

Growth of Twisted Bilayer Graphene by Chemical Vapour Deposition

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Twisted bilayer graphene is of interest to study due to the unique properties it can exhibit at different twist angles, such as superconductivity or non-linear optical effects. Bilayer graphene was grown on a copper substrate in a chemical vapour deposition system. The parameters of the system were varied and the resulting samples were studied in order to determine a link between each parameter and the average graphene crystal size as well as the nucleation density of the sample. Clear links were determined for parameters such as the temperature of the system and the growth time length, but other parameters did not demonstrate such a clear relationship. A few grown bilayer samples were studied in order to determine their twist angle, all of which measured a twist angle between 20° and 30°.

Introduction

Graphene is an allotrope of carbon composed of a single layer of carbon atoms arranged in a hexagonal structure. When growing graphene, a second layer can begin to grow beneath the first, which results in what is known as a graphene bilayer. This second layer will likely have a slight angular offset when compared to the first layer, which is characterized by the twist angle, which is the angle between the first and second layer of graphene. Due to the hexagonal structure of graphene, this twisting angle only varies between 0° and 30°, as every 60° of rotation simply returns the bilayer to a 0° twist angle, as can be seen below in Figure 1.

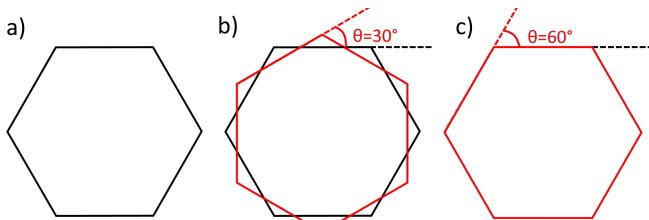
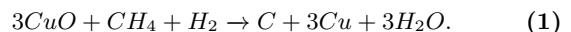


Fig. 1. Diagram of the twist angle between 2 layers of graphene. **a)** Depicts the original single layer. **b)** Demonstrates a 30° twisting angle between the original layer (depicted as the black hexagon) and the bilayer (depicted as the red hexagon). **c)** Demonstrates how after a 60° rotation of the bilayer, the resulting twist angle between the two layers returns to 0°.

These twisted graphene bilayers are of interest due to the special properties they can have [1] [2], such as superconductivity or non-linear optical effects, which all depend on the twist angle between the two layers.

To grow graphene, a process known as Chemical Vapour Deposition (CVD) is used. First, a substrate is inserted into a system at high temperature and low pressure. Next, a flow of gas is passed through the system for an allotted amount of time. As the gas interacts with the substrate, it will deposit molecules onto it. In our case, we use copper as our substrate, to which carbon atoms, coming from a methane (CH_4) source,

are deposited onto in order to form graphene. The chemical reaction describing this specific chemical vapour deposition is:



While hydrogen does not play a direct role in the reaction causing the formation of graphene, it instead acts as an etchant, removing impurities and lowering nucleation density, meaning the density of sites of growth for new graphene crystals. By decreasing nucleation density, it allows for the graphene crystals that do form, and subsequently the bilayers beneath them, to grow larger.

Once graphene bilayers have grown on the copper substrate, in order to view and characterize their twist angles, the graphene must first be transferred onto a silicon substrate. This is because the bilayers which grow beneath the top layer of graphene cannot be viewed when on a copper substrate. Raman spectroscopy is then used in order to specifically characterize the twist angle between the 2 layers. If only a less precise measurement of the twist angle is needed however, an analysis of the optical intensity of the single layer graphene compared to the intensity of the bilayer can be performed to classify the twist angle into a range of possible angles.

Materials and Methods

A. Copper pretreatment. As previously mentioned, graphene is grown on a copper foil through chemical vapour deposition. First, the copper foil must undergo a pretreatment process comprised of 2 chemical baths in order to remove impurities and suppress nucleation density. First, the foil is submerged in a methanol (CH_3OH) bath for 10 seconds, then rinsed with deionized water before being placed in a second bath of acetic acid (CH_3COOH) and left for 10 minutes. Once it is done in the acetic acid, the copper foil is rinsed again with deionized water, then dried using compressed nitrogen gas. At this step, a portion of the copper is removed in order to keep a control piece.

B. Chemical vapour deposition. Once the copper has undergone its pretreatment, it is ready for CVD. The entirety of the chemical vapour deposition system is depicted in Figure 2. The oven is heated to temperature and the copper foil is placed in a quartz tube, which is depressurized by a pump hooked up to the system. In order to control the rate of H_2 and CH_4 into the system, 2 flow meters controlled by a computer running a program in MatLab regulate the flow of both gases in standard cubic centimeters per minute (s.c.c.m.). One s.c.c.m. is equivalent to a flow of 1 cm^3 of gas at standard temperature and pressure per minute. Once the oven reaches the desired temperature and the system has been depressurized to 1 $mtorr$,

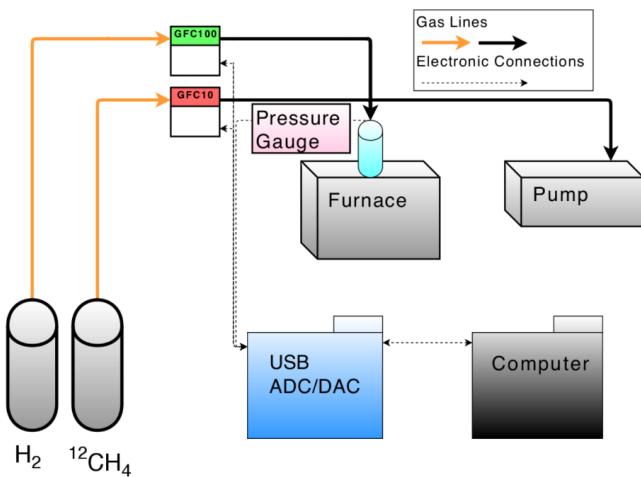


Fig. 2. Diagram of the experimental setup. The computer controls the flow rate of both H_2 and CH_4 through a flow controller. The pressure in the quartz tube is measured by a pressure gauge throughout the entire experiment. This figure is taken from Eric Whiteway [3], who built the setup.

the quartz tube containing the copper foil is inserted into the oven and the MatLab program is started, thus commencing the copper's annealing phase. The annealing process is done in order to remove internal stresses present in the copper foil. During the annealing process, only H_2 is passed through the system and the pump remains running in order to maintain a low pressure environment throughout the system. Once the copper has been annealed, it is onto the growth period where methane is introduced into the system in order to induce chemical vapour deposition. At the end of the growth period, the flow of methane is blocked and the quartz tube is immediately removed from the oven in order to avoid redeposition of copper on top of the graphene that has grown on the substrate. The system is then allowed to cool under a flow of H_2 similar to during the annealing phase. Once the quartz tube becomes cool enough to manipulate, the flow of hydrogen is blocked and the pump is stopped in order to repressurize the system to atmospheric pressure. The copper foil can then finally be removed from the system.

C. Classifying graphene samples.

C.1. Observation under a microscope. There is one last step to be performed if the graphene is to be observed on the copper foil under a microscope. Despite graphene only being a single atom thick, it still provides the copper with protection against oxidation, and so a hot plate is set to $200^\circ C$ and the copper is placed on it and allowed to oxidize for 5 minutes. This oxidation creates a difference in color between sections of bare copper, which turn a deep red from oxidation, and sections of graphene, which protect the copper from said oxidation and so remain a lighter shade. Once the sample is done on the hot plate it is finally ready to be observed under a microscope, where photos can be taken of the graphene crystals in order to judge the efficiency of the growth parameters.

C.2. Determination of crystal size. The average size of graphene crystals is an important characteristic of each sample. The size of each graphene crystal is characterized by 2 values: their inner and outer circle diameter. The inner circle is defined

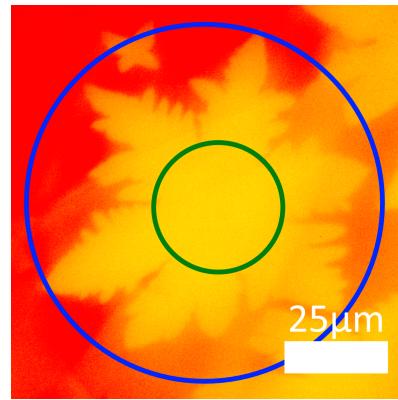


Fig. 3. Optical image of a graphene crystal with circles for size characterization. The red background is the oxidized bare copper and the yellow crystal is the graphene crystal. The green circle represents the inner circle of the graphene crystal and the blue circle represents its outer circle.

as the largest circle that can be inscribed into the graphene crystal and the outer circle is defined as the smallest circle that encloses the entire crystal. An example of the inner and outer circle of a crystal can be seen in [Figure 3](#).

C.3. Determination of nucleation density. Another necessary characteristic of each graphene sample is its nucleation density. The nucleation density is determined by counting the number of graphene crystals present in a set area and dividing it by said area. This is done at different locations throughout the sample in order to determine an average nucleation density for the entire sample.

D. Transferring graphene from the copper substrate to silicon.

If the intent of the graphene growth is to observe the bilayers rather than simply the crystal structure, the graphene must be transferred onto a silicon substrate. First, the copper foil with graphene is spin coated with poly(methyl methacrylate) (PMMA), which is a transparent thermoplastic. The spin coating applies an even layer of PMMA onto the top of our sample, thus allowing the graphene to bind to the PMMA once it has cured. In order to isolate the graphene from its substrate, the copper must be dissolved in a solution containing ammonium peroxydisulfate. After a few minutes in the solution, the underside of the sample must be rinsed with DI water in order to remove the graphene grown on the under side of the copper foil. This is needed since if the underside is allowed to remain, once the copper dissolves, it will contaminate the layer of graphene grown on the top of the substrate. Once the copper has been completely dissolved in the solution, a silicon wafer is used to remove the floating piece of PMMA containing our graphene. The whole sample is then rinsed using DI water, then left to dry. Finally, the PMMA is dissolved by submerging the sample in acetone, then the sample is rinsed with isopropyl alcohol and dried with pressurized nitrogen gas, leaving only the graphene on the silicon substrate. The entire process from CVD to transfer can be seen in [Figure 4](#).

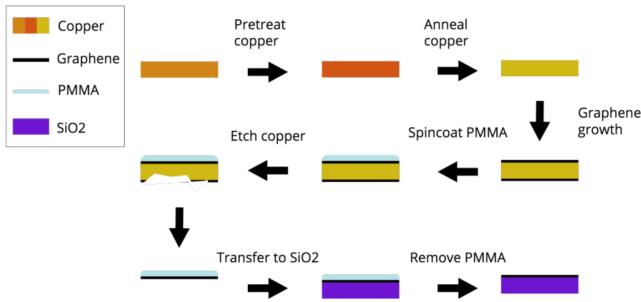


Fig. 4. The entire process in order to obtain a sample of observable bilayer graphene, from the pretreatment of the copper substrate, to the chemical vapour deposition, to the transfer to the silicon substrate. This figure is also taken from Eric Whiteway's paper [3].

E. Observing the twist angle.

E.1. Raman Spectroscopy. In order to determine the twist angle of a graphene bilayer using Raman spectroscopy, a monochromatic light interacts with said bilayer. This light interacts with molecular vibrations in the bilayer, which causes the energy from the laser light photons to be shifted up or down, creating a Raman spectrum. One section of the resulting Raman spectrum is known as the G peak. The intensity and full width at half max of this G peak varies depending on the twist angle of the graphene bilayer. The specific correlation between the properties of the G peak and the twist angle of the observed graphene bilayer has been studied both theoretically [4] and experimentally [5], and so by measuring the G peak, the precise twist angle can be determined.

E.2. Optical Intensity Analysis. If a precise twist angle isn't needed, a range of possible angles can be determined simply by analysing the optical intensity of a graphene bilayer sample [6]. By calculating the ratio between the measured intensity of the bilayer and the intensity of the single layer of a graphene crystal, the twist angle can be classified into one of three ranges: $0^\circ - 10^\circ$, $10^\circ - 20^\circ$ and $20^\circ - 30^\circ$.

Results

With so many parameters that can affect the growth of twisted bilayer graphene, it was impossible to explore them all. The parameters that were chosen to explore were growth time length, H_2 to CH_4 ratio, temperature of the system and the purity of the copper substrate as these were determined to be most likely to have an impact on the size of the resulting bilayers.

F. Effects of growth time length. To measure the effect of the growth time length on the resulting size of graphene crystals, multiple growths were performed under the same conditions, except the sample was left in the oven under flow of CH_4 for different lengths of time. The growth was performed using a $25\mu m$ copper foil with a purity of 99.8% (Alfa Aesar 46986) as the substrate. Alfa Aesar refers to the manufacturer of the copper foil, and 46986 is its product number. All the parameters for these growths can be seen in Table 1.

To determine the crystal size for each sample, the inner and outer circle diameter for 25 crystals spaced throughout the sample was measured. The average of these measurements

	Annealing	Growth	Cooling
Time (min)	30 ± 0.01	$0 - 2.3 \pm 0.01$	5 ± 0.01
CH_4 (s.c.c.m.)	0	3 ± 0.02	0
H_2 (s.c.c.m.)	20 ± 0.02	20 ± 0.02	20 ± 0.02
Temperature ($^\circ C$)	1050 ± 0.5	1050 ± 0.5	-

Table 1. Growth parameters for the CVD system to observe the effects of varying the growth time length on the resulting average graphene crystal size and nucleation density. The growth was performed on a $25\mu m$ 99.8% purity copper foil (Alfa Aesar 46986).

was then calculated and the error on the average was taken as the standard deviation. To determine the nucleation density of each sample, the number of nucleation sites in a $400\mu m^2$ area was counted at 4 different locations. These values were then averaged and the error was taken as the standard deviation. The average inner and outer circle diameter for graphene crystals as well as the nucleation density of each sample can be seen in Figure 5.

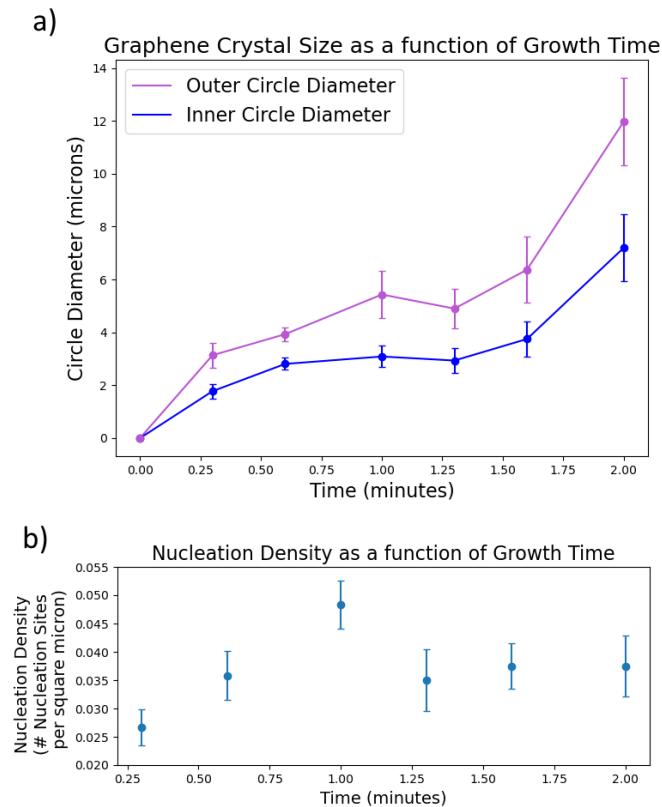


Fig. 5. The effect of varying the growth time length on a) the average inner and outer circle diameter and b) the average nucleation density of graphene crystals throughout the sample. It is worth noting that the sample with growth length time of 2.3 minutes produced a full coverage (crystals begin to meld together), and so the size and nucleation density was not measurable.

G. Effects of temperature. Similarly, to observe the effects of temperature, all parameters were kept consistent as the temperature was varied from $1020^\circ C$ to $1060^\circ C$ over multiple growths. The substrate also remained the same ($25\mu m$ 99.8% Cu foil) as in the growth time length variation. The full parameters can be seen below in Table 2

The resulting samples were analyzed using the same methods as in subsection F in order to determine the average inner

	Annealing	Growth	Cooling
Time (min)	30 ± 0.01	1.6 ± 0.01	5 ± 0.01
CH_4 (s.c.c.m.)	0	3 ± 0.02	0
H_2 (s.c.c.m.)	20 ± 0.02	20 ± 0.02	20 ± 0.02
Temperature (°C)	1020 – 1060 ± 0.5	1020 – 1060 ± 0.5	-

Table 2. Growth parameters for the CVD system to observe the effects of varying the temperature of the system on the resulting average graphene crystal size and nucleation density. The growth was performed on a 25μm 99.8% purity copper foil (Alfa Aesar 46986).

and outer circle diameter as well as the average nucleation density, which can be seen in Figure 6 .

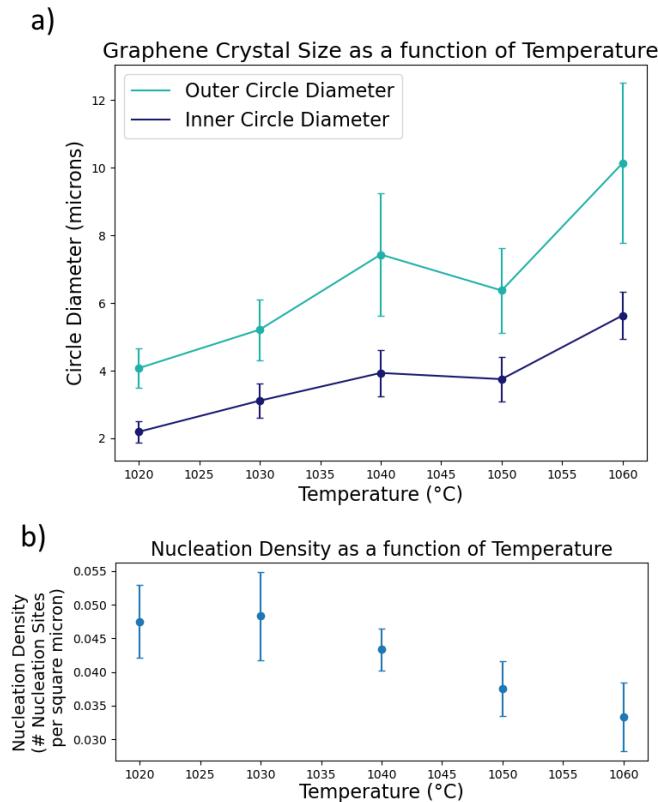


Fig. 6. The effect of varying the temperature on a) the average inner and outer circle diameter and b) the average nucleation density of graphene crystals throughout the sample.

H. Effects of different substrates. Other than the 25μm 99.8% purity copper foil (Alfa Aesar 46986) that was used for a majority of the samples grown, two other substrates were tested, both with higher purity. The first was a 25μm 99.999% purity copper foil (Alfa Aesar 010950) and the second was a 50μm 99.9999% purity copper foil (Alfa Aesar 042972). After growths comparing the 3 substrates, it was determined that the higher purity substrates did not have any significant difference in crystal size and nucleation density when growth parameters were kept constant. The higher purity substrates did however have an impact on the size of the copper grain. Copper grain is a consequence of the internal stresses of the substrate that breaks up the copper into different domains, known as copper grains. The effects of the more pure substrates on the grain size can be seen in Figure 7 .

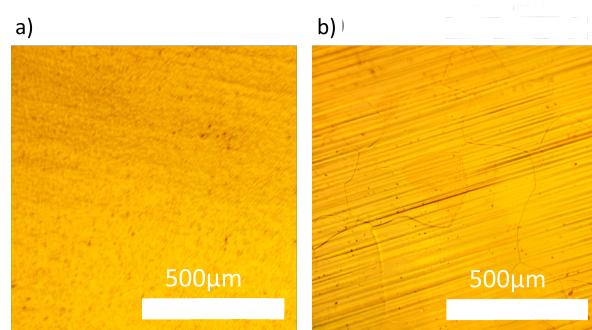


Fig. 7. Optical images to compare the grain size of 2 copper substrates. a) is full coverage of graphene on a 50μm 99.9999% purity copper foil (Alfa Aesar 042972). b) is full coverage of graphene on a 25μm 99.8% purity copper foil (Alfa Aesar 46986). On sample b) multiple copper grains can be seen, all delimited by what appears as cracks in the copper substrate. On the purer sample a) however, only 1 copper grain is visible in the image as no cracks can be seen.

I. An interesting growth. During one of the growths, the program controlling the flow of gas throughout the system malfunctioned and stopped the flow of H_2 during the annealing phase. Once the error was discovered, flow of H_2 was restored and the growth proceeded. This ended up producing a sample with a much smaller nucleation density which resulted in the formation of large graphene crystals on the copper substrate. Images of the sample can be seen in Figure 8 .

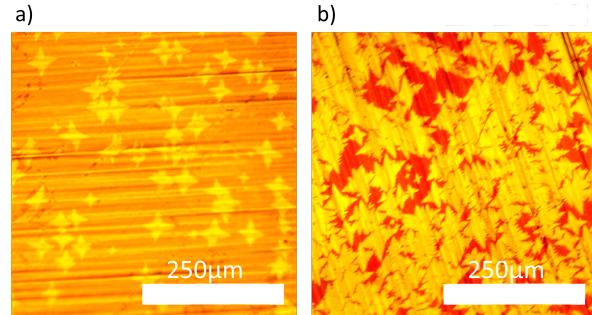


Fig. 8. Optical images of the sample resulting from a system malfunction during the annealing phase. a) is an image of a section from the under side of the sample whereas b) is an image of a section from the top of the sample.

After growing this sample, in an attempt to grow more samples with similar properties, multiple growths were run with parameters attempting to recreate what happened during the system malfunction. The parameters for one of these growths can be seen in Table 3 .

	Annealing		Growth		Cooling
Time (min)	10 ± 0.01	10 ± 0.01	25 ± 0.01	5 ± 0.01	5 ± 0.01
CH_4 (s.c.c.m.)	0	0	0	4 ± 0.02	0
H_2 (s.c.c.m.)	20 ± 0.02	0	20 ± 0.02	20 ± 0.02	20 ± 0.02
Temperature (°C)	1040 ± 0.5	1040 ± 0.5	1040 ± 0.5	1040 ± 0.5	-

Table 3. The parameters of a growth attempting to replicate the success of the malfunctioned growth. The annealing time is split into 3 sections in an attempt to replicate the section of time where flow of H_2 was blocked during the malfunction.

Unfortunately however, nothing near the results of the malfunctioned growth was ever able to be replicated.

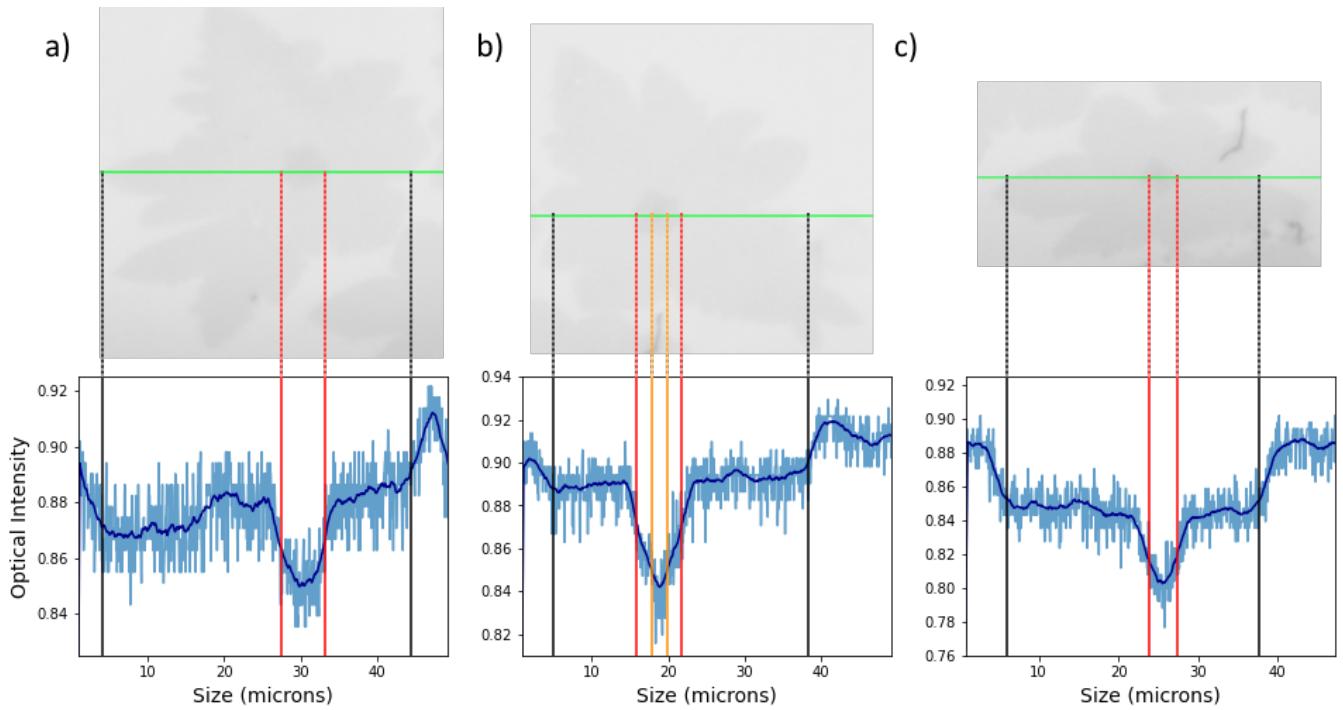


Fig. 9. Optical intensity of a slice passing through the center of 3 graphene bilayers. The slice of the image that the intensity is taken from is displayed in green over the image itself. The light blue lines on the optical intensity graphs are the raw intensity data whereas the darker blue lines are a smoothing of said data. The vertical black lines in the intensity graphs denote the edges of the first layer of the graphene crystal, whereas the vertical red lines denote the edges of the bilayer. The graphene crystal in **b**) also has vertical orange lines which denote the edges of a third layer of graphene grown under the bilayer. The graphene crystals in **a)** and **c)** however only have a bilayer of graphene.

J. Analyzing the twist angle optically. In order to measure the twist angle of some bilayers, first graphene was grown on copper following similar conditions to those outlined in subsection G. After transferring the samples to a silicon substrate, the bilayers became observable and images of 3 graphene crystals with bilayers were taken in black and white. The intensity of a slice of pixels passing through the center of each graphene crystal was measured in order to determine the ratio between the intensity on the bilayer compared to the single layer. This can be seen in Figure 9.

The intensity ratio of the bilayer over the single layer was determined to be 0.970 ± 0.010 for crystal a), 0.965 ± 0.008 for crystal b) and 0.957 ± 0.010 for crystal c). The error on each of these results is calculated by taking the standard deviation of the fluctuations in the single layer and bilayer sections.

Discussion

K. Growth time and temperature. Unlike most of the other parameters, the growth time length and temperature of the system were 2 parameters where the link between them and the resulting sample was clear. As the growth time increases, the size of the graphene crystals increases. This is as you would expect, as we are simply allowing for more time for carbon to be deposited onto the copper from the methane flowing through the system in order to enlarge the crystal size. Also as would be expected, the nucleation density does not seem to be correlated with growth time, as it remains fairly constant throughout the samples. Similarly, as we increase the temperature of the system, this also leads to an increase in the average size of the resulting graphene crystals. This is expected as the raise in temperature makes the system more

favorable for CVD, and so the crystals grow larger. Unlike the growth time however, temperature does seem to have an impact on the nucleation density of the sample, which is most likely due to the fact that a higher temperature makes the annealing process of removing impurities more effective. Therefore, as temperature increases, the nucleation density subsequently decreases.

L. Hydrogen and methane ratio. While only around a dozen samples were discussed in the results section, over 40 samples were grown using a variety of different parameters. The reason only a few of these samples were presented was because they were used to demonstrate a clear link between the variation of a parameter and the effect it has on the sample, such as temperature. The vast majority of samples however were used to explore the effects that the ratio of H_2 and CH_4 during the growth phase had on the resulting crystal size and nucleation density. Unfortunately, a clear link, or even a trend, was never able to be determined. Part of this was due to the sometimes large inconsistencies that occur between samples of the same substrate grown with the same parameters. As an example, Figure 8 from subsection I demonstrates this perfectly. The two images are of the same piece of copper grown in the same conditions, the only difference is that the section in image a) was grown on the bottom side of the substrate and the section in image b) was grown on the top of the substrate. Even under the exact same conditions, there is a vast difference in the nucleation density and dendricity between the two sections of the same sample. Due to the large differences even the same sample can display, there is need for a more thorough process of pretreatment and annealing before graphene is allowed to grow on the substrate in an attempt

to normalize the results from each group and increase the reproducibility of the experiment.

M. Twist angle analysis. Depending on the intensity ratio between the single layer and bilayer, the twist angle can be classified into a range of possible angles. Bilayer to single layer intensity ratios of $0.94 - 0.95$, $0.93 - 0.94$ and $0.95 - 0.96$ correspond to a twist angle of $0^\circ - 10^\circ$, $10^\circ - 20^\circ$ and $20^\circ - 30^\circ$ respectively [6]. From this, we can estimate that out of the bilayers presented in subsection J, all three of them have a twist angle of between 20° and 30° , though this estimation may not be correct as the error on the intensity ratios for each crystal is large when compared to the size of each range of intensity ratios corresponding to a specific range of twist angles. In order to properly determine the twist angles of these bilayers, the samples would need to be analyzed using Raman spectroscopy. Unfortunately however, due to time constraints this was not possible.

Conclusion

Twisted bilayer graphene was grown on a copper substrate in a chemical vapour deposition system. In an attempt to optimize the size of these bilayers, parameters such as the growth time length, the H_2 to CH_4 ratio, the temperature of the system and the purity of the copper substrate were all varied and the effects those variations had on the subsequent samples was observed. A correlation was able to be determined between the growth time length and the average size of the resulting graphene crystals, however the growth time length did not seem to have an effect on nucleation density. The temperature of the system also showed a correlation with the size of the resulting crystals, and as the temperature increased it was observed that the nucleation density slightly decreased. Varying the substrate used did not result in significant differences in either nucleation density or crystal size, but did produce larger copper grain when using copper foils of a higher purity. A clear link however between the ratio between H_2 to CH_4 and the resulting size and nucleation density of graphene crystals was not able to be determined. The twist angles of 3 bilayer samples were analyzed optically and were all determined to fall within the range of $20^\circ - 30^\circ$, though a more precise determination of these twist angles is possible using Raman spectroscopy.

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