (Lee, 2008). It has also been found to have a zero band gap allowing it to achieve high electrical conductivities, among other unique properties.

There are many processes that have been found to synthesize graphene. Each process has its benefits and its draw-backs. The first method used; mechanical exfoliation, was simple but highly effective. Mechanical exfoliation involves the physical tearing of the layers of graphene from the bulk material. To do this, an adhesive material such as ordinary Scotch[®] tape is placed onto a piece of bulk graphite. This initially adheres to small pieces of graphite at sizes less than five microns. After the initial adherence, the tape is then adhered to a second piece of tape. The two pieces of tape are then peeled apart. At the microscopic scale the graphite is being exfoliated; physically ripping layers apart. This is then repeated several times to further reduce the amount of layers the pieces contain until they are left with a few layers or a single layer. Currently, mechanical exfoliation provides us with some of the best samples of graphene. Samples created using mechanical exfoliation have given us measured properties of strength and conductivity closest to the ideal and theorized values (Kysar, 2013). One large problem with mechanical exfoliation is the defects formed during the physical tearing of the layers. Defects will negatively affect the conductivity and the strength of the material. Another problem with mechanical exfoliation is the randomness associated with the process itself. Uncontrolled

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variables such as inconsistent pressure on the samples during exfoliation cause very inconsistent results when attempting to create samples. On some attempts no samples may be found while others could yield a large amount of graphene (Novoselov et. al., 2005).

Other ways of exfoliation have been discovered such as liquid phase exfoliation (Coleman, 2008). This process works by dispersing graphite into a solvent. This graphite solvent mixture is then agitated. The surface energy of the solvents and the agitation lead to the exfoliation of the layers. If this is done enough the graphite may produce few layer graphene which is comparable to the graphene from mechanical exfoliation.

Chemical vapor deposition (CVD) involves the deposition of an element onto a substrate. The source for the element is usually a gas. This gas is run through a sealed vacuum chamber. In this chamber the gas is heated which causes the chemical decomposition of the gas. This allows part of the gas to be deposited onto the substrate. In the case of graphene, a hydrocarbon gas is used. The most common hydrocarbon used is methane (CH_4). When the gas is put though the vacuum chamber the carbon atoms are chemically broken apart from the hydrogen atoms. The carbon atoms are then deposited onto a copper substrate. These carbon atoms, when deposited, naturally form bonds and become graphene. The leftover hydrogen atoms form hydrogen gas which is then removed as a byproduct. Coleman, et al. found that CVD created large area samples, but the samples' conductivity and strength did not reach the same level of pristine graphene created through mechanical exfoliation (2008). Another problem associated with CVD is that a way to remove the carbon layer from the copper substrate has not been optimized.

To observe the thickness of the 2D samples, an atomic force microscope (AFM) has traditionally been used. An AFM uses the displacement of a small contact needle to obtain a measurement of the height of the material. One drawback of this process is that defects can be

created when the needle is dragged along the surface of the material. A recent advancement has been the process of raman spectroscopy. Raman spectroscopy utilizes the way light scatters when it hits a surface to provide information on the molecular structure of what is being observed.

Raman spectroscopy provides an immense amount of information not measureable with an AFM while also leaving no traceable effect on the material. A most notable advantage of raman spectroscopy is the ability to measure the amount of layers and approximate thickness of what is being observed. This information can confirm the existence of two dimensional materials.

Statement of Purpose

The purpose of the experiment is to create an easy method of creating mechanically exfoliated graphene for use in research. Though it cannot create samples as large as CVD, mechanical exfoliation still produces graphene samples with the highest quality. In this experiment, a possible option for creating a large amount of graphene samples for use in research was explored. This method involved a refinement of the original mechanical exfoliation process. The changes made involved automating the process to reduce the amount of uncontrolled variables the original method has. An automated roller was designed to allow variables such as the force applied on the material to be made consistent when compared to manual exfoliation. Raman spectroscopy was used to analyze the quality of the products. It was expected that automated mechanical exfoliation would increase the yield of graphene and result in a better distribution of graphite along the substrate.

Methodology

1) Silicon wafer creation

The substrate upon which the graphene would be placed on was created. The final products of this process were small square pieces of silicon on top of silicon dioxide which had a grid system marked on their surface using chrome on gold. This grid allowed us to mark and record the specific places the graphene or any other points of interest were found.

First, pre-made p-type doped silicon/silicon dioxide (Si/SiO₂) wafers with a (100) crystal orientation were obtained. The wafers' crystal orientation (the way the atoms connect at the molecular scale) and positive doping (the removal of an electron using a chemical process) were both to ensure a strong adherence to the graphite. They were first spin coated with a primer. After it was primer coated each wafer was then coated with SPR; a photoresist. Once the wafer was coated with photoresist, it was annealed for one minute. It was then placed onto the mask/wafer holder, and a platinum mask was placed on the other side of the holder. A vacuum suction kept them in place. The holder was then aligned with a mask of the grid pattern of cross-hairs and numbers. The grid pattern would eventually allow us to locate a specific area on the substrate. The wafer and mask were then exposed to ultraviolet light. The wafer was then washed with acetone for 15 seconds. This etched away the parts of the SiO₂ layer that were exposed to the ultraviolet light. Gold, then chrome, was deposited onto the wafer in the etched out areas, to make the numbers and crosshairs more visible when under a microscope. The wafers were then cut down to small square pieces of approximately one square centimeter in size.

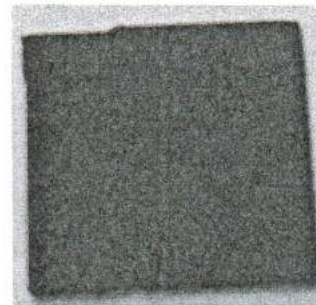


Figure 1: One piece of the silicon wafer cut into a square centimeter used to create the samples.

2) Mechanical Exfoliation

To create the control group of samples, the original manual exfoliation process was used. Scotch[®] tape, an acetate-based adhesive, was placed on a bulk piece of graphite, which was a higher quality than that which is used in pencils. The bulk graphite was formed in layers similar to slate. The tape was slowly peeled off by hand. A second piece of tape was aligned with the

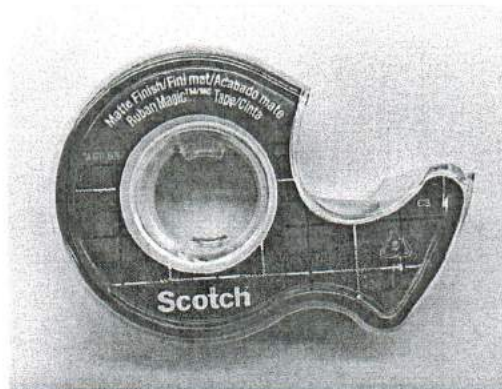


Figure 2: The scotch[®] tape used in the experiment.

original piece (adhesive sides facing). The pieces of tape were rubbed together gently then peeled away from each other. This was repeated five to six times until a good amount of graphite had been coated on each piece of tape. Once graphite was evenly coated on each piece, one was placed with the graphite side down onto the Si/SiO₂ substrate created earlier. The tape was rubbed onto the wafer for about 10-15 minutes. Afterwards, the tape was removed and the sample examined under a microscope.

3) Roller Design and Testing

A prototype roller was used to create the automated roller samples of graphene, as shown in figure 3. Solidworks[®] 3D modeling software was used to design the roller. Each piece of the roller was modeled individually, and then an assembly was created. The motor, motor clamps, shafts, gears, shaft clamps, bearings, springs, washers, standoffs, and rubber roller were purchased. The main body, the sample roller, and the holder for the sample roller were 3D printed. The assembled roller was then tested. Scotch[®] tape was placed onto a graphite sample in a similar fashion to the way it is done in the manual mechanical exfoliation method. The tape was peeled off the graphite, and then adhered to a piece of double sided tape. The double sided

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tape was attached to the rubber roller with the side with the graphite facing outward, and the silicon substrates placed on to the substrate roller. The substrate roller assembly which included the roller and the holder was then placed onto the roller. The springs would suspend the substrate roller assembly while a screw would maintain pressure. The roller was allowed to rotate for approximately 10 minutes, which in turn exfoliated the graphite while transferring it onto the Si/SiO₂ substrate.

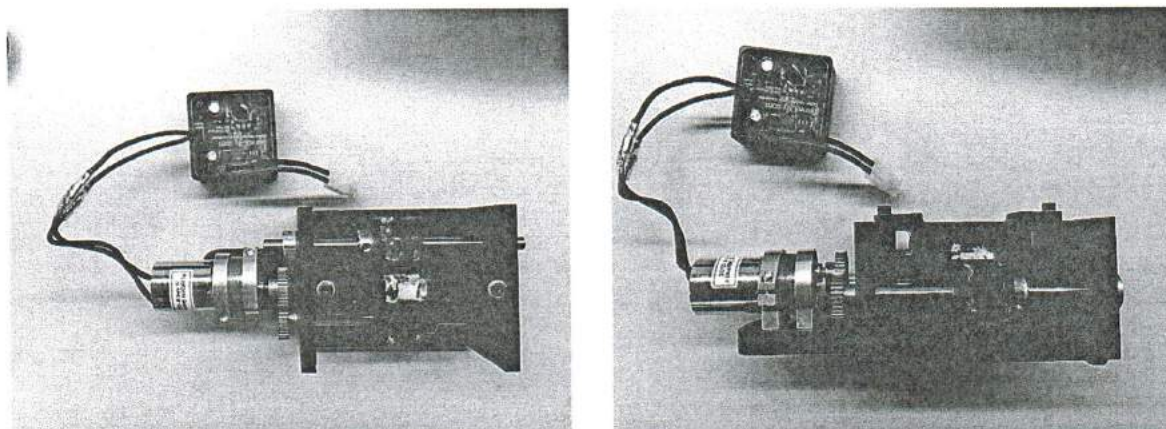
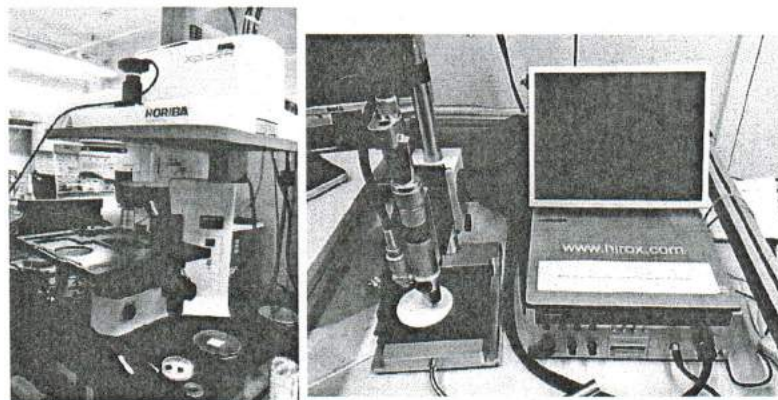


Figure 3: The top (left) and side (right) view of the roller with the controller attached.

4) Monolayer identification and confirmation

After samples were created using the automated roller and standard mechanical exfoliation, they were examined under a microscope. Different locations on the wafer were identified using the grid system referred to earlier. While looking through these areas, possible monolayers were identified. Once all possible monolayers were identified, raman spectroscopy was used to confirm that they were indeed monolayer samples. A comparison between the mechanically exfoliated samples and the automated roller samples was conducted.

Figure 4: The two main pieces of equipment used to obtain data: the Hirox microscope (left) and the Horiba scientific Xplora (Raman spectrometer) (right).



5) Device efficiency analysis

Two sets of data were collected from the manual exfoliation process, and two sets of data were collected from the automated exfoliation process. Using the grid system on the samples, a 10 by 10 area was chosen. In this area the amount of graphite pieces were counted. The average number of graphite pieces for each square was calculated. This gave an approximate comparison between mechanical and automated exfoliation as a higher amount of graphite transferred would yield a higher chance of obtaining any graphene samples. Another set of data was collected to compare the average sizes of the graphite pieces. Using a smaller 5 by 5 area, within the 10 by 10 area, the average sizes of the graphite pieces were measured in two of the samples. To get the averages for each square a program in the microscope was used. This program allowed us to outline a piece of graphite which then uses the information provided by the outline to find the area of the piece. This was done for each piece which was then added together to find the sum total. This was done for each square area. The average size for each piece in a square was then found by dividing the total area covered by graphite in one square by its corresponding graphite count. The various data taken was put into excel. Then the descriptive statistics option within program was used to find the information needed to perform a statistical analysis. The automated and manual processes were then compared with a one-tailed t-test assuming equal variances.

Results

Figure 5 is a visual representation of the amount of graphite per segment. This data was collected by counting the visible graphite pieces in a specific segment on the grid. This was done for a ten by ten area on a given sample. The graphs provide a visual that allows a comparison of the relative distribution of the graphite on a ten by ten area on the sample. As can be seen both manual samples have areas with little to no pieces of graphite, while other areas in comparison have a much higher amount. The automated samples both have a large amount of graphite pieces and have smooth distribution without any anomalous peaks.

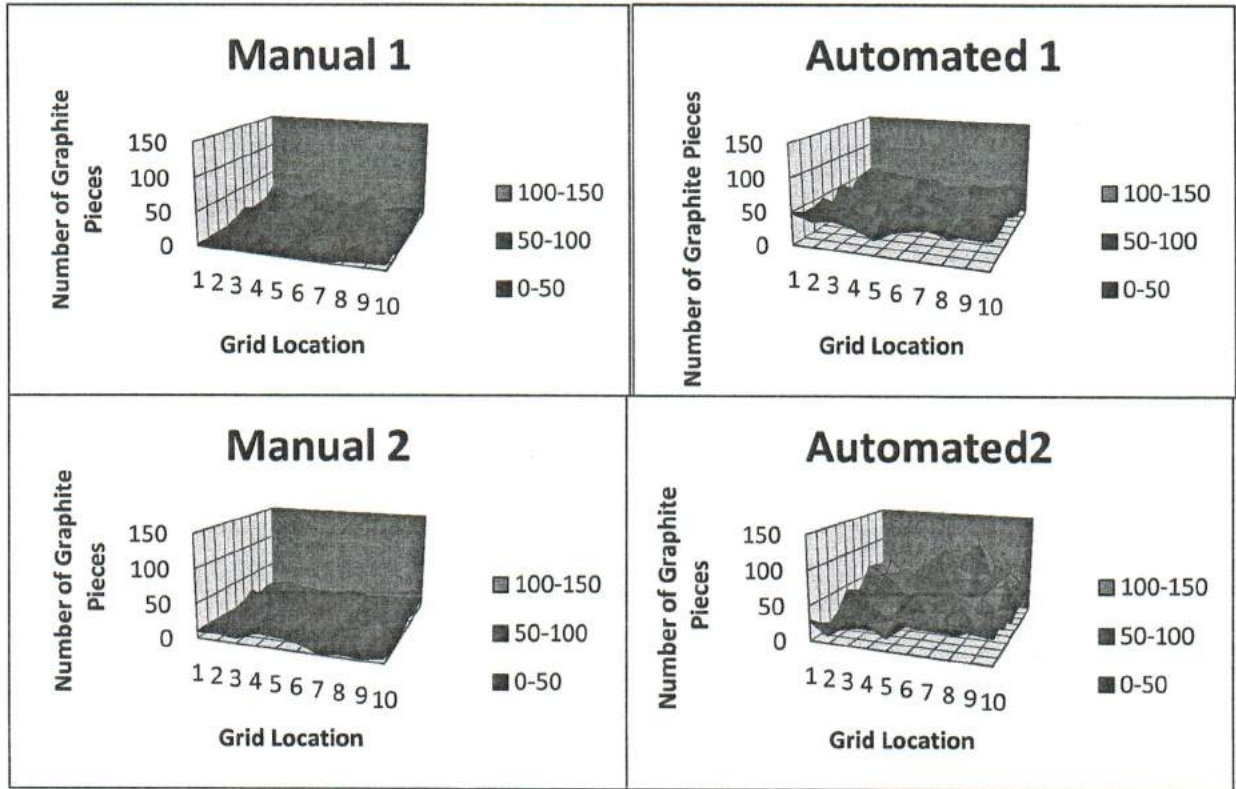


Figure 5: Density of graphite pieces. The relative heights detail the number of graphite pieces found in one area.

Raman spectroscopy was used in order to confirm that few layer graphene was indeed created using the mechanical exfoliation process. Using raman spectroscopy to characterize graphene involves locating two characteristic peaks. One peak, called the G peak, is located at a raman shift around 1600 cm^{-1} and a second peak, called the 2D peak around 2700 cm^{-1} . These two peaks define the readings given by graphite. Monolayer graphene will have a G peak with a specific ratio of its full width at half maximum to the full at half maximum of the 2D peak. The graph below shows the raman spectroscopy data for a sample of graphene. This sample is estimated to be around tri-, bi-, or mono-layered. This is shown through the smoothness of the peak and their relative sizes.

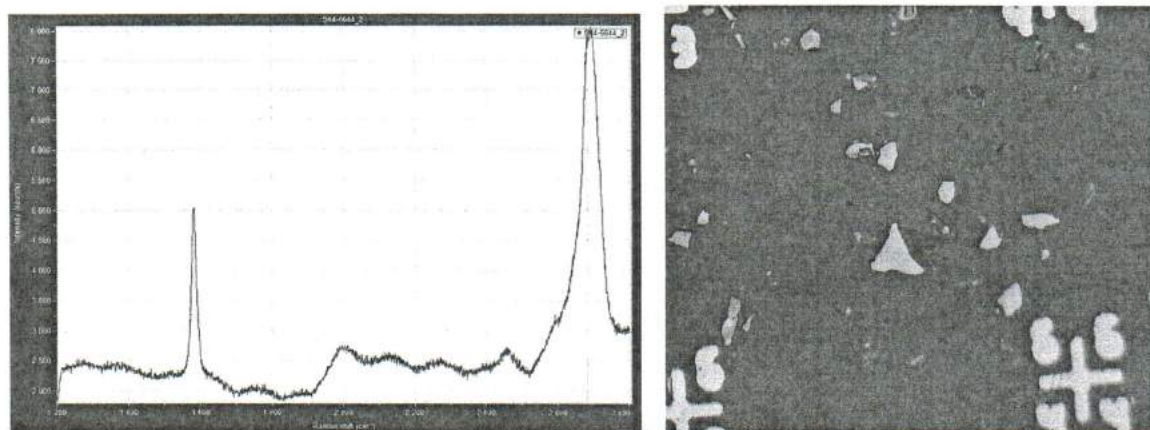


Figure 6: Raman spectroscopy data for a few layer graphene samples on sample 44(left). The sample observed (right).The distance between the center of each crosshair is approximately $25\text{ }\mu\text{m}$.

There was a clear increase in the amount of flakes transferred in the automated process based on what could be seen under the microscope. This was then supported by the one-tailed student's t-test which yielded a p value $<.001$. This tells us that there was a statistically significant difference in the amount of flakes transferred. The calculated confidence interval also tells us an approximate range where the difference of two given samples is going to lie. For the

amount of graphite flakes the 95 percent confidence interval was 28.06 pieces to 30.56 pieces. This means that it can be said with 95 percent confidence that the difference in the number of graphite pieces between any given manual segment and automated segment will be found in this range.

	<u>Manual</u> n=200	<u>Automated</u> n=200
<u>Mean</u>	7.37 pieces	36.68 pieces
<u>Standard Deviation</u>	5.53 pieces	13.53 pieces
<u>One-tail P value</u>	<.001	
<u>95% Confidence interval</u>	28.06 pieces - 30.56 pieces	

The average of the total area covered by graphite in each one by one segment in a five by five area on the grid was found using the microscope and analyzed with the same method used in analyzing the amount of pieces. Based on a one-tailed t-test there was no significant difference in the total area covered by graphite by the two exfoliation processes ($p=0.279$).

	<u>Manual</u> n=25	<u>Automated</u> n=25
<u>Mean</u>	202.277 μm^2	180.887 μm^2
<u>Standard Deviation</u>	33.915 μm^2	12.694 μm^2
<u>One-tail P value</u>	0.279	
<u>95% Confidence interval</u>	6.827 μm^2 - 35.952 μm^2	

Lastly the average size of each piece in each segment was found by dividing the total area by the total amount of flakes in the corresponding one by one segment. When the average area of the flakes in each sample was found a one-tailed t-test was once again performed. The data was

shown to be statistically significant with a p value that was $<.001$. This tells us that there was a significant difference in the size of the flakes between the two methods. The automated method created flakes with a much smaller size when compared to the manual method. The confidence interval shows that the difference between any two flakes in the two methods will be between $4.432 \mu\text{m}^2$ and $35.285 \mu\text{m}^2$.

<u>Table 3: Graphite Average Area</u>		
	<u>Manual</u> n=25	<u>Automated</u> n=25
<u>Mean</u>	24.561 μm^2	4.702 μm^2
<u>Standard Deviation</u>	13.978 μm^2	1.871 μm^2
<u>One-tail P value</u>	$<.001$	
<u>95% Confidence interval</u>	$4.432 \mu\text{m}^2 - 35.285 \mu\text{m}^2$	

The results show a clear increase in the amount of flakes transferred, as shown in table 1, but with a reduction in their size, as shown in table 3. This increase in amount is a desirable effect but the smaller size could cause problems for other applications. It was also displayed through the raman spectroscopy data that graphene was synthesized during the process.

Discussion

Clear benefits were seen in automating the process of mechanical exfoliation. There was a measurable increase in the amount of graphite pieces transferred using automated exfoliation. The distribution of these pieces was also much more even throughout the samples. There are still, however, problems present. Keeping the amount of pressure used to perform mechanical exfoliation constant did prove to increase the amount of flakes, but it decreased the size of the flakes. The increase in the amount of flakes is desirable trait of automating the process; however the reduction in size may be problematic for various applications. There was also a slight

variation between each of the distributions of the two automated samples. This may be because the roller may have less but more consistent pressure while the manual process has inconsistent but large pressure overall. The slight variation between the two roller samples may also be attributed to the method used to attach the wafers to the device. A revisitation to the design of the roller may need to be done to further control the variables present. Some options would be to change the method used to attach the samples to the roller. The layers were stuck onto the middle roller using a small amount of acetate-based adhesive on the back. An inconsistent application of adhesive may alter the amount of pressure between the middle roller and the outer rollers, which may have led to the differences between both automated samples with respect to the tape residue.

Conclusion

The objective of this study was to find a way to refine the process of mechanical exfoliation. To do this, a roller to automate the process was designed, created, and tested. There was a great difference between the samples created through standard mechanical exfoliation and automated mechanical exfoliation. The amount of graphite in each automated sample was clearly larger but the size of the flakes was much smaller. The graphite flakes were also much more evenly distributed throughout the roller sample. A more consistent method of attaching the wafers to the roller must be developed, as it may have been the cause of some of the variance between the two automated samples. A large amount of tape residue was found in in both the automated and manual samples. Other types of adhesives that would be worth testing include but are not limited to rubber, synthetic rubber, acrylic, and silicon-based adhesives. A different adhesive may have different effects on the transfer and exfoliation of graphite. Different adhesives may also leave different amounts of residue on the substrate during transfer. The next steps to take would be to redesign the roller to allow control over temperature, roller speed, and

pressure. A successful design will make the production of mechanically exfoliated graphene samples much easier. These samples could be used to research the application of 2D materials and may lead to continued production of smaller, more powerful electronics.

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