Adhesion of Microspheres to Graphene coated substrates

Radhika Patil

Indian Institute of Technology Gandhinagar

Guide: Prof. Nicholas Boechler

Department of Mechanical Engineering

University of Washington

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Contents

Figures

Acknowledgement

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Introduction

Meta-materials are materials engineered to have properties that have not yet been found in nature. These materials are fabricated from the materials found naturally, but using various fabrication techniques. These artificially fabricated materials exhibit novel and/or enhanced properties, for example conductivity, elasticity, adhesion, etc.

Experiments are conducted in lab to analyze behaviors of systems with microspheres on them, especially resonance frequencies. For some experiments the test sample in the lab is an Aluminum coated glass slide which has microspheres mounted on it. The adhesion of these microspheres to the substrate (i.e. Aluminum) is modeled as a spring mass system. Waves are generated in this system by creating laser interference fringes on the sample. Thus changing the adhesion would mean changing the spring constant of the system.

Figure 1: Microspheres on Aluminum coated glass slide

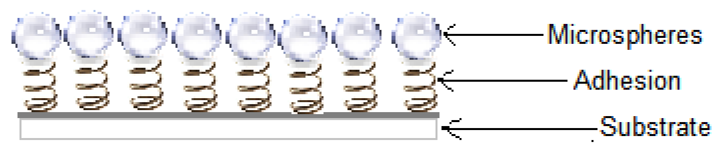


Figure 2: Modeling of adhesion as spring

One of the ways to change this adhesion of microspheres to substrate was thought to be introducing a thin layer of another material in between the microspheres and substrate.

Graphene is an allotrope of Carbon. It is a two dimensional array of carbon atoms arranged in a hexagonal lattice structure where each carbon atom is a vertex of the hexagon.

Graphene is a very interesting material as it exhibits many extraordinary properties. Graphene can be monolayer or multilayer.

If graphene could be introduced in between the microspheres and aluminum, it might be able to change the adhesion of the microspheres to aluminum.

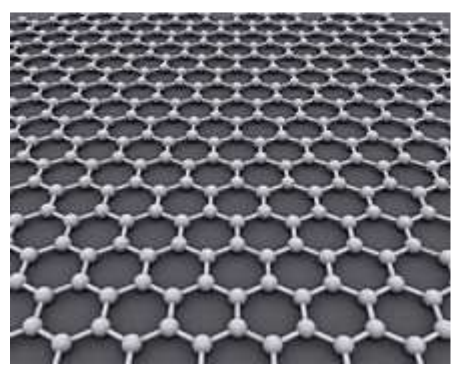


Figure 3: Structure of Graphene

Source: Wikipedia.org

Graphene Transfer Techniques

Graphene was first produced using a piece of graphite and a scotch tape. Now, Graphene is usually produced by Chemical Vapor Deposition (CVD) process. CVD Graphene is generally grown on metals like copper or nickel. These metals can be either foils or just a layer of the metal on SiO_2/Si wafer.

There are several methods to transfer CVD Graphene from the metal to required substrate, mainly mechanical or chemical. Some of the common ones are-

1) Tape transfer
2) PMMA transfer
3) PDMS transfer

The Tape transfer method is mainly a mechanical process with very little chemical use. It basically involves sticking the tape to Graphene and then transferring this Graphene to the required substrate by pasting the tape onto it.

The PMMA and PDMS methods usually involve the material to be spin coated on the Graphene. After removing the metal from the Graphene and placing it on the desired substrate, the PMMA or PDMS is dissolved in suitable solvents so that Graphene remains behind on the substrate.

The tape transfer is easier and cleaner, but it is highly dependent on the pressure applied and so in turn is vulnerable to human errors and defects due to its mechanical nature. But the Graphene Transfer Tape was already available in the lab. So it is easier and economical to use it.

The Graphene used in this project is CVD Graphene bought from a manufacturer, Graphene Supermarket.

1) Graphene on Nickel/SiO_2/Si Wafer (Multilayer)
2) Graphene on Copper Foil (Monolayer)

Figure 5: Graphene on copper foil

Source: Graphene Supermarket

Figure 4: Graphene on Nickel/SiO2/Si Wafer

Source: Graphene Supermarket

Cleaning the Aluminum coated glass slide and making them hydrophilic

Before transferring Graphene or mounting microspheres, the substrate needs to be cleaned and made hydrophilic. The Aluminum coated glass slide is cleaned and made hydrophilic using following procedure-

1) Clean using distilled water
2) Soak in isopropanol for 15 minutes
3) Soak in acetone for 15 minutes
4) Soak in Hydrogen peroxide at 70-80^{o}C for 20 minutes
5) Plasma treat the slide *(optional)*

Making the substrate hydrophilic facilitates the mounting of microspheres and transfer of graphene.

Same procedure works for making a simple microscopic glass slide hydrophilic.

Graphene Transfer Tape

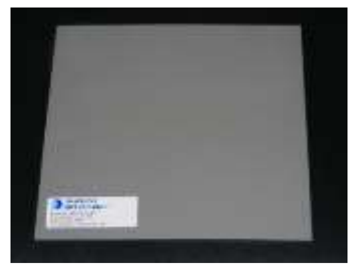


Figure 6: Thermal Release Graphene Transfer Tape

The Graphene Supermarket provides a product called 'Graphene Transfer Tape'. This is a thermal release tape, that is, it loses its adhesion properties when it is heated. The procedure for using this tape to transfer graphene is given on the Graphene Transfer Guide.

The procedure was modified slightly as the desired results were not obtained.The procedure used was as follows.

1) Cut out a 1''x1'' piece of the thermal release tape.
2) Peel off the transparent cover and place the sticky side on the graphene coated side of the sample.
3) Press hard for the tape to stick to the graphene.
4) Soak the sample in water if its wafer for 5 minutes, or not if it's a foil. Peel off the metal if it's a wafer.
5) Place the tape in 100ml freshly prepared 1M $FeCl_3$ at 40^{o}C (To etch away the base metal, leading to only graphene being left on the tape) for 20-30 minutes.
6) Clean the tape with Distilled water.
7) Place the tape with graphene on the substrate to transfer on with graphene facing down. Press hard and put on some weight for 20 minutes. Put the substrate and tape in preheated oven at 100^{o}C for 10 minutes.
8) The tape automatically peels off and turns opaque whitish in color.
9) Graphene is transferred and seen as a darker layer on the substrate.

Figure 7: Heated Ferric Chloride

Using Aluminum Coated Glass slide as substrate and [Graphene on Ni/SiO2/Si Substrate] from Graphen Supermarket

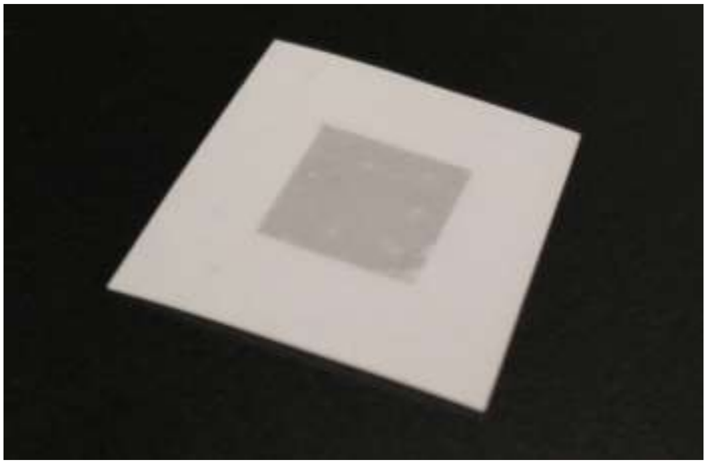


Figure 8: Graphene on the Thermal Release Tape

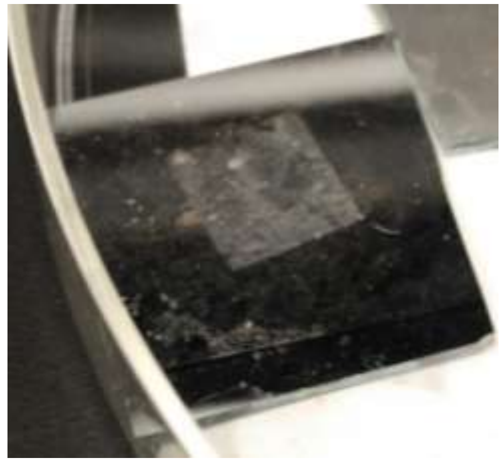


Figure 9: Graphene on the Aluminum coated glass slide

The Tape Transfer Method is used to Transfer Graphene from $Ni/SiO_2/Si$ wafer to Aluminum coated glass slide. It is observed-

The tape does transfer graphene to aluminum, but the aluminum coating incurs holes, that is, regions where the aluminum coating is removed from the glass slide. This does not change with longer heating so that the tape is automatically detached from the substrate and does not need to peel off. The 'holes' are present only in the region with graphene present. There are no holes outside the graphene coated region.

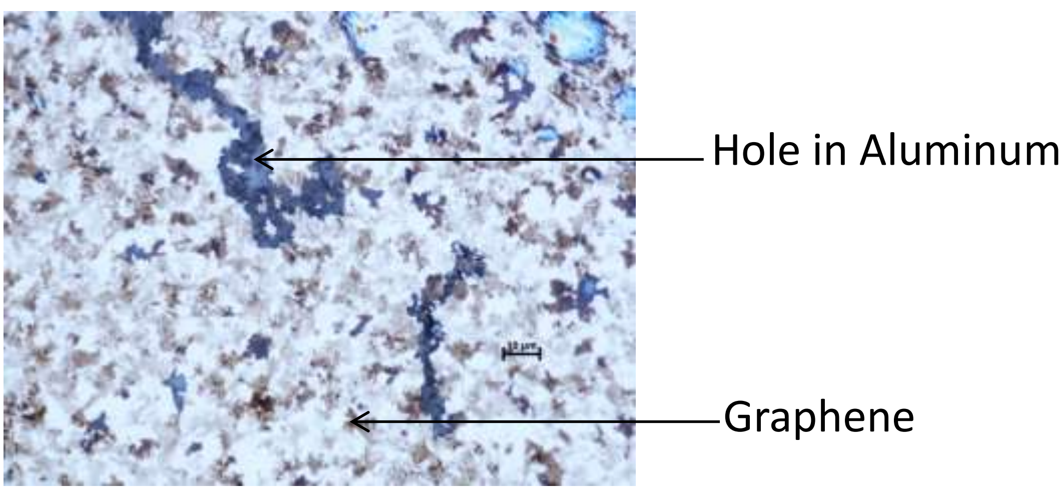


Figure 10: Aluminum coated glass slide with Multilayer Graphene - Reflection mode

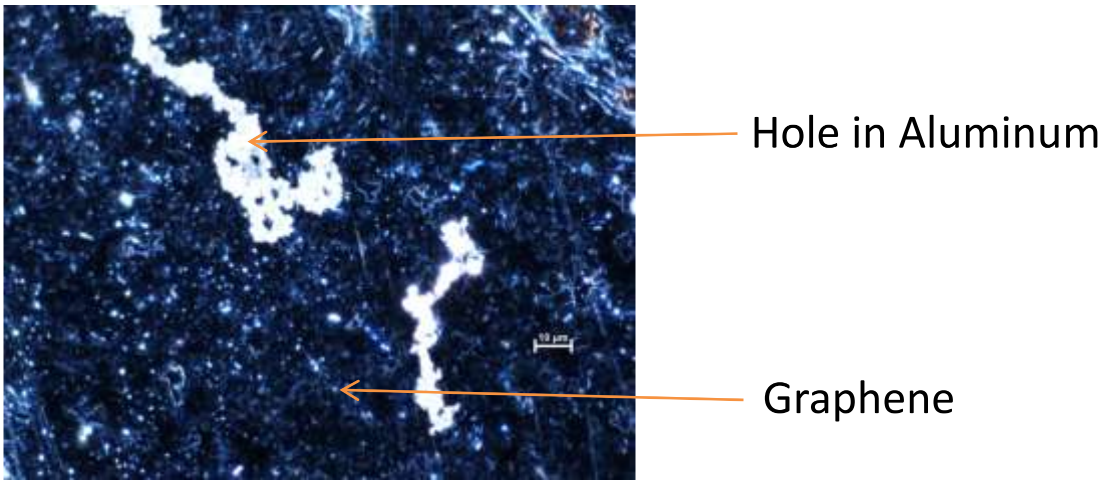


Figure 11: Aluminum coated glass slide with Multilayer Graphene - Transmission mode (lights on)

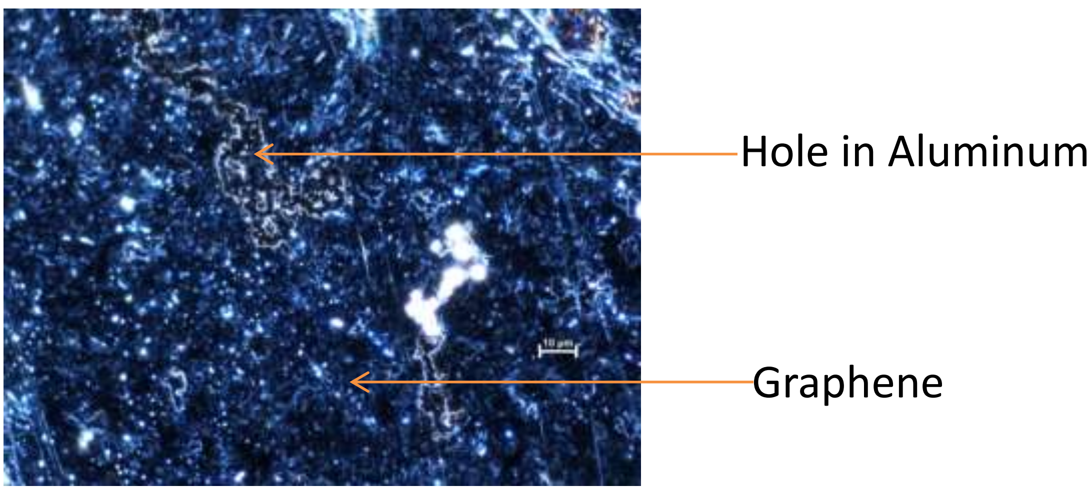


Figure 12: Aluminum coated glass slide with Multilayer Graphene - Transmission mode (lights off)

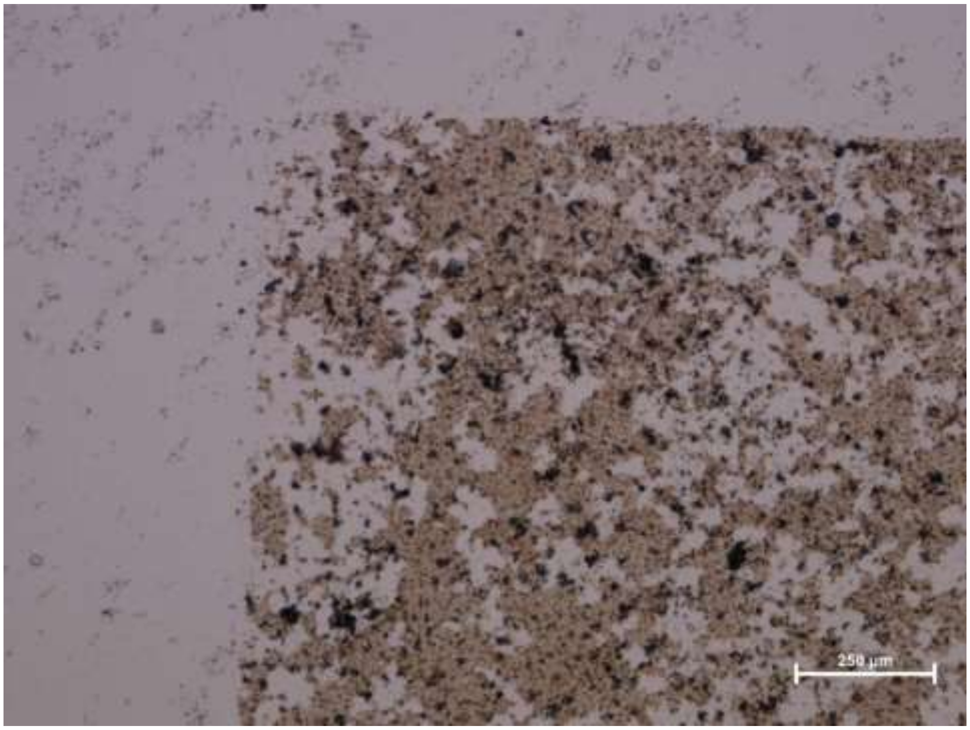


Figure 13: Multilayer Graphene on Aluminum coated glass slide (Graphene – Aluminum interface)

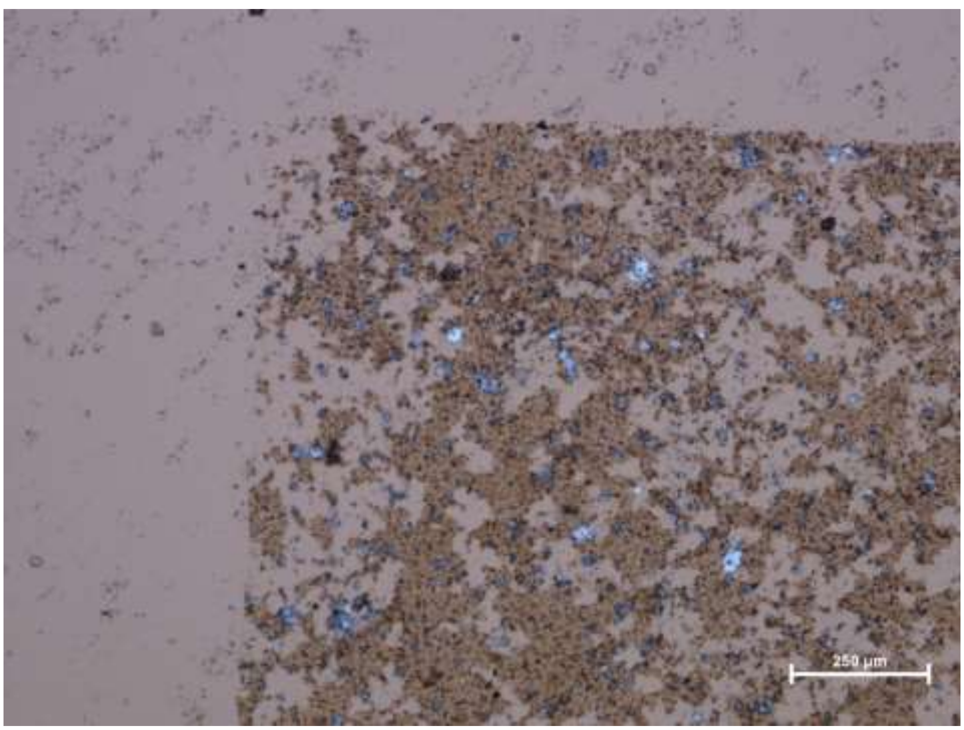


Figure 14: Multilayer Graphene on Aluminum coated Glass slide (holes in Al visible as white dots)

Mounting Microspheres on substrate using the Vogel Technique

This technique involves floating microspheres on water allowing them to form two dimensional lattices and scooping them using our substrate to transfer the lattice to the substrate. The glass slide used to drop microspheres into the water is also made hydrophilic before using.

Polystyrene microspheres are used.

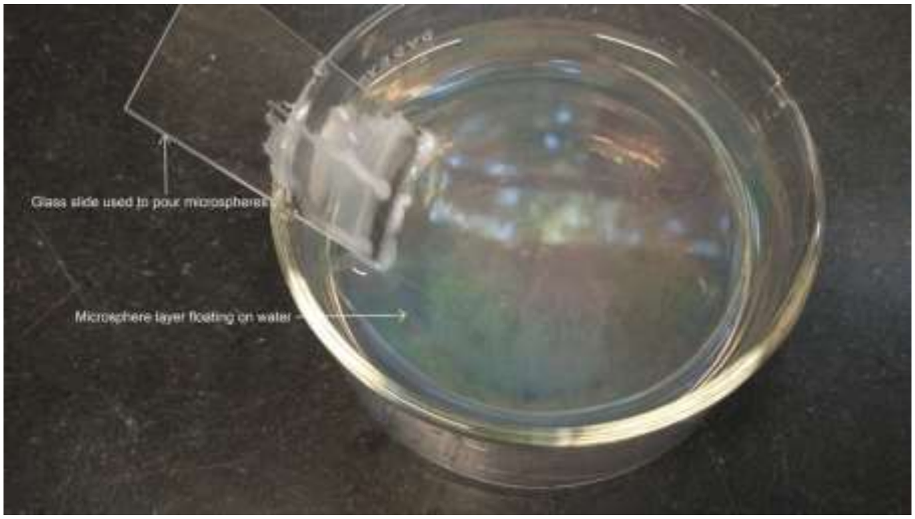


Figure 15: Vogel technique for mounting microspheres

In spite of the holes in the Aluminum coating, microspheres were mounted on the sample using the Vogel technique. Monolayers of microspheres with close pack structure are required. The better the packing, the more colorful the sample looks.

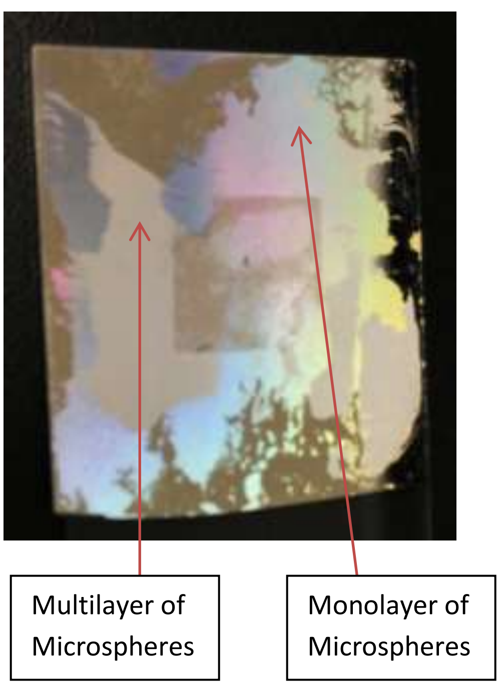


Figure 16: Microspheres on Sample with Graphene

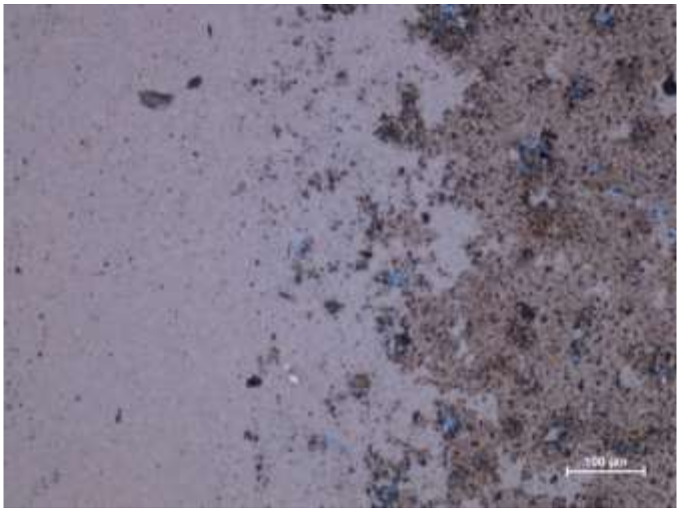


Figure 17: Graphene on Al coated glass slide with 1 micron Polystyrene spheres (Graphene –Aluminum Interface)

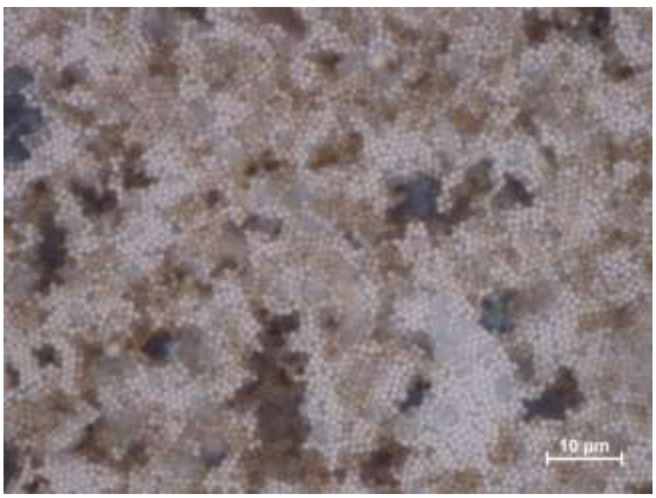


Figure 18: Graphenen on Al coated glass slide wiht 1 micron Polystyrene spheres (Graphene region)

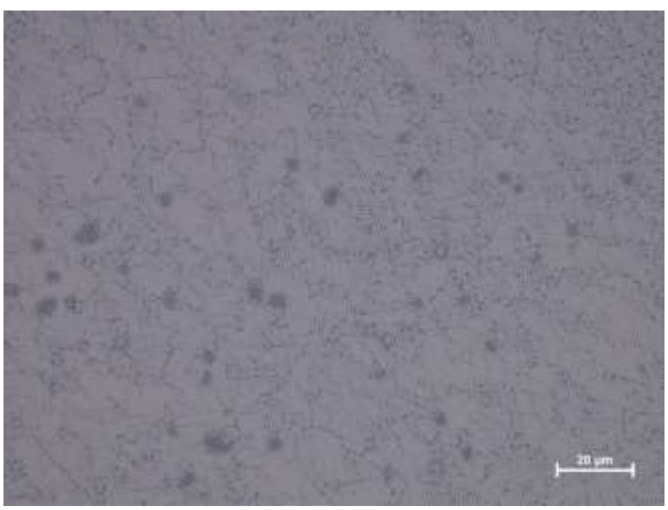


Figure 19: Microspheres on Aluminum coated glass slide

Transient Grating (TG) Tests on the Sample.

The sample with graphene and microspheres on Aluminum coated glass slide was tested under transient Grating test. This involves a high power laser beam split using a transient grating apparatus of particular width of grating. Two laser beams from this grating are directed to form interference fringe pattern on the sample. Because of these interference fringes, the area with high laser intensity heats up and expands while the darker region does not. This induces waves in the sample. The waves involve longitudinal waves, Rayliegh waves, and microsphere resonance.

The tests on sample with graphene yielded following results.

'Front' implies tests performed with microspheres facing the lasers

'Back' implies tests performed with glass facing the laser and aluminum or graphene or microspheres facing to the other side of glass

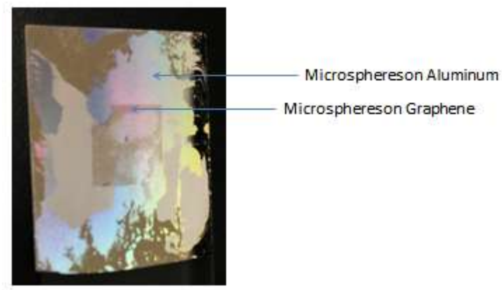


Figure 20: Testing regions on the sample

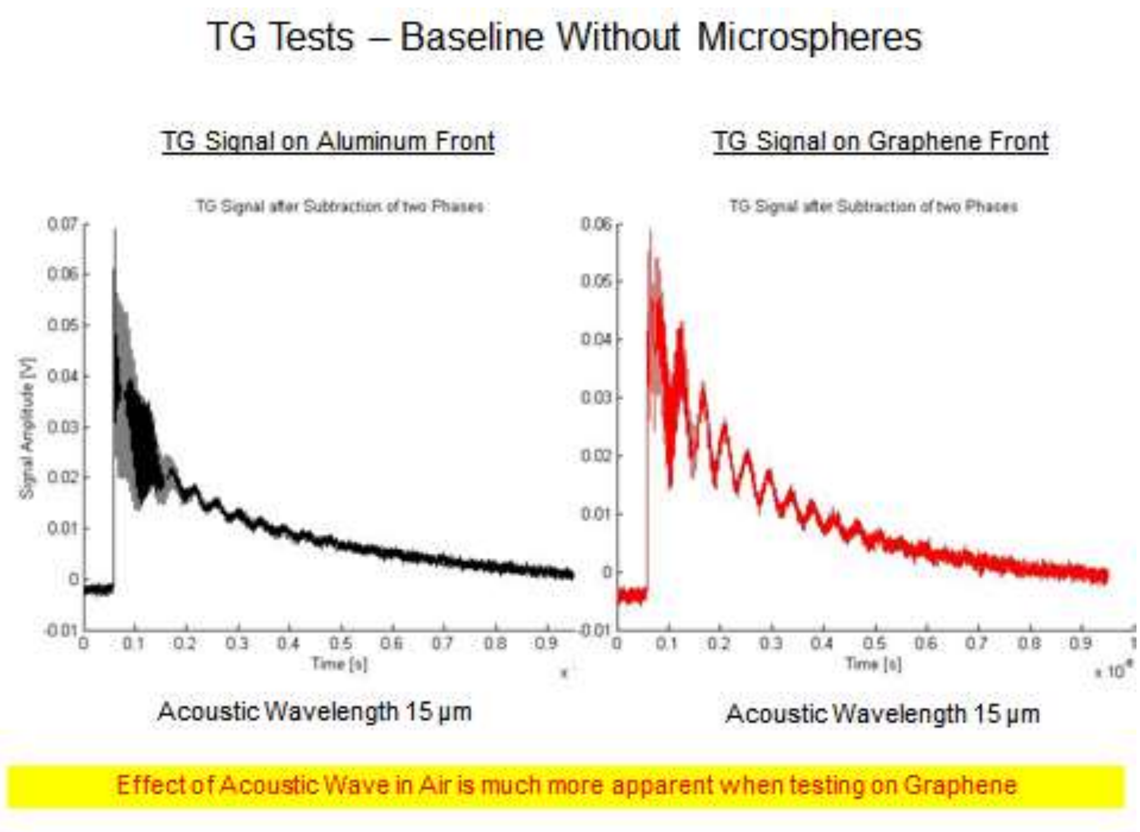


Figure 21: TG test signal on bare Aluminum and Graphene on Aluminum (Front)

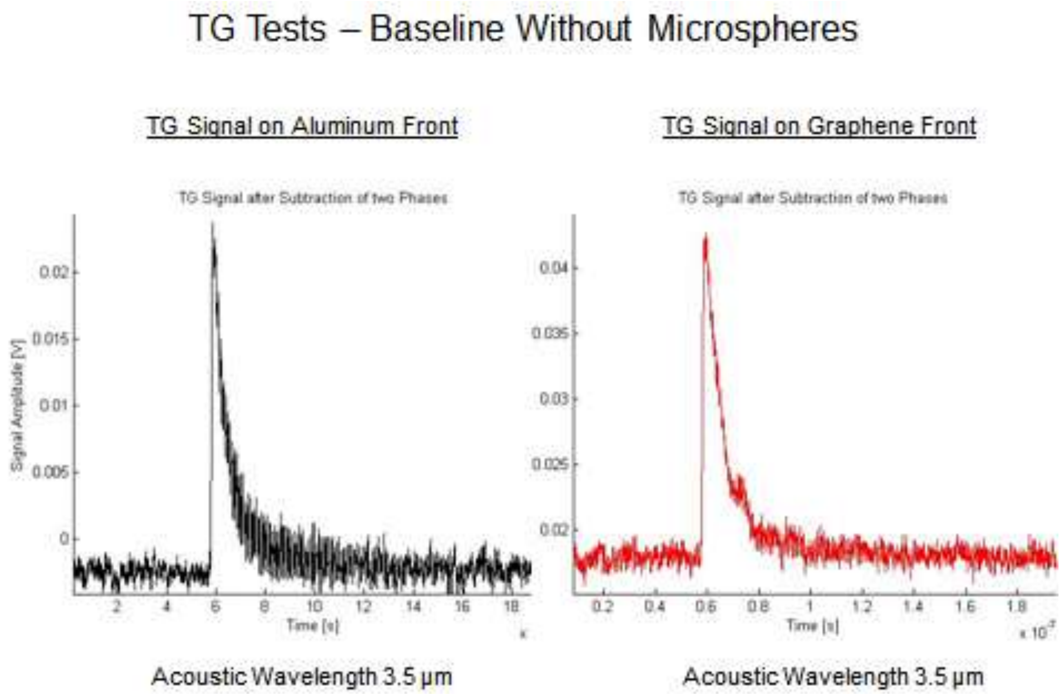


Figure 22: TG test signals on bare aluminum and Graphene on Aluminum (Front)

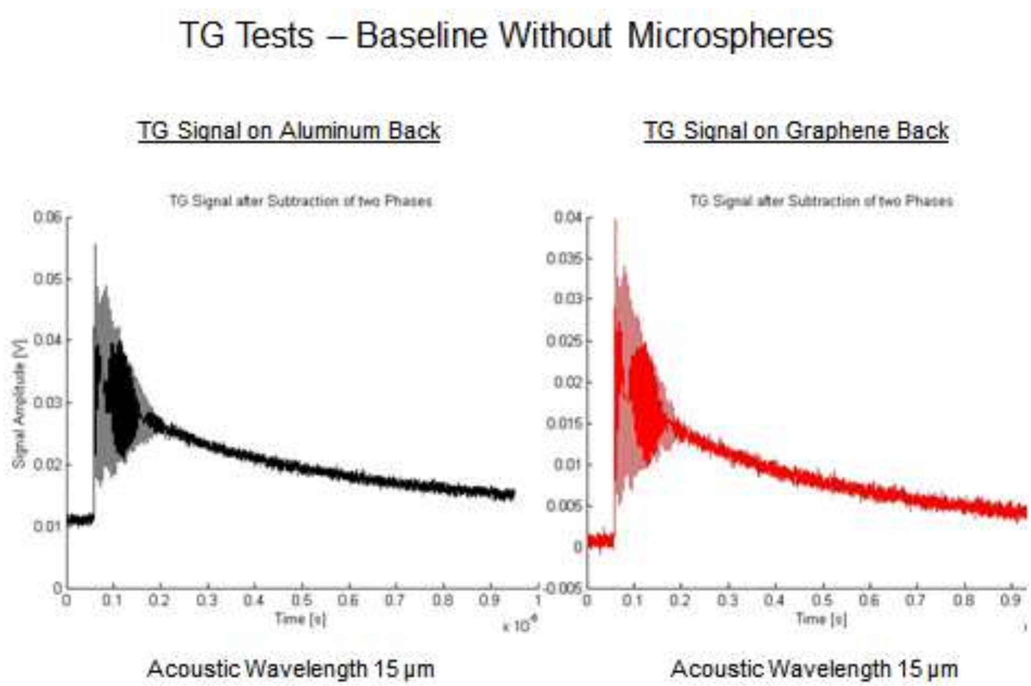


Figure 23: TG test signals on bare Aluminum and Graphene on Aluminum (Back)

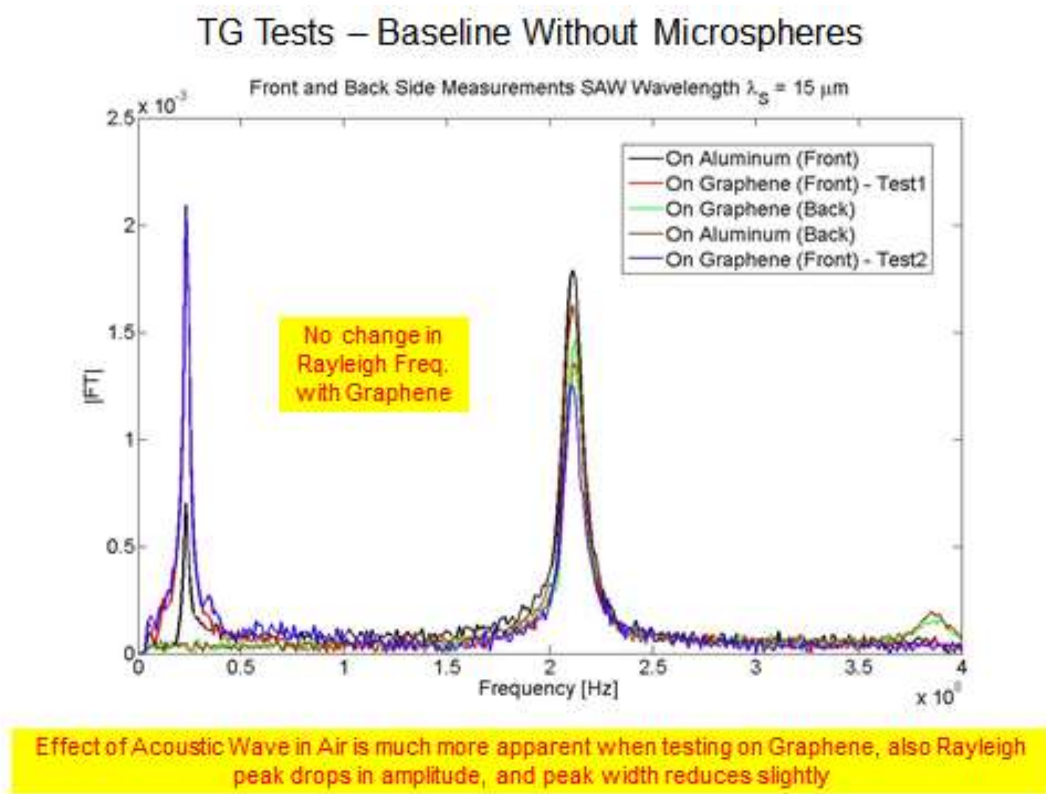


Figure 24: Fourier Transform of TG test signals

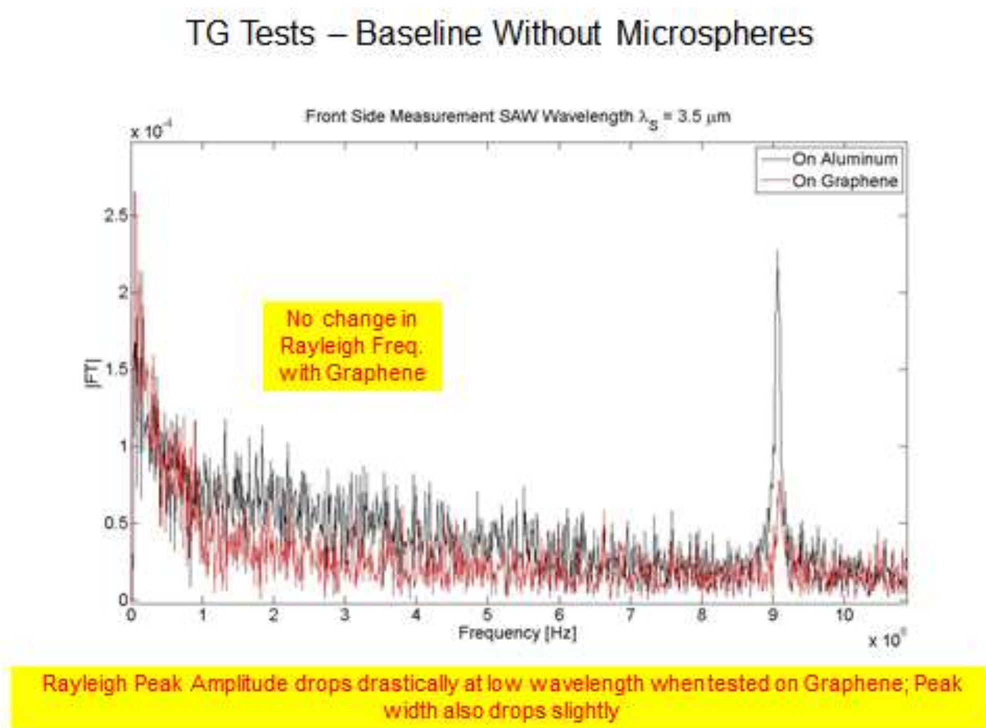


Figure 25: Fourier Transform of TG test signals

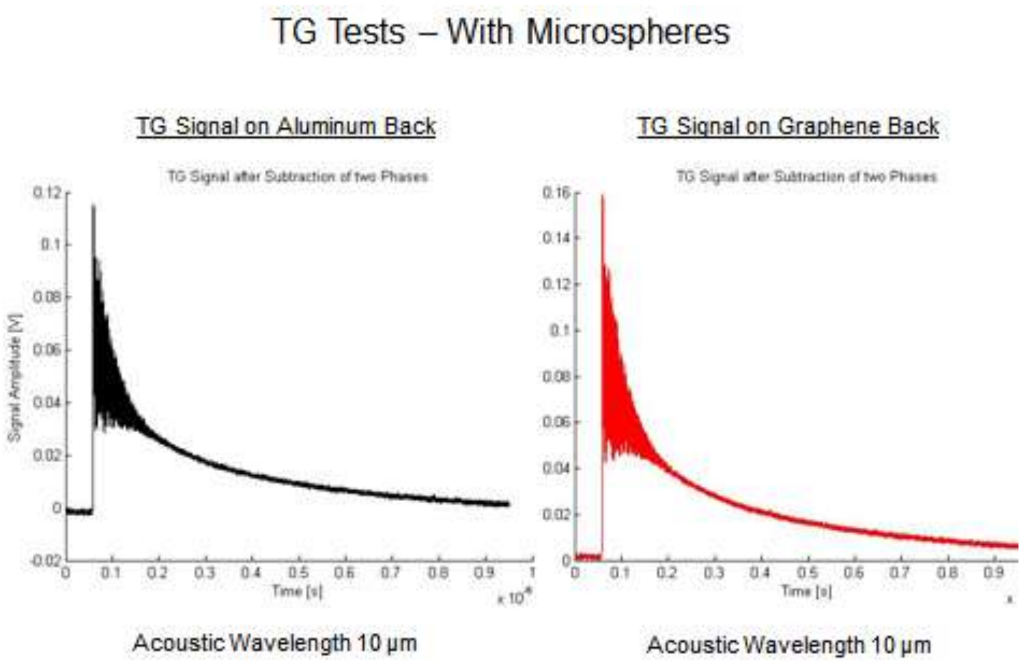


Figure 26: TG test signal on aluminum and Graphene on aluminum with microspheres (Back)

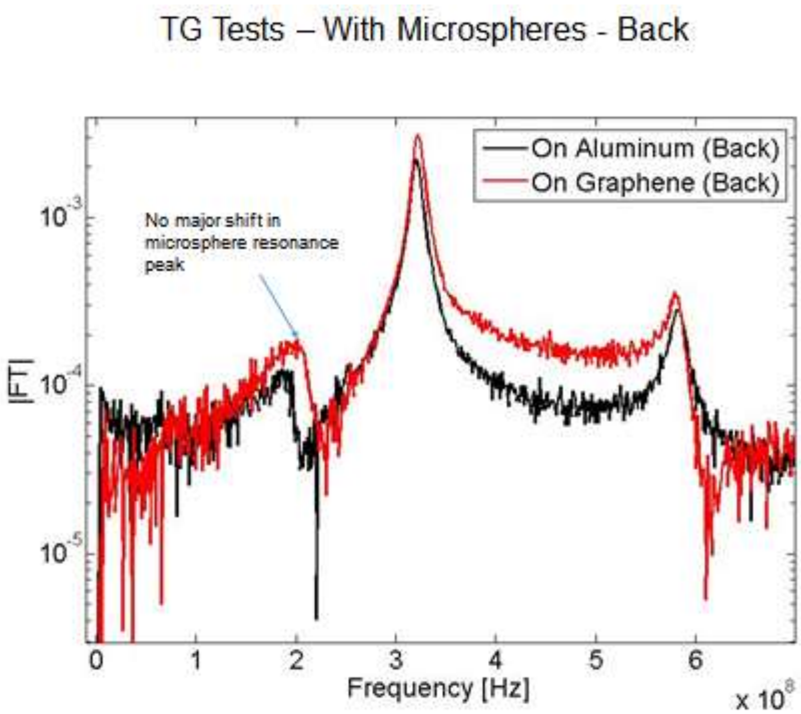


Figure 27: Fourier Transform of TG test signal on aluminum and Graphene on aluminum with microspheres (Back)

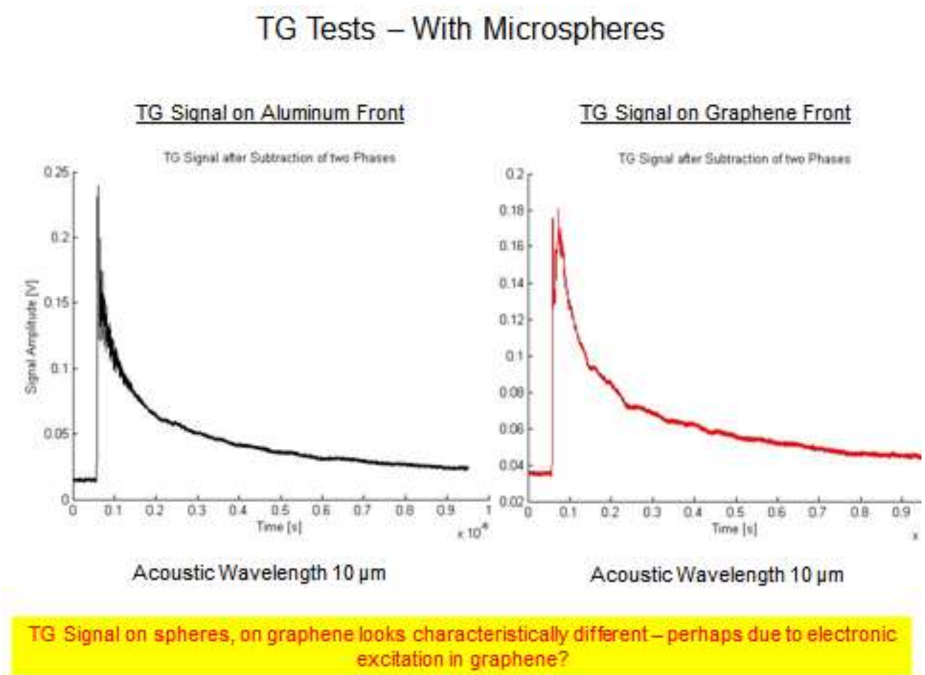


Figure 28: TG test signal on aluminum and Graphene on aluminum with microspheres (Front)

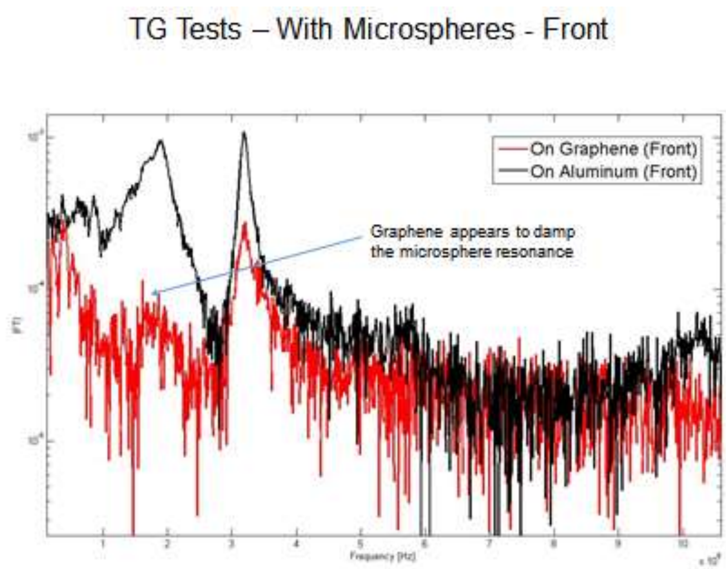


Figure 29: Fourier Transform of TG test signal on aluminum and Graphene on aluminum with microspheres (Front)

The tests did not show the desired shifts in microsphere resonance frequence due to presence of Graphene. A possible reason for this could be the holes in the Aluminum, or also the multilayers or uneven coverage of Graphene.

Transfer of Monolayer Graphene using Thermal Release Tape from

To eliminate the possibility of error due to multilayers, monolayer Graphene could be used.

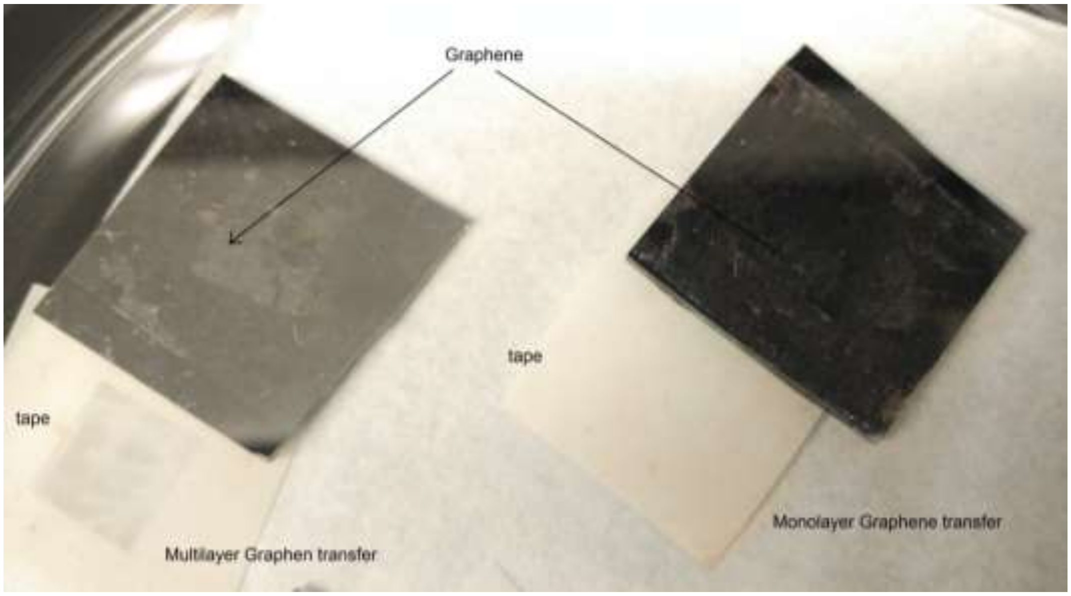


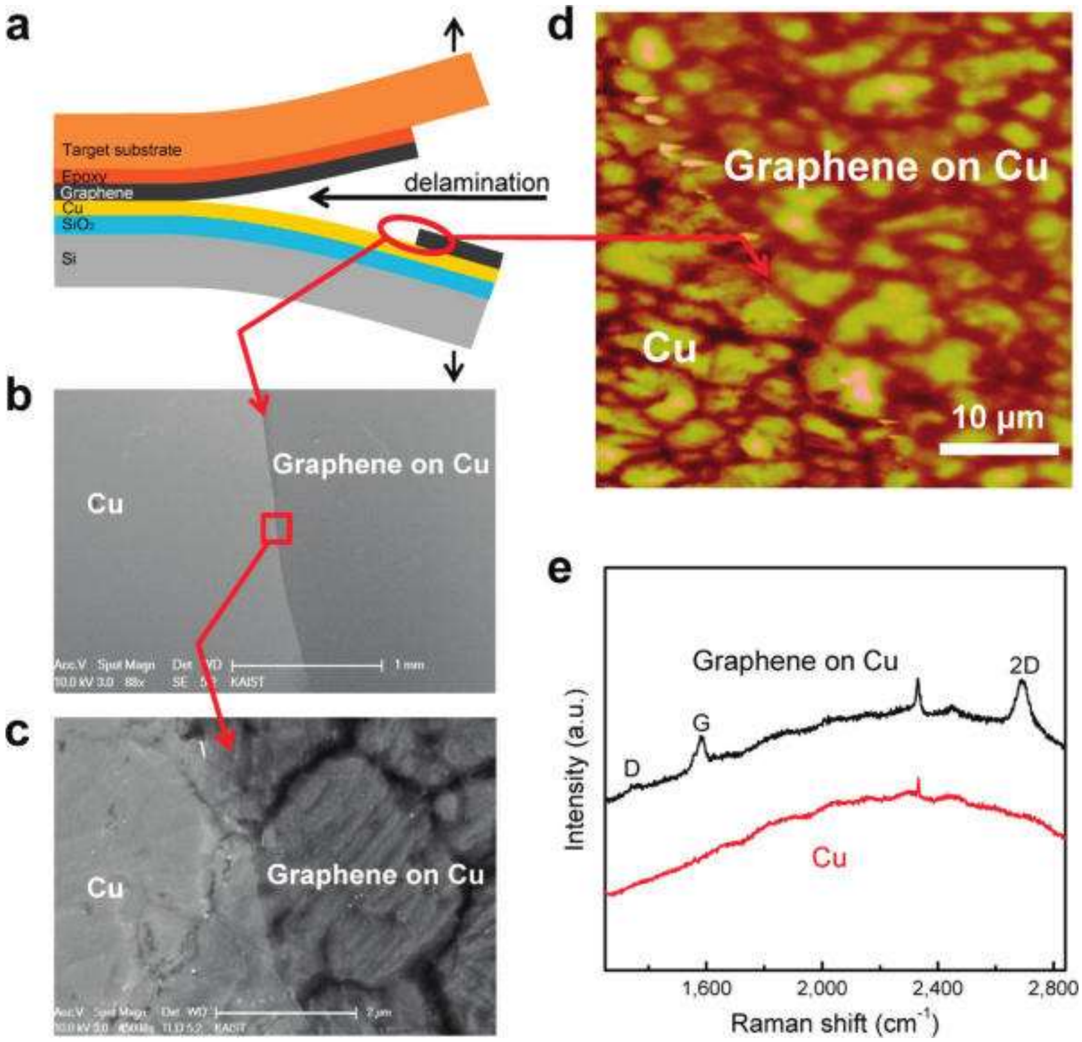
Figure 30: Multilayer (from Ni) and Monolayer (from Cu) Graphene transferred to Aluminum coated glass slide

Monolayer Graphene is obtained from the Copper foil sample. The Thermal Release Tape is used to transfer this Monolayer Graphene from copper to aluminum coated glass slide. It is found that monolayer Graphene is not visible under optical microscope with its maximum 100x zoom. Therefore, it's difficult to be sure of the transfer, without any definite proof of it.

Imaging Graphene

Presence of Graphene is usually detected by Raman spectroscopy or SEM scan. Raman Spectroscopy is a more definite indicator as it gives shifts in peaks for intensity vs. wavelength or wavenumber graphs with presence or absence of Graphene. Scanning Electron Microscope (SEM) can also revel the presence of Graphene, but there is a possibility of error caused due to the grain boundaries of the base metal. But still it is possible to use SEM.

(CVD Graphene grown on copper foil starts growing at the grain boundaries of copper due to activation energy difference. CVD Graphene on Nickel on the other hand starts growing by infusion into the Nickel surface. But this could also imply that the CVD Graphene whether monolayer or multilayer samples, have a complete coverage of Graphene on the metal surface. – *source: Grapphene Supermarket phone call with technical expert*)



Etching-free selective mechanical transfer of large-area monolayer graphene. (a) Schematic of selective graphene transfer to a target substrate using the mechanical delamination process. (b) Low-magnification (the scale bar is 1 mm) SEM image of a selectively graphene delaminated copper surface. (c) High-magnification (the scale bar is 2 μm) SEM image. (d) AFM image of a selectively graphene-delaminated copper surface. (e) Raman spectra of the graphene-delaminated bare copper (the lower spectrum) and of the graphene-covered copper (the upper spectrum).

Figure 31: Imaging Graphene by SEM and Raman Spectroscopy is possible

Source: Taeshik Yoon, W. C.-S. (2012). Direct Measurement of Adhesion Energy of Monolayer Graphene As-Grown on Copper and Its Application to Renewable Transfer Process. Nano Letters American Chemical Society.Mounting microspheres directly on the copper foil coated with CVD Graphene

Microspheres on Monolayer Graphene

Inorder to be sure of the presence of Monolayer Graphene below the microspheres, the copper foil itself was mounted with microspheres. The copper foil was pasted on two glass pieces which were inturn pasted on another glass slide, to keep the foil free standing, for testing purposes.

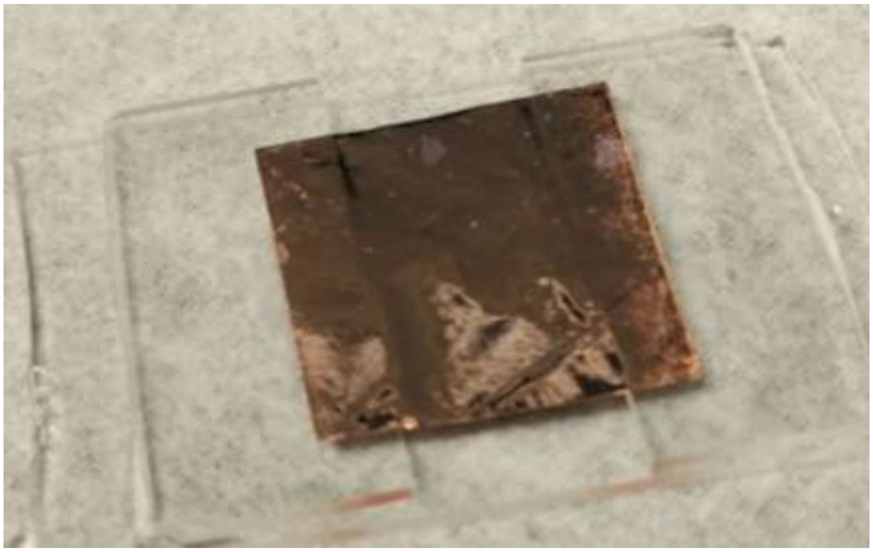


Figure 32: Copper foil with Graphene mounted to be free standing

Microspheres were then mounted on the foil using the Vogel technique as before.

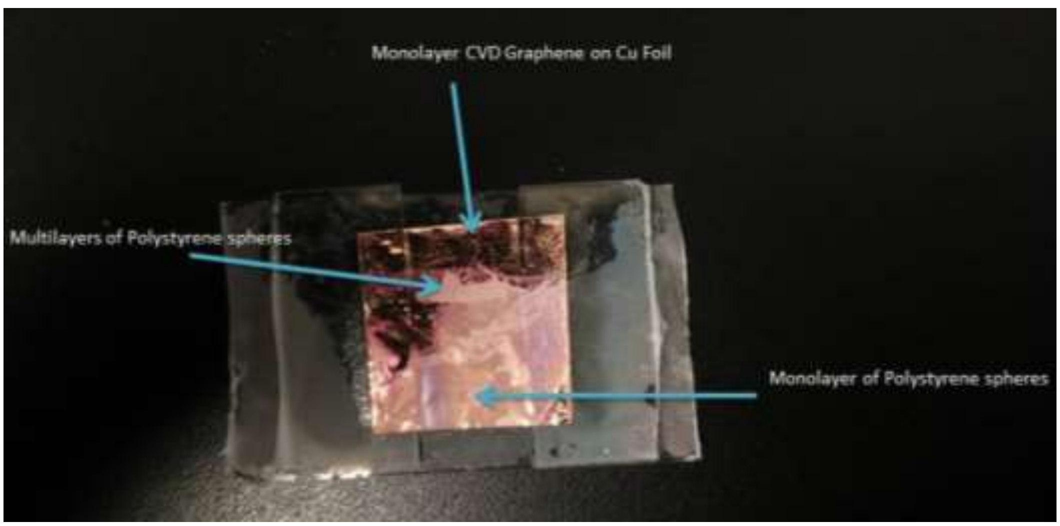


Figure 33: 1 micron diameter polystyrene microspheres mounted on 20 micron thick copper foil with monolayer CVD graphene

This sample has areas with microspheres as well as without microspheres. But the Graphene is present all over.

The sample required for the tests is as below-

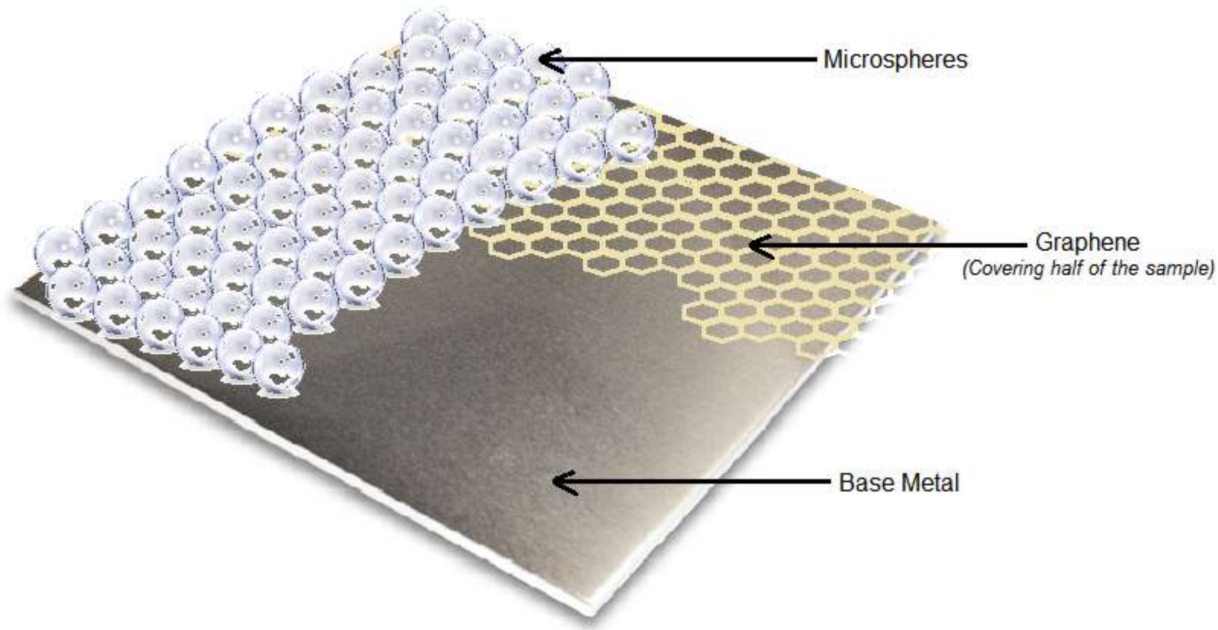


Figure 34: The way sample is required

This necessitates either transferring Graphene on half of the plane substrate, or removing the Graphene from half area of the sample of copper foil before mounting microspheres.

Removing Graphene from the copper foil

Oxygen Plasma Treatment

Graphene could be removed by Oxygen plasma treatment, which oxidizes the impurities on any surface rendering it pure and more hydrophilic. But over exposure to plasma treatment could also oxidize the base metal leaving behind an oxide layer.

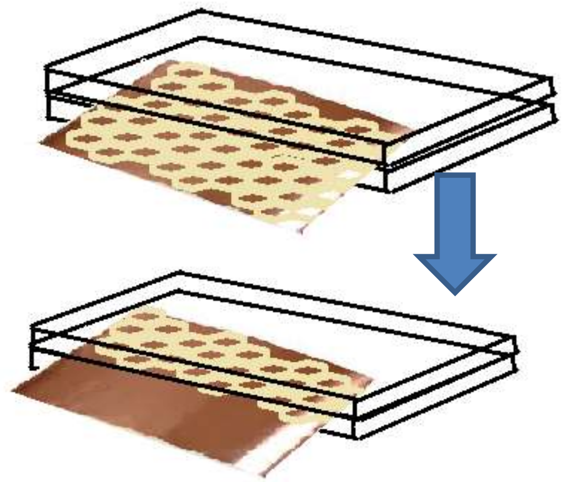


Figure 35: Oxygen Plasma Treatment of partial area

In order to remove Graphene from half of the area of the copper foil sample, a piece of the Graphene coated Copper foil was placed between two glass slides and the slides were held together using tape, to prevent exposure to plasma.

This process was tried for two times with different power ratings, 200W and 60 W for 2 minutes for two separate samples.

The used rating proved higher than required as the plasma treated region of copper turned red and black in color. This may be Cu_2O and CuO layer being formed on the surface.

Figure 37: Oxygen plasma treatment, 200W 2 minutes

Figure 36: Oxygen Plasma treatment, 60W 2 minutes

Mechanical Tape Removal

Another way to remove Graphene that was tried is pasting the Graphene Transfer Tape on the foil, pressing it to let the Graphene stick to the tape, and peeling off the Tape. But this method also requires conformation using Raman Spectroscopy of SEM to be sure of the removal.

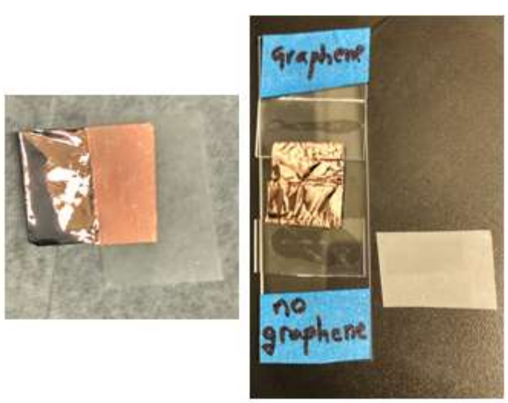


Figure 38: Graphene on copper foil removed by tape

Graphene transfer using floating Graphene

Graphene could also be transferred to the desired substrate by etching away its base metal, copper, and allowing it to float in the etchant, before picking it up on the substrate.

This method was also tried, but it is difficult to pick up monolayer Gaphene and so did not succeed

Figure 39: Copper foil with graphene in $FeCl_3$ etchant, Graphene floating on the etchant after etching away copper

This method might be useful to transfer graphene to Aluminum coated glass slide without creating holes in the Aluminum. But the difficulty lies in picking up the graphene from the etchant, especially if it is monolayer, which is difficult to even see floating.

Radius variation samples using Polystyrene microspheres

For testing purposes, samples of microspheres of different radii on Aluminum coated Glass slide are required. Samples of various radii of polystyrene microspheres made using Vogel technique, and the observations were-

1 micron diameter

- Good packing is achieved (high light diffraction leading to colorful sample)
- Complete water surface is covered with microspheres before the surface starts to buckle
- Angle of entry of spheres (i.e. the slide) is 45^o.

2 micron diameter

- Both hydrophilic and hydrophobic slides tried for pouring the spheres into the water (usually its hydrophilic)
- Spheres sink into the water instead of floating turning the water cloud
- Angle of entry of spheres (i.e. the slide) is 45^o.

Figure 40: Microspheres sinking into the water

5 micron diameter

- Reasonable lattice packing observed
- Many impurities and defects also observed
- Multilayer regions of microspheres formed

10 micron diameter

- Spheres float up to some amount forming random arrangement. Lattice arrangement is not formed.
- They sink after some more amounts are poured in.
- Spheres do not easily enter water and are accumulated at the water-air-glass edge.
- Angle of entry of spheres (i.e. the slide) is 45^o.
- With lowering the Angle of the slide to 26.5^o makes the entering of spheres into water - easier, but no appreciable difference is observed in the sample quality.

Conclusion

Efforts were made to transfer Graphene on to desired substrate, mounting microspheres on the Graphene and test it under transient grating apparatus. The transfer succeeded in some cases while in others it may have succeeded but more analysis is required. It might be possible to transfer Graphene using other chemical methods.

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