

Low noise electrical measurement setup for graphene and molecules in a gas atmosphere

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Abstract

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This thesis consists of two parts. The first part is mainly theoretical and explores the properties, production and characterization of graphene; discussing different techniques used as well as the wide range of electronic applications. The second part is experimental and analyses a low noise electrical measurement setup for the field of nano-electronics; describing optimization measures to lower the level of various noise sources. The noise level was successfully decreased by four magnitudes. An accurate electrical measurement station has been built up, with the possibility to conduct measurements in different gas environments.

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Abstract

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Introduction

In 2004, Andre Geim and Kostya Novoselov succeeded in isolating the first 2D material, something long thought impossible. Using mere adhesive tape they cleaved a sample of graphite repeatedly until only a one atom thick sheet of carbon atoms was left, known as graphene. This material is not only the strongest material known to man; it also conducts electricity better than copper and outperforms all other materials in terms of heat conduction. By proving that 2D materials can be stable and showing that carbon atoms arranged in this manner shows relativistic effects and possesses these extraordinary properties, Geim and Novoselov were awarded the 2010 Nobel Prize in physics [Geim et al, 2007], [Deshmukh, Singh, 2011].

During the past few years, graphene has drawn a significant amount of interest in the research field due to its unique properties, making it a rising and promising material for a wide range of electronic applications ranging from super-fast transistors to highly sensitive gas sensors [Neto et al, 2006].

1. Graphene

Properties

Graphene is an allotrope of carbon and consists of a monolayer of carbon atoms arranged in a two-dimensional honeycomb pattern, not much different from an infinite layer of benzene rings. It's the building block for all other graphitic materials i.e. fullerenes, nanotubes and graphite, see figure 1. Pristine graphene is a semi-metal or zero-gap semiconductor [Royal Swedish Academy of Sciences, 2010].

The interaction between the special structure of graphene and the electrons causes the electrons to behave as if they were massless [Neto et al, 2009]. Furthermore, the electrons move at an effective speed of 300 times less than the speed of light, allowing relativistic effects to be observed in room temperature in the absence of huge particle accelerators [Neto et al, 2006]. Another remarkable property of graphene is its unexpectedly high transparency; it absorbs only 2.3% of white light, rendering it practically invisible and making it a strong candidate for optical devices.

Some additional observable effects worth mentioning are the quantum Hall effect, extremely high electron mobility with low scattering and the minimum conductivity point. Graphene thus works as an ultimately simple particle accelerator and offers opportunities to investigate quantum field theories never seen before [Geim et al, 2007].

Graphene has also shown highly adjustable properties, creating great opportunities in nano-engineering where material properties are changed to modify the behavior. As an example, experiments have shown that, contradicting the physics of other materials, the conductivity of graphene increases when defects are introduced [Jafri et al, 2010].

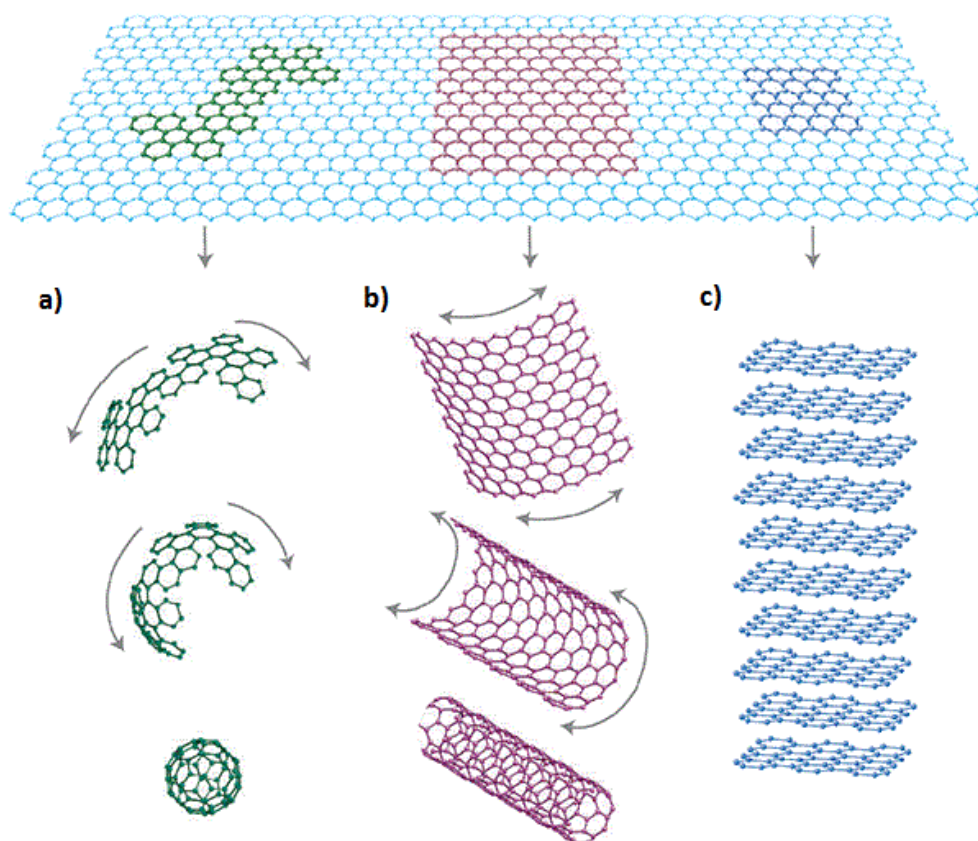


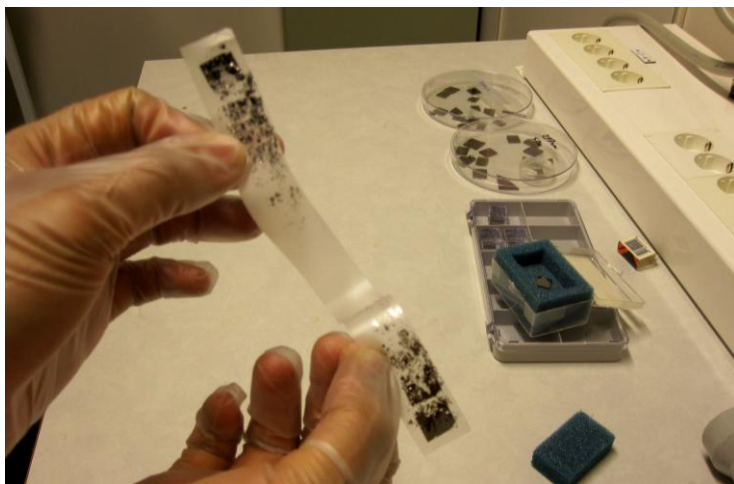
Figure 1. Graphene (top) is the base for all other graphitic forms i.e. a) fullerenes, b) nanotubes and c) graphite.

Production

When graphene first was discovered, no complex machines or advanced techniques were used. With the help of ordinary sticky tape, the Geim group succeeded in isolating a single sheet of atoms. This method is referred to as mechanical exfoliation and is a straightforward and simple way to produce graphene. Below, you can follow my attempt to mechanically exfoliate and characterize graphene.



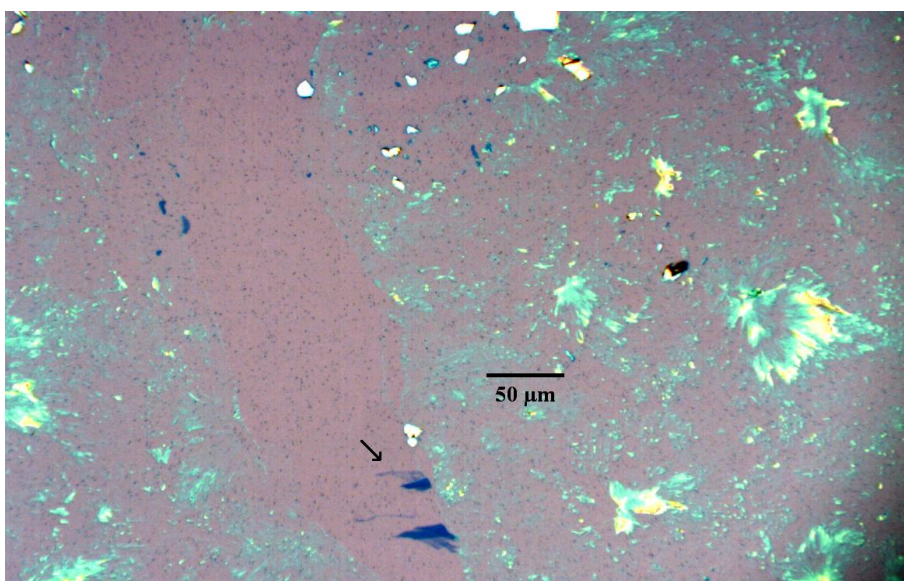
First, a piece of Highly Oriented Pyrolytic Graphite, HOPG, is placed on a piece of sticky tape. The tape is then folded to sandwich the sample and when peeled apart, the sample cleaves into two thinner parts.



This is repeated until only very thin areas remain.



Transfer the sample onto a silicon substrate by laying it on the silicon and gently rubbing it for a couple of minutes. Slowly remove the tape and start hunting for flakes in a light optical microscope.



Among all graphite fragments, hopefully there are some graphene layers. These are typically in the size of 10 micrometers across.

Mechanical exfoliation is a surprisingly simple method and produced samples are relatively easy to make. However, for mass production and large-scale use, mechanical exfoliation is lacking since it is time consuming, only produces small flakes and cannot mass-produce samples with identical outcomes. But for fundamental research and measurements, the sticky tape method produces satisfactory and uncomplicated results.

In recent time, other techniques have been researched and developed for this purpose, such as chemical exfoliation, epitaxial growth and chemical vapor deposition. These methods are more specialized for mass-production of bigger graphene flakes but still, more research has to be made before a reliable method can be established [Soldano et al, 2010].

Characterization

Optical Light Microscopy

The first step in finding graphene is by looking for potential candidates in a regular optical light microscope. The optical light microscope uses white light and different objectives to magnify small samples up to a resolution of 10^{-7} m. When an interesting area has been found, the location is marked out and an image of the area is taken with the microscopes charge-coupled device (CCD) camera. This is done at different magnifications to easily find the way back to the same area.

But firstly, how can we even see a single layer of atoms such as graphene?

Graphenes optical properties make it practically invisible, absorbing mere 2.3% of visible light. During the exfoliation, the graphene flakes are deposited onto a substrate consisting of a silicon wafer with an oxidized top layer. The top layer of the substrate is silicon dioxide with a carefully chosen thickness, typically 300nm, in order to create a maximum optical contrast between the silicon substrate and the graphene layer. Because of the difference of path the incident and reflected light has to travel through these layers, the thin flakes become visible under a regular optical microscope [Di Cristo, 2010], [Deshmukh, Singh, 2011]. Flakes on the sample appear in colors ranging from gold and dark purple for thicker flakes to light blue and pink for very thin layers, see figure 2. Optical light microscopy only provides a first, qualitative view of the sample to find interesting areas which are then further analyzed using atomic force microscopy and Raman spectroscopy.

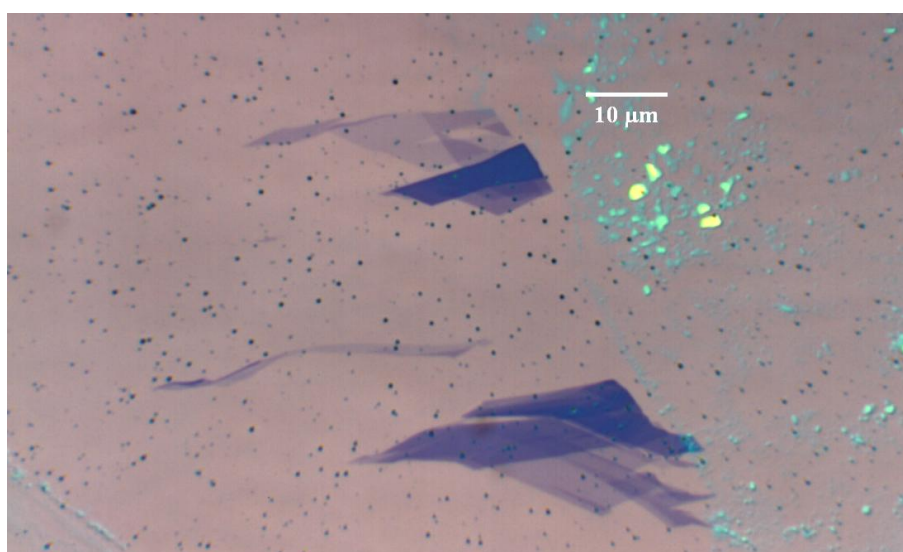


Figure 2. Mechanically exfoliated sample seen in a light optical microscope at 100 times magnification. Thicker graphite flakes are gold and dark purple, graphene flakes are light, transparent purple.

Atomic Force Microscopy

Atomic force microscopy, AFM, sweeps the sample surface using a cantilever with a fine silicon tip, which gives a very high resolution in the order of fractions of a nanometer. When the tip is brought close to the sample surface, forces between the tip and the surface lead to a deflection of the cantilever. The deflection of the cantilever caused by mechanical contact force, electrostatic force, magnetic force etc. is then measured by a laser spot, thus constructing a topographic image.

There are two modes used, contact mode and non-contact mode. For measuring thin graphene flakes, the non-destructive non-contact mode is used. In this mode, the tip does not contact the surface. Instead, the cantilever is oscillated at close to resonant frequency slightly above the surface. Being affected by forces from the sample changing the frequency, the height of the tip is adjusted to maintain a constant frequency, creating a topographic image of the surface [Di Cristo, 2010], see figure 3. This method determines the actual thickness of the flake and everything thinner than 10 Å is considered to be mono-layer graphene.

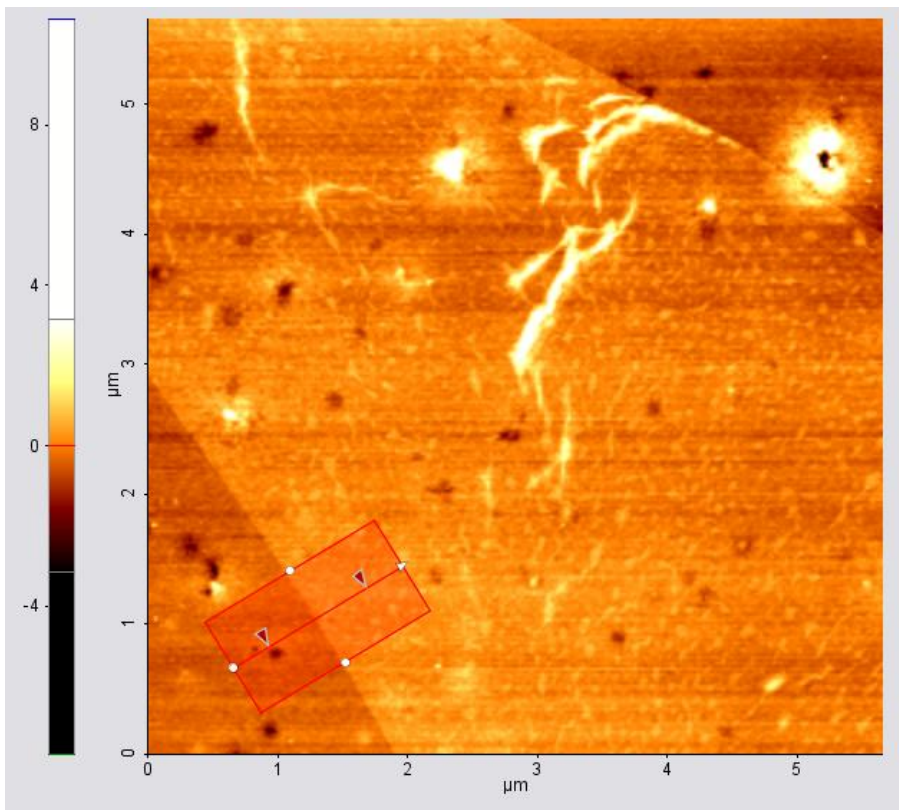


Figure 3. Graphene flake (lighter orange) on silicon substrate (darker orange), scanned in AFM. Measured thickness to 6 Å, confirming this is mono-layer graphene.

Raman spectroscopy

Raman spectroscopy is used to study low-frequency modes and is based on inelastic Raman scattering. Monochromatic laser light is used to excite the sample, thus shifting the energy of the laser light. The shift and the intensity are measured, creating the Raman spectroscopy. The advantage of using this method is the characteristic spectrum of graphene. It also provides information on the flake thickness since one can distinguish from mono-, bi- and multi-layer graphene given that they all have their own characteristic spectrum.

There are two characteristic peaks for graphene, called the G peak and the 2D peak. The G peak appears at 1580 cm^{-1} and is present in all graphite forms. The 2D peak is sharp, narrowed and centered around 2640 cm^{-1} for mono-layer graphene and the shape broadens and shortens for thicker flakes [Moral, 2010], see figure 4.

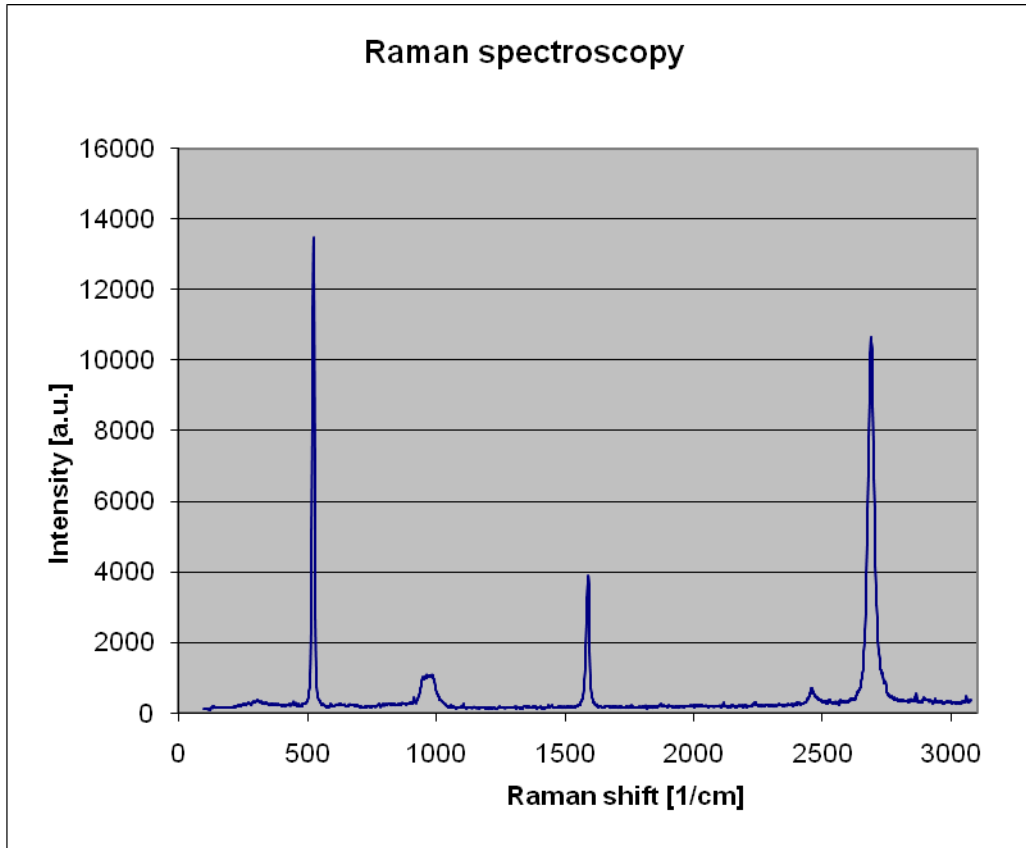


Figure 4. Raman spectroscopy of mono-layer graphene. The 2D peak is seen at 2640 cm^{-1} and the G peak at 1580 cm^{-1} . The other two peaks come from the silicon substrate.

2. Measurement setup

Theory

Current-Voltage curves

To conduct a current-voltage measurement, a voltage is applied over an electronic device and the resulting current is measured. These curves are referred to as I-V curves. The simplest I-V curve is that of a resistor and is, in accordance to Ohm's law, a linear relationship between applied voltage and measured current. This is however the simplest case and typically, these curves have a non-linear behavior. With this curve, one can see the basic parameters and material characteristics of a device and consequently use this to model the behavior by changing or doping the material for desired characteristics.

Noise

Electrical noise is present in all circuits and devices and can vary greatly since it can be produced from different sources such as thermal noise, vibrations and electromagnetic fields. Noise is an unwanted oscillation of the electric signal and great efforts are made to bring it down to an acceptable level. Since nano-electrodes generally have an extremely high resistance, very precise and accurate current measurements are required for the low currents, sometimes as small as pA (10^{-12} A). This means that if the noise signal exceeds this level, no sensible measurements can be made. In practice, noise can originate from cables and connections, external fields, leakage currents and mechanical vibrations, so these have to be analyzed thoroughly to be minimized [Maple Systems Inc.].

Faraday cage

To optimize a sensitive measurement setup, one has to lower all kinds of noise as much as possible. A good first step is to shield the setup with a Faraday cage. A Faraday cage is simply an enclosed box made of a conductive material that can lead electric charges. This construction has the capacity to shield against external electromagnetic fields since the charges on the conducting surface will rearrange such that the field inside the cage will be cancelled, see figure 5 and 6. For best effect, the Faraday cage should be grounded to earth so that electromagnetic forces affecting the cage can be conducted into the ground, thus keeping the inside unaffected [Gamry Instruments, 2010]. During the project, I built a Faraday cage, using aluminum sheets, to shield the measurement station, see figure 6.

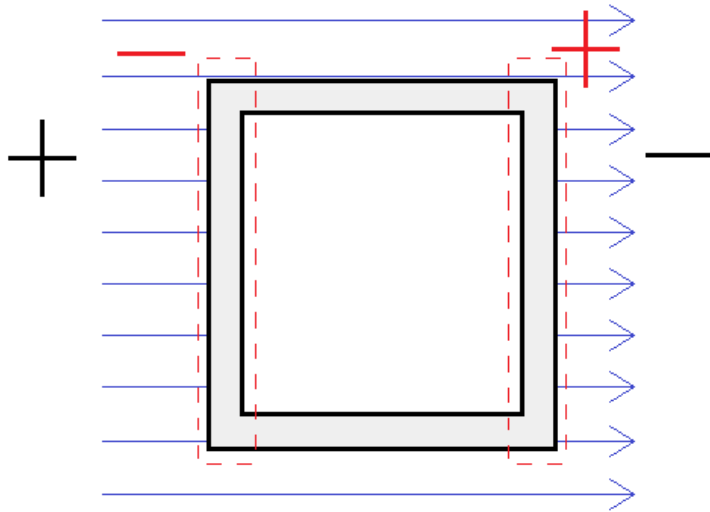


Figure 5. The Faraday cage principle. The charges on the conducting surface redistribute to effectively cancel the electromagnetic field on the inside, thus shielding the interior.



Figure 6. The Faraday cage made for shielding the measurement station, made of aluminum.

Initial setup

- Probe station - probes with 5 μ m Tungsten needles, platform with chamber and lid.
- Light optical microscope with magnification up to 180X.
- Keithley 6430 Sub-femtoamp Remote Sourcemeter with Pre-Amplifier, used to conduct current-voltage measurements with a resolution of 10^{-17} A.
- LabTracer, PC software, used to control Keithley 6430.

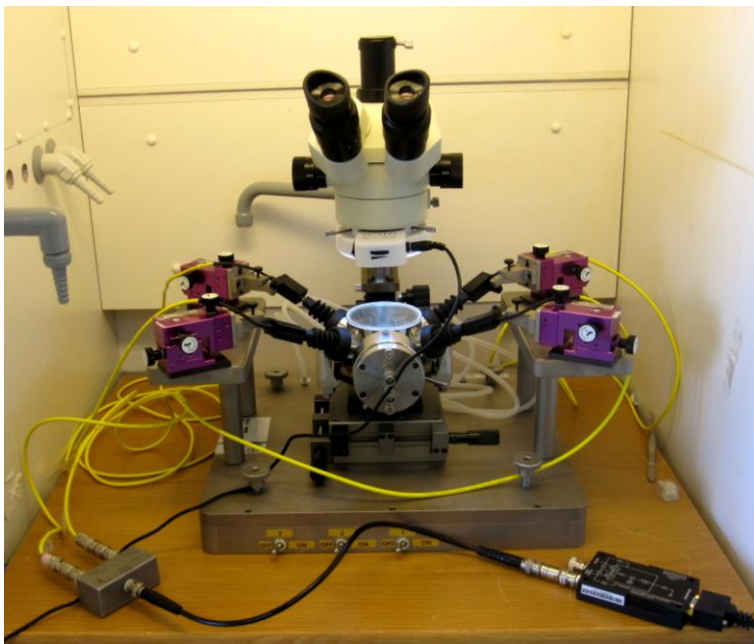


Figure 7. Initial setup of the measurement station

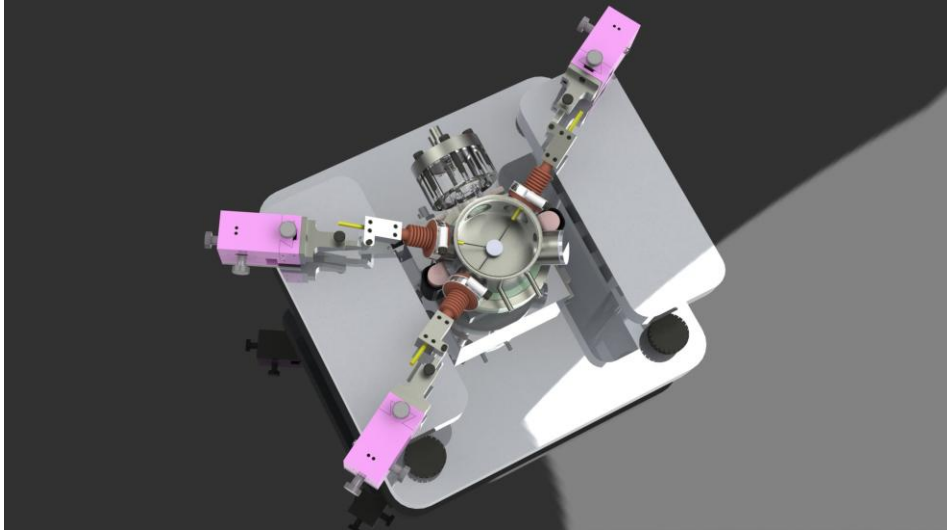


Figure 8. Probe station seen from above. Drawn in CAD by Masih Noor.

Experiment

The first I-V measurements were made with the initial measurement setup, with the needles placed on isolated gold pads. The most accurate, although slowest, settings were chosen i.e. maximum integration time and maximum number of repeat filters. The measurements are showing noise in the order of 10 nA, see figure 9, which is very high for nano-electronics.

Since the equipment is highly sensitive for noise, the setup was systematically tested for noise in every connection where the noise was present in all parts of the system, see figure 9. As an example, the long cable adds cable noise to the system and the box could potentially act as an antenna, each resulting in additional noise. Alternative solutions (various banana connectors and splitters) were tried, although with no improvement. One major improvement was made when the electric cord to the microscope light was plugged out; it was inducing an electric field which was picked up by the probes. This reduced the noise level by one order.

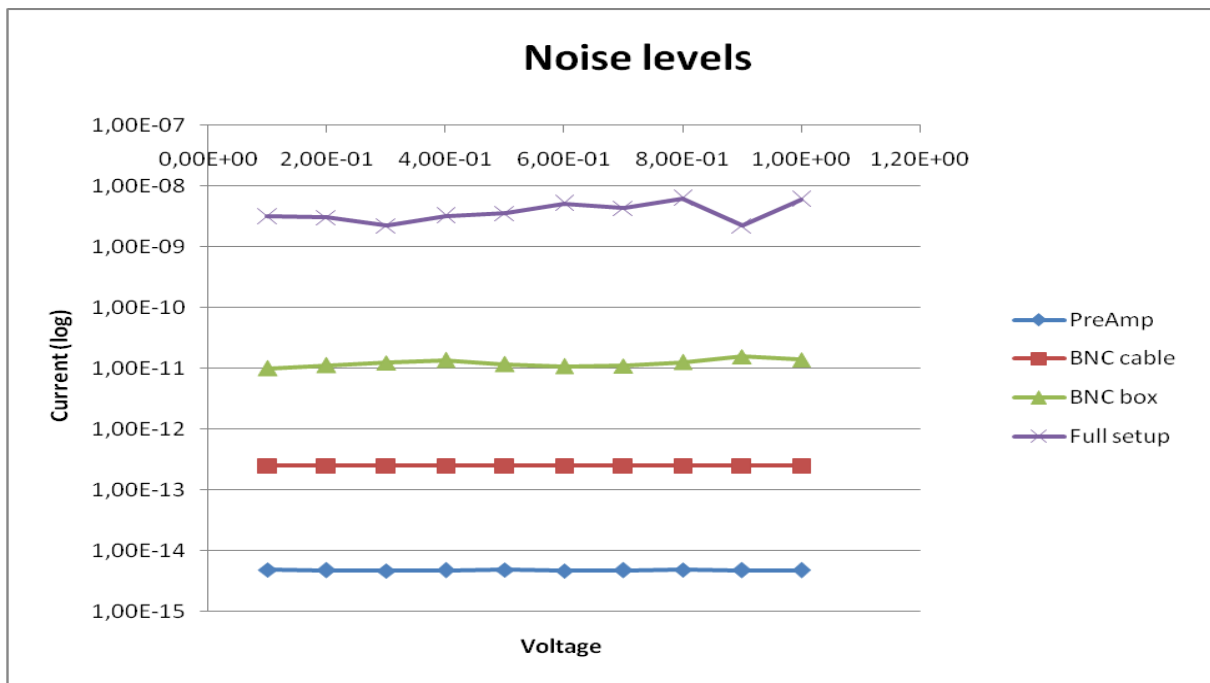


Figure 9. Semi-log I-V graph for the different parts of the system.

As a next step, a Faraday cage was installed and grounded to shield the measurement station from external fields. This showed a significant result, with the system noise level measured to 1 pA range, see figure 10. Grounding contra ungrounding the cage showed considerable difference, as expected.

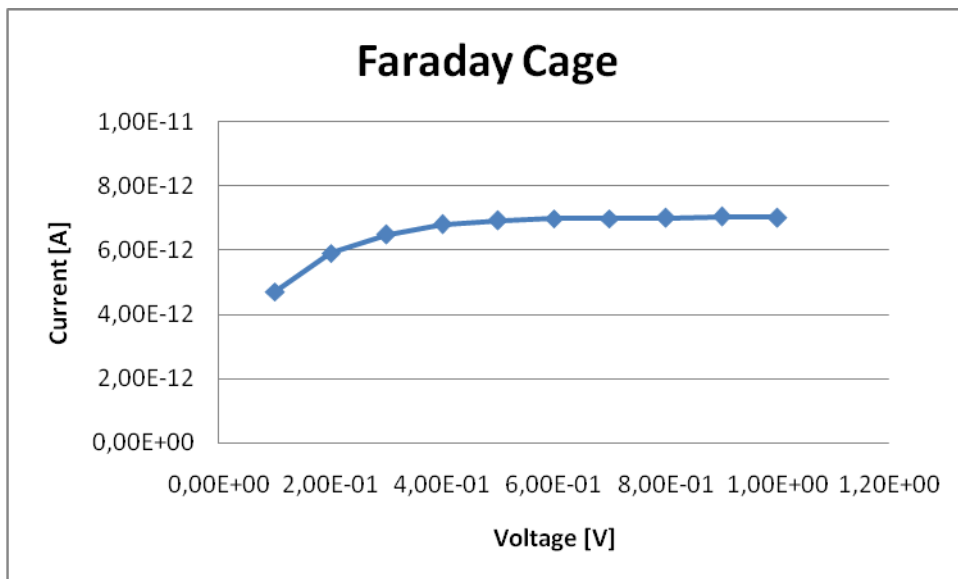


Figure 10. I-V graph with the Faraday cage installed.

Next, a granite base plate and vibration dampers were installed in order to prevent vibrational noise. The granite was chosen because of its stiffness since the previous wooden base allowed mechanical vibrations to transfer onto the system. The noise level was measured to the range of 1 pA, see figure 11.

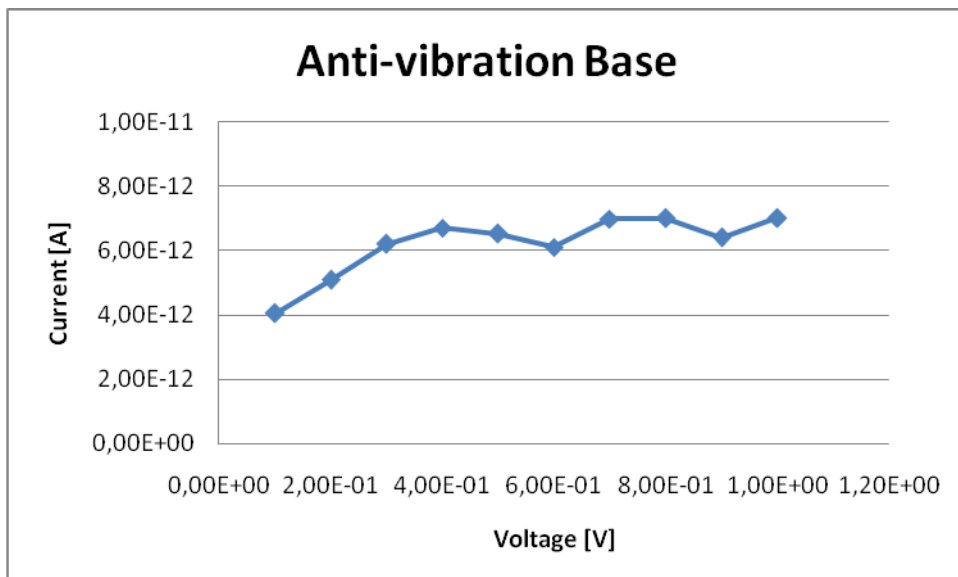


Figure 11. I-V graph with the anti-vibration base.

There is no significant difference to be observed with the anti-vibration base, simply because there were no noteworthy vibrations present. However, the setup is now more rigid and resistant to bigger mechanical vibrations such as low-frequency vibrations and door slams.

Final setup

The final noise level was measured to less than 1 pA, a decrease by more than four orders.

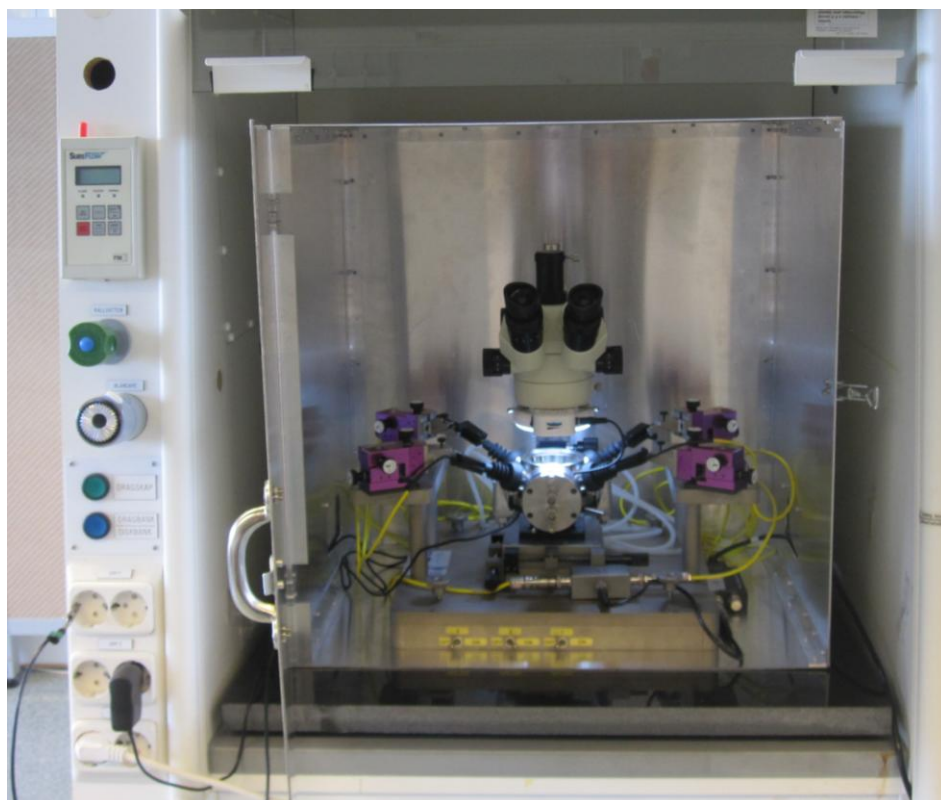


Figure 13. Final setup with grounded Faraday cage and anti-vibration base.

Discussion

This thesis explored the properties of graphene and the setup and optimization of a low noise measurement station.

Graphene is a rising material of ultimately simple form; mere carbon atoms arranged in a single sheet of hexagons. It is a highly versatile and exciting material with several properties superior to those in other materials. These unique properties can also be enhanced and doped to modify graphene into what is needed in different applications, making it a very useful material. Even though graphene has seen a tremendous progress in the past few years, stable mass-production still remains a main issue. However, a dramatic progress in developing new techniques for mass-production is expected, such as chemical exfoliation and chemical vapor deposition. This tells us that it won't be too long until we will see the first products based on this ground-breaking material.

To start studying and experimenting on nano-electronics, one needs the right equipment to work with. For this reason, an electrical measurement station has been set up. In this field, it is crucial to conduct precise and accurate measurements, therefore all noise signals have to be minimized. This is a long and constant battle since noise can originate from a great many sources. There are many diverse techniques and measures to minimize different kinds of noise and this project has mentioned some of them. The noise level for the entire measurement setup was successfully decreased from the starting noise level of 10 nA to the final 1pA.

It is now possible to conduct electrical measurements with low noise on graphene and molecules. A supplementary setup using Keithley 6221 Current Source and Keithley 2182A

Nanovoltmeter was also installed, as was a gas setup, for future differential conductance measurements in different gas environments.

In summary, graphene is one of the lightest, strongest and most conductive materials. It was awarded a Nobel Prize simply because graphene is one of the most promising materials of today with a wide range of upcoming applications ranging from strong composite materials and high-speed quantum experiments to gas sensing and high-capacity batteries. Graphene is still very new, discovered only a few years ago so there is much to be discovered and more research to be made. It will certainly be interesting to see what the near future for graphene will bring, both in fundamental science and in real life technologic applications.

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Figures

Figure 1 taken from *Graphene*, 2010

Figure 8. Provided and made in CAD by Masih Noor