Graphene Refinement using High Temperature Anneals

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Abstract

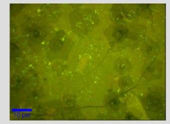
Graphene's intrinsic properties of being a good conductor as well as having efficient optical transmission make it a potentially useful material in photovoltaic cells as a transparent conducting electrode. One problem preventing graphene from being fully utilized stems from contaminates created and deposited during the transfer process of multiple graphene layers. After synthesis, TRT (Thermal Release Tape) is applied to the graphene supported on the copper growth substrate. TRT utilizes a unique formulation of adhesive that is temperature sensitive so that it will release when heated. Upon removing the growth substrate in a chemical bath, the TRT is used to transfer the graphene to substrates of interest. Unfortunately, the TRT also transfers small quantities of adhesive along with the graphene, thus creating a contaminant-laden area. To improve the properties of the transferred graphene films, the contaminants must be removed. In this study we investigate the ability for high temperature anneals to remove the residual adhesive. It is found that higher temperature anneals, while increasing the defect intensity within the graphene, also appear to increase the consistency of multiple layer application. This analysis is achieved by comparing Raman Spectroscopic maps of the FWHM of the G' peak (2680 cm^{-1}) associated with the graphene layer. This consistency correlates with lower resistance values that were achieved using a four-point probe measurement. Although high temperature anneals increase the D/G peak ratio in the Raman Spectra, the resistance values still decrease. Overall, this study gives the first indication that higher temperature anneals may be capable of removing contaminants without sacrificing graphene conductivity

Summary

- Higher temperature anneals increase D/G ratio but still allow samples to achieve low resistance
- G' broadening shows how poor additional layers transferred onto the sample as evident from the maps of the Raman Spectra
- Anneals in the range of 350°C to 450°C show the most potential for removing containments without destroying the graphene which will allow for a cleaner transfer of additional layers
- 4 layer graphene samples can achieve resistance values as low as 204-288.2 Ω/Sq. The best results achieved by a four layer sample was the 350°C anneal group which had a resistance of 204 Ω/Sq.
- Absorption data shows partial transfer between second and third layer graphene sheets.
- The best 4 layer samples were annealed to 350°C and 450°C and had resistance values of 204 Ω/Sq. and 207 Ω/Sq. respectively
- UV-Vis absorption tests show inconsistent jumps in transmission rates. This evidence, along with Raman Mapping Spectra show a large amount of defects created by the transfer process.

What is Graphene?

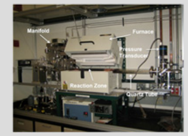
- Basis for sp^2 carbon nanostructures
- Forms in a planar honeycomb lattice of hexagonal rings
- Can support relativistic properties of conduction electrons in a single graphene layer
- Strong fit for transparent conducting electrodes for use in photovoltaic systems

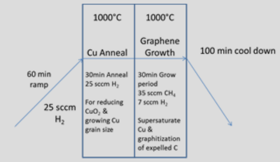


This is a picture of a 2-Layer graphene sample. The bright flecks are the containments from the TRT.

Graphene Anneal Process

Annealing the transferred graphene removes containments introduced into the sample by the TRT. This is beneficial when applying additional layers to the samples. For this study, anneals were accomplished using a programmable furnace to run ramp rate, anneal time, and temperature. The samples were placed on quartz plates and inserted into the system. Ramp rates were set to 2° C/min and anneal times lasted for 8 hours. The environment was held between 1.5-1.8 Torr with a H_2 flow rate of 25 sccm.



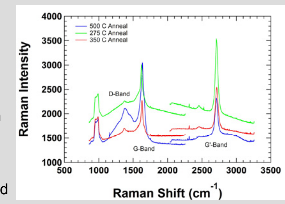


Graphene Synthesis

- Growth substrates consisted of 25 µm thick copper cut into 1.5"x2" sheets
- After the system evacuated, the furnace ramped from room temperature to 1000° C in 60 minutes
- Once the temperature was reached, the system would anneal the copper for 30 minutes to reduce CuO_2 and increase Cu grain size to help promote graphene growth
- During the growth period, the graphene becomes supersaturated with carbon from the methane gas
- Once the saturation limit is reached, carbon would begin to pool on the surface of the copper substrates forming the graphene
- Temperature is lowered at a rate of 10° C/min to prevent the substrate from cracking the graphene layer
- Samples are removed from the system and TRT is applied to allow transfer to other substrates

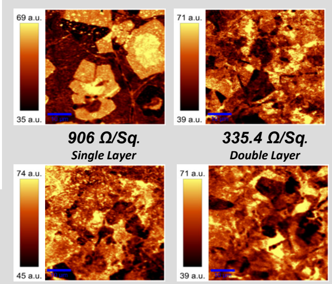
Using specific Raman Spectroscopy signatures to identify properties of Graphene material

- There are three peaks of interest when using Raman Spectroscopy to look at graphene[1]
  1. G-Band (1585 cm^{-1}) – Raman signature of sp^2 carbon systems.
  2. G'-Band (2500-2800 cm^{-1}) – Raman signature of sp^2 carbon as well as an identifier for the amount of graphene layers.
  3. D-Band(1250-1400 cm^{-1}) – Raman signature used to quantify the amount of disorder in a carbon system.
- Higher temperature anneals create a larger ratio between D and G peaks
- Using a Lorentzian curve fitted to the G' region, we are able to see how well additional layers transferred to the sample, as inferred from the FWHM
  - Single layer graphene has a FWHM value of 30-35 cm^{-1}
  - Maps plot FWHM as a function of intensity
  - Sections get brighter as width of the FWHM increases



Above: Raman spectra of single layer graphene annealed to various temperatures. As you can see, D/G increases as temperature increases.
Right: Raman Maps using the a Lorentzian curve fitted to the FWHM of the G' region. The brighter the area, the thicker the graphene

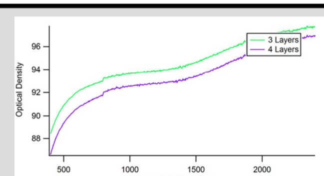
Maps of the Raman Spectra
525° C Anneal



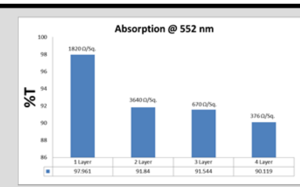
906 Ω/Sq. *Single Layer* — *335.4 Ω/Sq.* *Double Layer* — *316 Ω/Sq.* *Triple Layer* — *232 Ω/Sq.* *Quadruple Layer*

Absorption

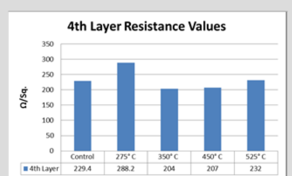
- Graphene has a relatively flat absorption curve making it a useful material for transparent electrodes
- A single layer of graphene will absorb ~2.3% of light in the visible spectrum
- Uneven jumps between layer application give evidence to defects and contaminations in the graphene
- The four layer sample with a resistance of 376 Ω/Sq. had a transmission rate of 90.119%
- Annealing the material had no effect on transmission rates



Note the relatively flat absorption curve, this is an advantage graphene has over metal oxides (TCP's). A wider range of wavelengths can be used in any system that uses transparent conducting electrodes, making it more efficient.

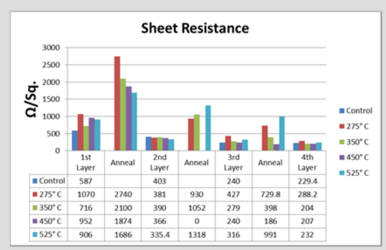


	1 Layer	2 Layer	3 Layer	4 Layer
	97.961	91.84	91.544	90.119



	Control	275° C	350° C	450° C	525° C
4th Layer	229.4	288.2	204	207	232

Final sheet resistance values for graphene samples with four layers



	1st Layer	Anneal	2nd Layer	Anneal	3rd Layer	Anneal	4th Layer
Control	587		403		240		229.4
275° C	1070	2740	381	930	427	729.8	288.2
350° C	716	2100	390	1052	279	398	204
450° C	952	1874	366	0	240	186	207
525° C	906	1686	335.4	1318	316	991	232

4pt Probe Measurements

- The measurement of sheet resistance with the four point probe used the following equation:

$$\rho_s = \frac{V}{I} * C$$

  C is the Correction factor which is dependent on sample size
  For this study, a correction factor of 4.53 was used
- A current of 4.53mA is put through the sample to cancel the correction
- Using Ohm's Law, resistance of the graphene can be measured

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1. Jorio, Ado, Gene Dresselhaus, and Riichiro Saito. Raman Spectroscopy in Graphene Related Systems. Weinheim, Bergstr.: Wiley-VCH, 2011. Print.

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