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 contaminants 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 anneal 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.

What is Graphene?

- Basis for sp² 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

Graphene Synthesis

Annealing the transferred graphene removes containments introduced into the sample by the TRT. This is beneficial when applied to additional layers in the samples. For this study, anneals were accomplished using a programmable furnace to run ramp, 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 last for 8 hours. The environment was held between 1.5-1.8 Torr with a H₂ flow rate of 25 sccm.

Graphene Anneal Process

• Growth substrates consisted of 25 µm thick copper cut into 1.5x2” 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 CuO2 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 layer.
• Anneal temperatures are lowered at a rate of 10° C/min to prevent the substrate from cracking the graphene layer.
• Contaminants 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. G-Band (1585 cm⁻¹) – Raman signature of sp² carbon systems.
  2. G’-Band (2500-2800 cm⁻¹) – Raman signature of sp² 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.

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.

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 containments 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.

4pt Probe Measurements

- The measurement of sheet resistance with the four point probe used the following equation:
  \[ R = \frac{4}{\pi \rho L} \]  
  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.