LA-UR-15-24259

Approved for public release; distribution is unlimited.

Title: My Spring with Graphene

Author(s): O'Leary, Timothy Sean

Intended for: Report

Issued: 2015-06-08

**My Spring with Graphene**

Timothy O'Leary

**Abstract**

Graphene is a two-dimensional structure, one atom thick, with many uses in the world of technology. It has many useful electrical properties, is a very strong and durable material, and can be used to protect different types of substances. The world would be able to use these properties to further the strength of cars, protect metals from oxidation, increase computer speeds, use to improve superconductors, and whatever future uses that scientist invent or discover. We sought to optimize the growth and transfer of graphene. We grew graphene on copper foils by heating the foil in a furnace, and having various gases flow through a tube, where the copper foil was placed. We varied some of the concentrations of gases, along with having different times for heating the copper foil, different times for graphene growth, or a combination of the two. The focus of our experiment was to specifically grow monolayer single crystal graphene, which means that we do not want multiplayers of graphene, and do not want multiple crystals growing to form a bigger crystal. Our goal was to grow large single crystals from the growth experiment. We used a few different types of transfer methods that ranged from: using heat and pressure to press the graphene on different materials, using a polymer to cover the graphene with a method to destroy the copper, but leave the graphene and polymer intact, and using a type of heat tape with a combination of varying pressures to transfer the graphene, and then destroy the copper foil. To discover if we grew graphene we used different techniques involving lasers and microscopes to take different types of measurements. Discovering the best way of growing and transferring graphene will help with managing the cost of the future uses of graphene.

**Introduction**

Graphene is a two dimensional structure that has many uses in different fields. Two types of graphene exist, monolayer and multilayer graphene. Multilayer graphene is Graphene between two and nine layers. There are many purposes and prospects in various fields. It has a high carrier mobility [1], protection against oxidation [2], and also uses in the medical industry [3]. Graphene was first discovered in 2003 at the University of Manchester [4], by the scotch tape method. Later graphene has been grown through various methods, such as the use of Chemical Vapor Deposition (CVD), exfoliation, Nanotube slicing, along with many other methods. Depending on the purpose of the graphene, determines the type of graphene that is desired.

**Experiments**

There were two main projects that I worked on. First, I focused on growing graphene on Cu substrates, and to transfer the graphene to varying substrates for different projects. This involved growing, transferring, and characterizing graphene on different types of substrates. The main goal was to grow large area single crystal monolayer graphene. The second project involved optimizing the different transfer procedures. This involved finding the best strength of etchant to dissolve the Cu, how much PMMA was required to cover the Cu, and how many times the PMMA needed to be washed after being in the etchant.

Experiment 1:

Growth:

The foil was cut from a sheets of Cu stored in desiccators. We placed the Cu foil in acetic acid for a set period of time. We then transferred the Cu foil in a portable desiccator to and from the experiment.

We grew graphene by Chemical Vapor Deposition (CVD). CVD is a gas cylinder system that pumps a controlled amount of gas through a furnace. Copper (Cu) foil and Cu foam were used in the experiments.

When using the Cu foil, we annealed the sample for varying times ranging from two to ten hours. Along with different anneal times, we also used different deposit times for $CH_4$. The most reliable way to grow single crystal is to anneal the Cu sample in temperatures exceeding 1000°C, with annealing times greater than two hours [3]. We knew if we had single crystal monolayer graphene layer by the characterization methods that will be discussed later.

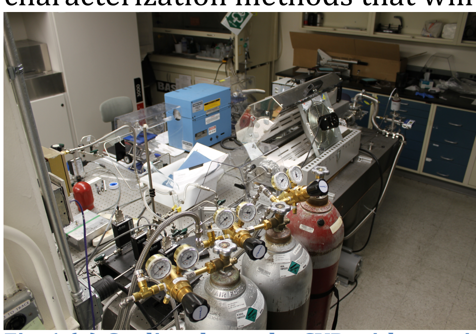

**Fig. 1 (a) Cooling down the CVD with a rapid cool down. Fig. 2 Au foam in CVD before annealing.**

Transferring

We used two different types of transfer methods. We used a thermal release tape pressure method, and a PMMA etchant method. When transferring graphene on the Cu, we first cut the foil into smaller pieces. Then put the sample piece on a spin coater with a drop of PMMA.

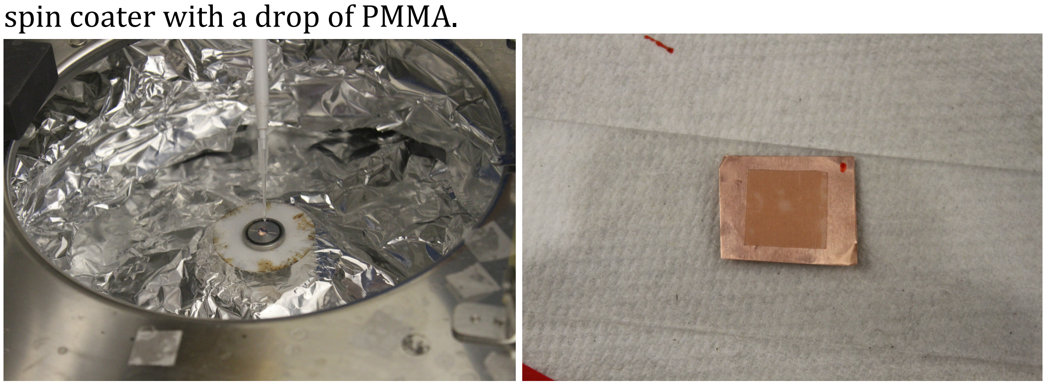

**Figure 2 (a) Left, Spin coating the PMMA. (b) Right, TRT on Cu.**

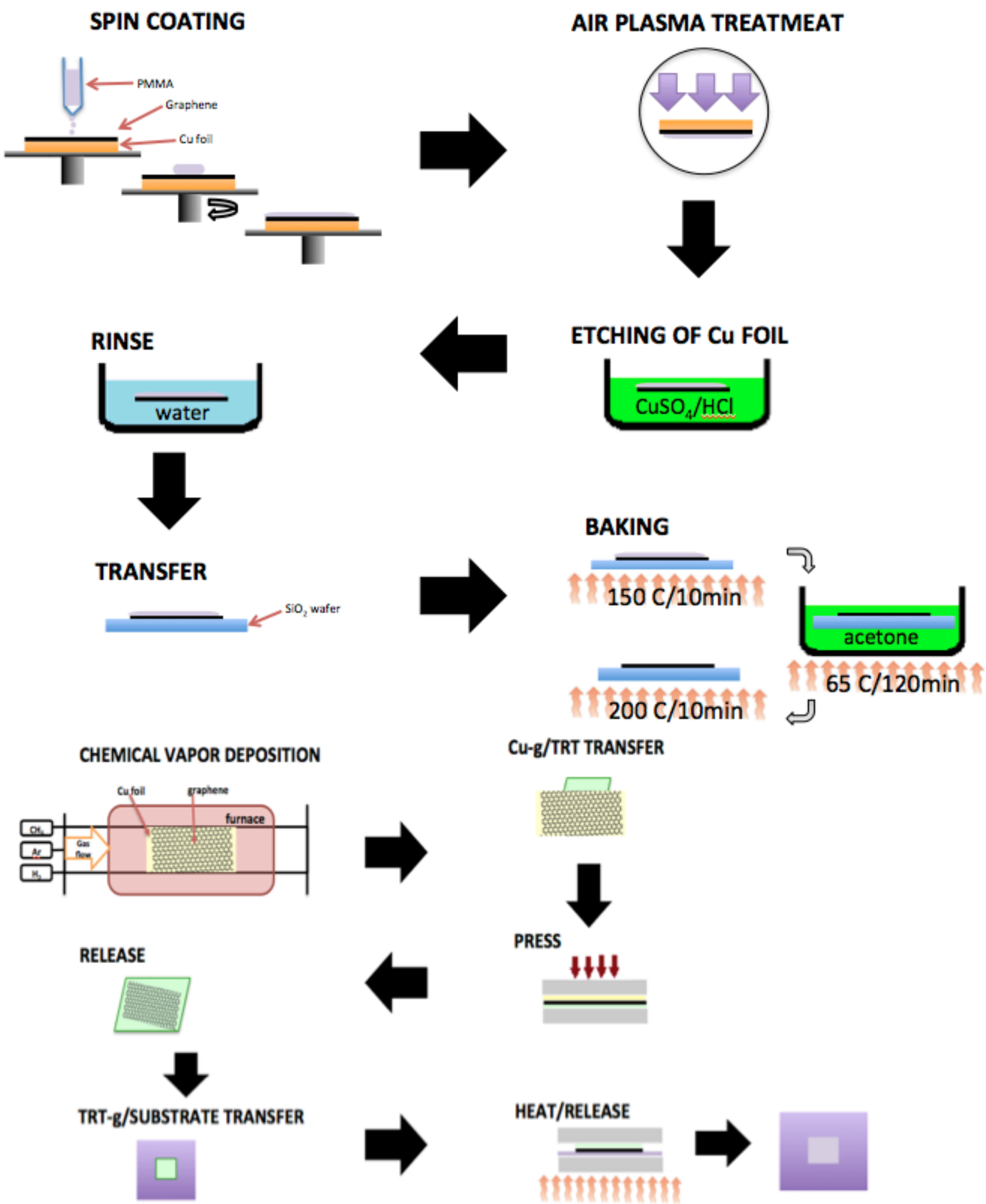


**Figure 3 (a) Top, wet PMMA transfer. (b) Bottom, Dry TRT transfer.**

Characterization

We characterized the samples through Raman spectroscopy, scanning electron microscope, optical microscope, and UV-Vis spectroscopy. Through Raman we look for specific peaks D, G, and 2D peaks. The D peak tells us about defects, the G peak is about ratio between the G and 2D peaks gives the information about the number of layers. When there is a stronger 2D peak than a G peak, then that suggests monolayer graphene. While a larger G, or similar peak intensity signifies multilayer graphene.

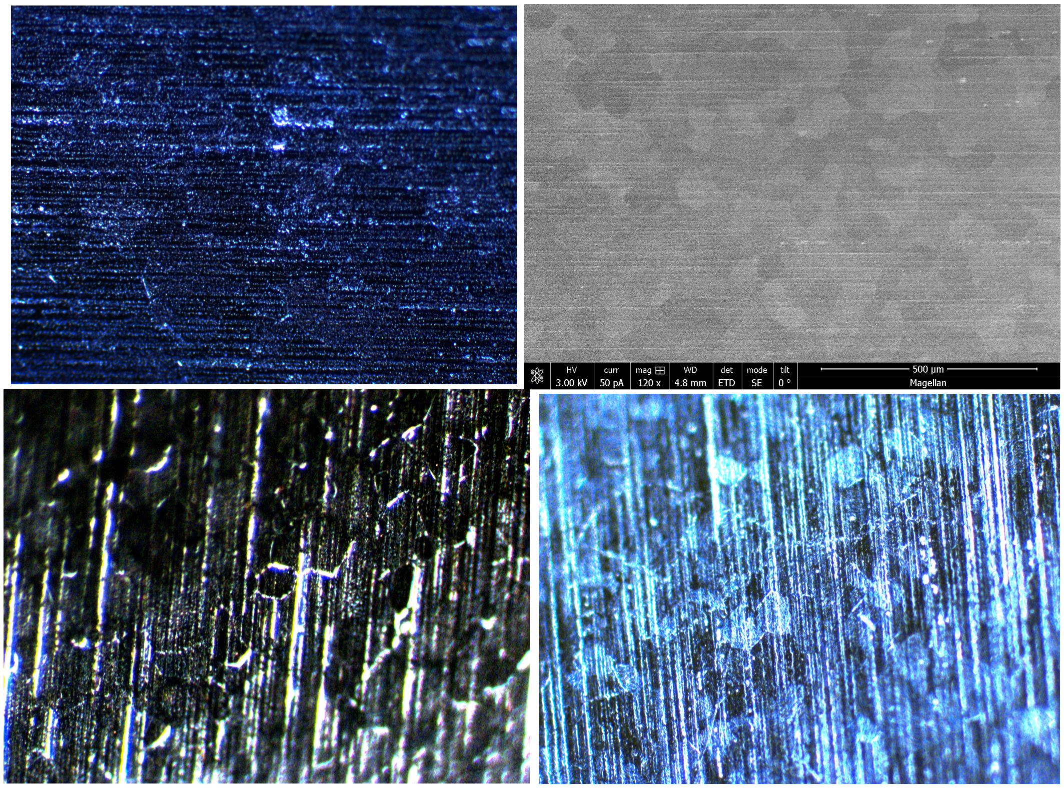


**Figure 3 (a) Top left control Cu annealed with no CH4. (b) Top right SEM of Cu after CVD. (c) Bottom left Optical Microscope (OM) of the grain boundaries. (d) Bottom right another OM image of grain boundaries.**

We used SEM and OM to look for grain boundaries between the graphene flakes. When using the UV-Vis we measured transmittance and absorption. After using this method, we discovered that transmittance was more reliable for our experiments.

Experiment 2:

For optimization, we sought to find the amount of PMMA required where the PMMA would not go on the opposite side of the Cu foil, but still completely cover the sample. We found that the initial amount of PMMA often went to the opposing side of the sample, which hindered the etchant process. We tried varying amounts of PMMA, and found that it often went to the other side. After trying many amounts in various regions on the sample, we were introduced to a type of blue tape that would prevent the PMMA from spinning onto the other side.

When transferring the substrates, it was when necessary to wash the acid off the PMMA in deionized water (DI water). We initially washed the PMMA twelve times. We sought to know how many washes were necessary for the acid to be cleaned from the polymer, and no longer change the PH in the DI water. After using PH test strips, we found that only six washes were needed, instead of the twelve.

## Conclusion

The future of graphene in the world is pivotal to the progress in many industries. Consistently growing the type of graphene and finding a quick and reliable method of transfer is vital to that progress. Through characterization we grew monolayer graphene, but are still trying to grow large area single crystal monolayer graphene.

## References


1. Wei Wu, Qingkai Yu, Peng Peng, Zhijong Liu, Jiming Bao, and Shin-Shem Pei, "Control of thickness uniformity and grain size in graphene for transparent conductive electrodes," Nanotechnology Vol.23(3), 2012 Jan 27
2. R. Silva (private communication)
3. E. Dervishi (private communication)
4. C.N.R. Rao, Urmimala Maitra, and H.S.S. Ramakrishna Matte; Synthesis, Characterization, and Selected Properties of Graphene,