Fabrication and Characterization of Graphene Micro-structures for Plasmonic Applications

By: Zeyan Xu

School of Physics, Georgia Institute of Technology

Advisor: Dr. Zhigang Jiang

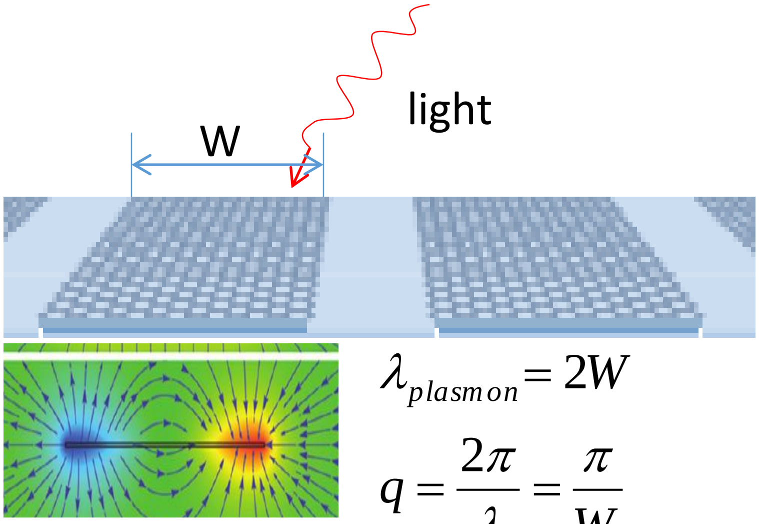
Date of Submission: 7/30/2014

Abstract

The goal of the project is to investigate the plasmon cross-talk effect in graphene nano-structures using magneto infrared spectroscopy. We first grew CVD graphene on copper substrate on a 1cm × 1cm scale. Infrared transmission measurements were done on silicon substrates with different doping levels, and also on SiC, to determine the best suited substrate for magneto IR experiments. We then performed trial experiments to find the recipe of photolithography on both Si and SiC, and decided to use SiC. After we found a promising recipe which gave us desired patterns, we transferred graphene on it and performed photolithography with the same recipe. Reactive ion etching is then used to remove any unwanted graphene and define the micro-array patterns that we desire. Once we obtained the graphene nano-structure sample, we brought it over to the National High Magnetic Field Laboratory at Tallahassee, FL for IR testing. However, due to the accident of equipment failure and time constraint of the program, we were unable to obtain a comprehensible result of the test. Nevertheless, according to theory we should observe that the geometric correction depends solely on the sample dimension and is independent of the polarization of the incident IR light. Once this is confirmed, it should enable us to gain a better understanding of magneto-plasmons in quasi-neutral epitaxial graphene nano-structures, which is crucial for designing graphene-based plasmonic devices.

Introduction

Recently, a new material called graphene has attracted a great deal of attention. Made of a single layer of carbon atoms arranged in honeycomb lattice, graphene has extraordinary mechanical, chemical and physical properties. The most astonishing among them is the linear low energy band, which means electrons in graphene obey Dirac equations and are massless Dirac fermions. This unique electronic property makes graphene a playground for many novel physics phenomenon which were previously inaccessible. Specifically, a great deal of research efforts has been put into the field of graphene plasmonics. Plasmons are the collective behavior of electrons in response of external electromagnetic waves (See Fig. 1). Thanks to the unique electronic properties of graphene, graphene plasmon bears much higher light confinement ratio and has much longer life time comparing to traditional Ag/Si plasmon (table 1). Also, since the Fermi level in graphene can be easily tuned using a back gate or some other types of doping, graphene plasmon enjoys more tunability.



$$\lambda_{plasmon} = 2W$$

$$q = \frac{2\pi}{\lambda} = \frac{\pi}{W}$$

Figure 1. When light is shine on the graphene ribbons, the electrons will move in accordance with the external electrical field. This creates an effectively changing dipole, and is called the plasmon.

In past experiments, it was observed that the energy of the upper-hybrid mode (UHM) absorption of graphene nano-ribbons (GNR) is polarization dependent. That is, when applying infrared (IR) light to the sample, the absorption in x-axis differs greatly from that of y-axis. The IR absorption is directly related to the plasmon energy. It is interesting to see whether the same effect is true in other geometries of the graphene patterns. To answer this question, we fabricated graphene arrays of disks with different sizes and spacing, and performed infrared magneto spectroscopy measurements. Although the device is fabricated using graphene grown from chemical vapor deposition method, the results are expected to provide insights to epitaxial graphene on SiC, which holds great potential in mass production of graphene plasmonics devices.

	Light confinement $\lambda_{light}/\lambda_{plasmon}$	**Propagation loss-length**	**Tunability**
Ag/Si	**~20**	**~0.1 $\lambda_{plasmon}$**	**Limited**
Graphene	**~200**	**~10 $\lambda_{plasmon}$**	

Table 1. Some properties of graphene plasmon comparing with traditional Ag/Si plasmon.

Methodology

The first step towards the project is to obtain graphene samples. There are multiple ways to make graphene including: CVD (chemical vapor deposition), mechanical exfoliation, epitaxial graphene growing on SiC substrate, precipitation from metals. Each of them has their own advantages and disadvantages. However, it is unfortunate that we still have not found a way to grow it on a large scale. The method that my research group uses is via CVD growth. I have developed a comprehensive user guide of the equipment and it can be found in Appendix. We grew multiple pieces of graphene and kept the good ones to later transfer onto silicon carbide.

The way we used to examine the purity of graphene is by doing Raman spectroscopy. Raman spectroscopy operates under the theory of Raman scattering. Different chemical bonds will absorb and reflect unique wavelength of light due to the structure of the bonds. When we run this test, we are expected to see C=C bond peak (2D peak) as well as a G-peak.

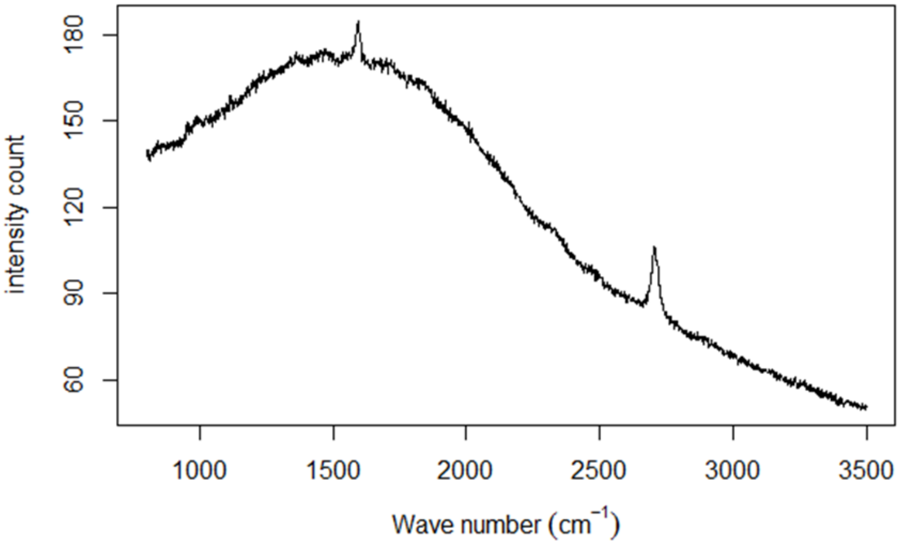


Figure 1: Raman spectroscopy of graphene sample

This happens because when light hits the edge of the sample it bounces back and forth and performs differently as other photons. As figure 1 shows, the peak with the wave number value of about 1600 is the D-peak, and the peak at 2700 is the 2D peak. It is ideal that the 2D peak has an area underneath double the area under the G-peak. And this is exactly what we observed in the figure above.

After making enough graphene samples, we went on and test the best suited substrate for IR testing. We tested different doping of Si and SiC wafer, and we concluded that SiC works the best with IR light.

The next step was photolithography. The general idea was that we obtain a mask with desired patterns and we “print” it onto the sample. This was traditionally been done with e-beam lithography, but this time we use photolithography because it’s faster and more promising. To do this, we mainly use three equipment in the cleanroom: the spin coater, the mask aligner, and the therm-plasma RIE. The spin coater is used to spread out photoresist evenly on the wafer. The recipe we used was 6000 rpm for 1 minute, with another 10 seconds for ramp up and ramp down each. Afterwards, we put it on the oven and baked it at 115^{o} for another minute. The mask aligner is used to align the mask and the wafer in order to do the lithography process. In my case, I used 2 micrometer of hexagonal pattern, and after multiple experiments, we determined to use 80 as doping parameter (the exposure time is also dependent on the intensity of the machine.)

We then immediately develop the pattern using MF. We developed in MF for 5 seconds at first, then we look under the microscope to see if we get the pattern. If not, we do for 2 or 3 seconds more and see again. Usually 8 seconds will be enough for development. We then wash the sample with DI water, and dry with nitrogen gun.

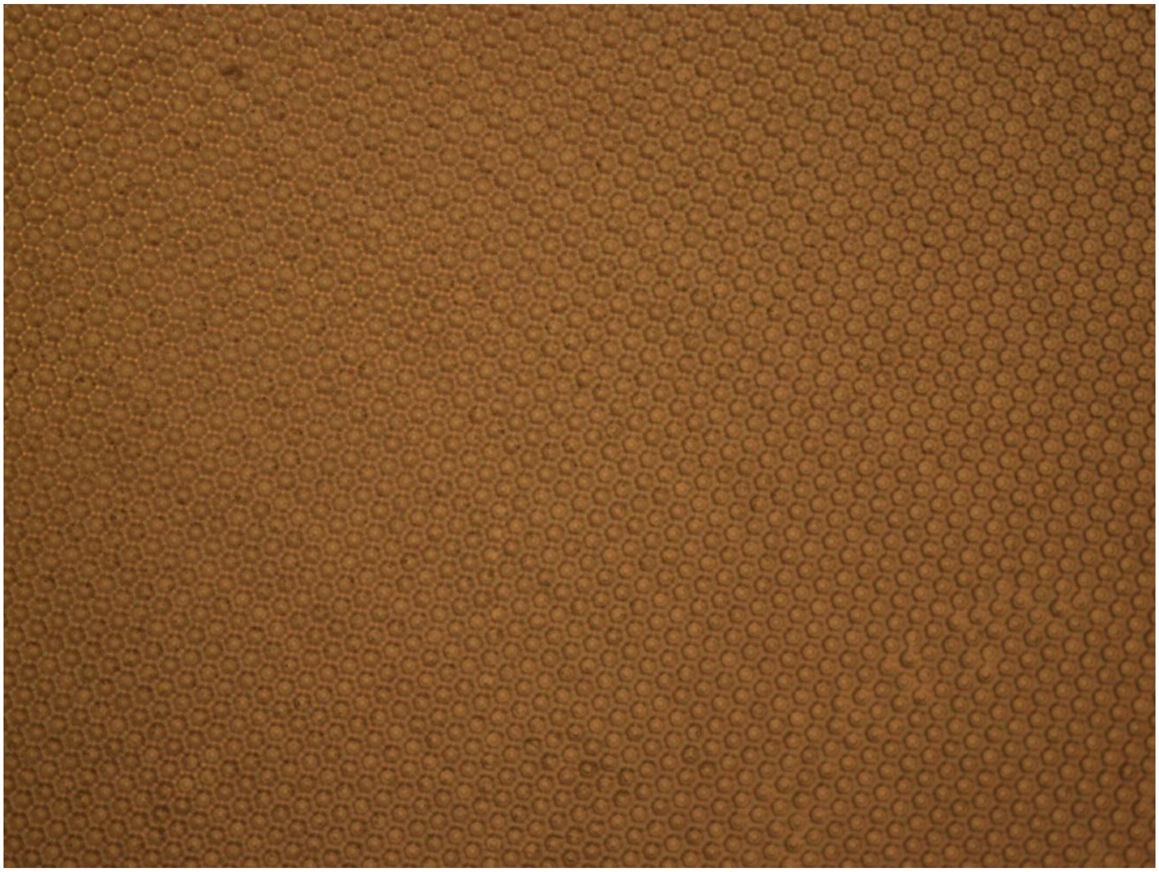


Figure 2: hexagonal pattern obtained by photolithography

Figure 2 is the result that we get from the microscope. Although there are a few defects, the pattern isn't perfect everywhere, it would be a great substrate for graphene since the piece of graphene is so small that it won't cover all area of the substrate above. Also, we are able to recognize the hexagonal pattern instead of circles.

Lastly, we use therm-plasma RIE to etch away all the unwanted graphene remaining parts.

After obtaining the substrate, we then transfer our graphene sample onto the substrate. We brought this sample over to the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida to test, along with 3 other samples of different materials fabricated from Sandia Laboratories. The main equipment that we used at NHMFL was the SCM3. There, we used liquid helium to cool the system down to 4K and applied varies magnetic field to test plasmon energy at different strength of magnetic field.

To set up the system, first, we put the sample inside the probe which was later sent into the detector, as shown in figure 3:

Figure 3: sliding probe down into the fridge

The probe itself was almost 4 meters long, and we had to slide it an inch or two at a time, since there is very high pressure as we go down. At the same time we had to watch closely at the pressure reading inside. The slightest mistake could lead to a leak and will make the system impure and not make a good vacuum inside. (When we were finished with the experiment, we had to do the same thing but in reverse).

After the whole probe was down in the fridge, we measure the resistance of the sample and therefore determine the temperature down there. If the resistance is low, that means the temperature in there is relatively high, and vice versa. After we know that there wasn't anything wrong with the system internally, we adjust the stand for IR source so that it can align with the probe orthogonally.

An image of the final setup of the experiment is shown in Figure 4:

Figure 4: SCM3 at NHMFL

The box on top left is the IR source. The IR light was sent through the tube on the top onto a mirror in the cube in the top right corner. In the cube there are two mirrors that are orthogonally positioned, once the IR light travelled to the mirror, it was then reflected downwards by the other mirror, and that went directly onto our sample. The vertical tube below the mirror goes down about 3-4 more meters, and samples are stored at the end of the tube and surrounded by liquid helium.

We run tests with a program written with LabVIEW. With that, we can easily change the strength of the magnetic field, scan the samples, and maintain all the data, which is shown in figure 5.

Results

After we run the test multiple times with a different magnetic field strength each time, we get a plot shown as figure 5 below:

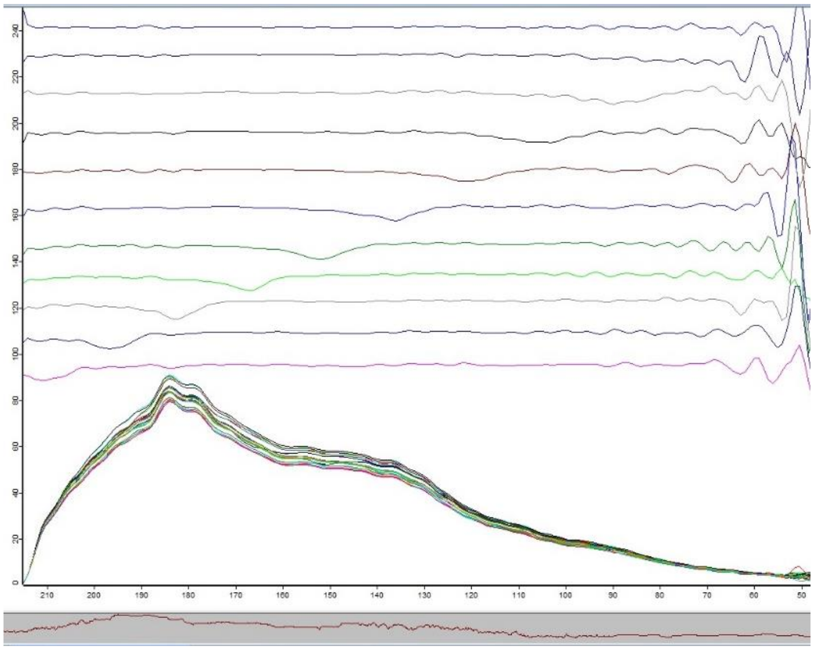


Figure 5: magneto infrared spectroscopy measurements

The raw data is plotted at the lower half of the graph. The y-axis is the transmittance of the IR light, and the x-axis is the wavenumber of the incident light. It is difficult to see the difference between various magnetic fields. Instead, we plot the transmittance normalized to the zero field data. This is shown on the upper half of the graph. We can clearly see there is a dip in transmittance, moving from the left end of the x-axis at low field, to the right end of the x-axis at high field. The noise at the very right end is due to the low transmittance in the wavenumber range, and that part of data should be discarded. This normalized transmittance curve at different magnetic field is the main result of our measurement. It is evident that the dip in the curve deserves more discussion.

Discussion

The transmittance dip is due to the cyclotron resonance (CR) of the electrons. It is known in electrodynamics that when put in a magnetic field, the electrons are no longer free and will detour their paths due to Lorentz force. When the magnetic field is strong enough, the electron energy band will collapse into Landau Levels, and the electrons will be effectively moving in a circle with quantized energies. At these energies, the IR light will resonant with the Landau Level, causing the cyclotron resonance and hence the dip in the transmittance spectrum. If the CR is the only effect present, then theoretical calculation shows that the dip should have a perfect Lorentzian shape. However, a careful scrutiny to our data shows that this is not the case. One possibility of the deviation is that the plasmon motion is coupled to the Landau Levels, forming a so called upper hybrid mode. Further analysis of the data is needed to decouple the components of the transmittance dip, and this analysis shall reveal useful information about the plasmon dispersion of the sample.

Conclusion

In conclusion, I have been highly active in Dr. Jiang’s research group and participated in all aspects that I discussed above. I learned to grow graphene, to use cleanroom equipment and finally, to operate the SCM3 at HMFL. I learned that for whatever I do, the procedures were to be performed repeatedly before I make a successful sample or to collect some useful data. It takes great patience and determination. I also learned to work my daily schedule around the experiments, sometimes it requires researchers to make personal sacrifices to ensure that the experiment goes smoothly. I realized that equipment failure is inevitable in any experiments. The machines are not 100% reliable and researchers should always be able to judge the situation critically and to react to any malfunction of the machines as soon as possible.

This experiment would be more effective if the equipment at the NHMFL did not malfunction which wasted 4 out of 6 testing days. Also, due to the physical setting of the equipment, as figure 4 shows, the IR source stands on an unstable stand, whenever there were any movements around the area it creates noise which was partially responsible for the noise to the right of figure 5. If we were able to have a clean observation in contrast to figure 5, we could possibly have observed more valuable information that could lead to a more promising result.

Appendix

CVD Graphene Operation Manual

- Cut 2 pieces of 1cm x 1cm copper pieces. Try to keep the surface of copper smooth and unbend.
- Use tweezers to put 2 copper pieces on a piece of semicircular quartz container. Put the container on top of another one and slide both of them to the center of the quartz tube. Be careful sliding them using the metal sticks, make sure not to touch copper sample nor flip the containers. (See figure 6)
- Connect pump to the quartz tube. Make sure not to hurt the end of the quartz tube since it is fragile and breaks can result in an imperfect vacuum inside the tube. After the pump is stabilized, further secure it with 3 screws, screw in from the pump end with a screw driver, screw it in until the ends of the screws are showing on the other end.

- Supply liquid nitrogen to the container connected to the pump. If using the compressed gas container, open the gate, the first few minutes there will only be gas coming out, and then liquid will follow. Put the tube at the opening of the container and let liquid flow in. don’t put a large portion of tube inside because that part can freeze and break inside. Keep supplying until it almost fills the container; if using the metal container to supply liquid nitrogen, put a funnel at the opening and pour in liquid nitrogen. When done, block the opening with a piece of cloth (or whatever).

Figure 6: Furnace of CVD graphene

- Open the switch at the pump by the quartz tube; open the pump switch (on the wall); slowly rotate and open the valve by the container of liquid nitrogen. There will be noise made by the pump. Turn on the top box which shows the pressure inside the tube. (It usually starts on the magnitude of a few Torr and decrease to 10-1 Torr; in the next step it will increases again to about 4 Torr). When the noise gets smaller, open the valve more, until the valve is opened all the way; close up the top part of the thermal instrument.

- Turn on the middle box on the side which controls the flow of H2/Ar gas. When the pressure reading is about 10-1 Torr, use a screw to set the flow of the left most channel to 20 sccm (or desired value). Turn on the switch above that to allow gas flow.

Turn on the bottom box which controls the temperature. Long press the left most button, use the other 2 buttons to get to CLC mode, press the left button again to confirm. This will set the desired temperature to 1000oC. Give it about 35 minutes to get to the desired temperature.

- When the temperature stabilize at 1000oC, open the 2nd switch on the top of the middle box to introduce CH4 flow. We don’t have to make any modifications to the flow flux since it is already set at 1 sccm. Open the valve on the left (second from the left) the let in the CH4. Let it flow for however long you need, usually 3~4 minutes. Turn of the CH4 switch and close the valve.
- Turn down temperature since the CVD process is over. Long press the left button on the bottom box, use the other 2 buttons to get to reset mode, press the left button again to confirm. This will set desired temperature back to room temperature which is 25oC.
- When the system is cooled down to 800oC, we can open the top of the thermal instrument to catalyze the cooling down. When it is about 200oC, we can shut down all the equipment which we have been using: start with tighten the valve by the liquid nitrogen container; then the pump switch on the wall; finally, close the switch close to the quartz tube.
- Tune the flow rate of H2/Ar back to 200 sccm, because it makes it easier for the air pressure inside the tube to go back to atmospheric pressure. Watch the pressure reading on the meter, when the pressure inside is 1atm or slightly greater, turn off the switch on channel 1 for H2/Ar. Disconnect the pump. Use metal stick to pull out the copper container from the tube. The copper now should be coated with grapheme on both sides.

Take caution:

- Use gloves when in lab at all times, to prevent oil from our hands from contaminating samples, and also to protect us from hazards.

- Watch carefully at the pressure meter on the last step, failure to do so will cause exploding of the tube.
- Be careful when pouring in liquid nitrogen, human body can be burnt from the low temperature of liquid nitrogen.
- Make sure that there is always liquid nitrogen in the container at all times of the operation.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. DMR 0820382. The author would like to thank the MRSEC REU program and Dr. Leyla Conrad for providing this opportunity to experience doing research at such state-of-art facility. The author is also thankful for the faculty advisor Dr. Zhigang Jiang and the graduate students in the group especially Xunchi Chen and Yuxuan Jiang for their technical guidance and support.

References

[1] Poumirol, Jean-Marie, Wenlong Yu, X. Chen, Claire Berger, W. A. De Heer, M. L. Smith, T. Ohta et al. "Magnetoplasmons in Quasineutral Epitaxial Graphene Nanoribbons." *Physical Review Letters* 110, no. 24 (2013): 246803.
[2] H.G. Yan, X. Li, B. Chandra, G. Tulevski, Y. Wu, M.Freitag, W. Zhu, P. Avouris, and F. Xia, Nat. Nanotechnol.7, 330 (2012).
[3] I. Crassee, M. Orlita, M. Potemski, A.L. Walter, M.Ostler, Th. Seyller, I. Gaponenko, J. Chen, and A.B.Kuzmenko,Nano Lett.12, 2470 (2012).
[4] J.N. Chen et al.,Nature (London) 487, 77 (2012).
[5] Z. Fei et al.,Nature (London) 487, 82 (2012).
[6] A.N. Grigorenko, M. Polini, and K.S. Novoselov,Nat.Photonics 6, 749 (2012).
[7] M. Jablan, H. Buljan, and M. Soljacˇic,Phys. Rev. B 80,245435 (2009).

[8] F.H.L. Koppens, D.E. Chang, and F.J.G. de Abajo,Nano Lett.11, 3370 (2011).

[9] A. Vakil and N. Engheta,Science 332, 1291 (2011).

[10] M. Sprinkle, M. Ruan, Y. Hu, J. Hankinson, M. Rubio-Roy, B. Zhang, X. Wu, C. Berger, and W.A. de Heer, Nat.Nanotechnol.5, 727 (2010)

[11] Pirkle, A., J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace. "The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO2." Applied Physics Letters 99, no. 12 (2011): 122108.

[12] Colombo, Luigi, Robert M. Wallace, and Rodney S. Ruoff. "Graphene growth and device integration." Proceedings of the IEEE 101, no. 7 (2013): 1536-1556.