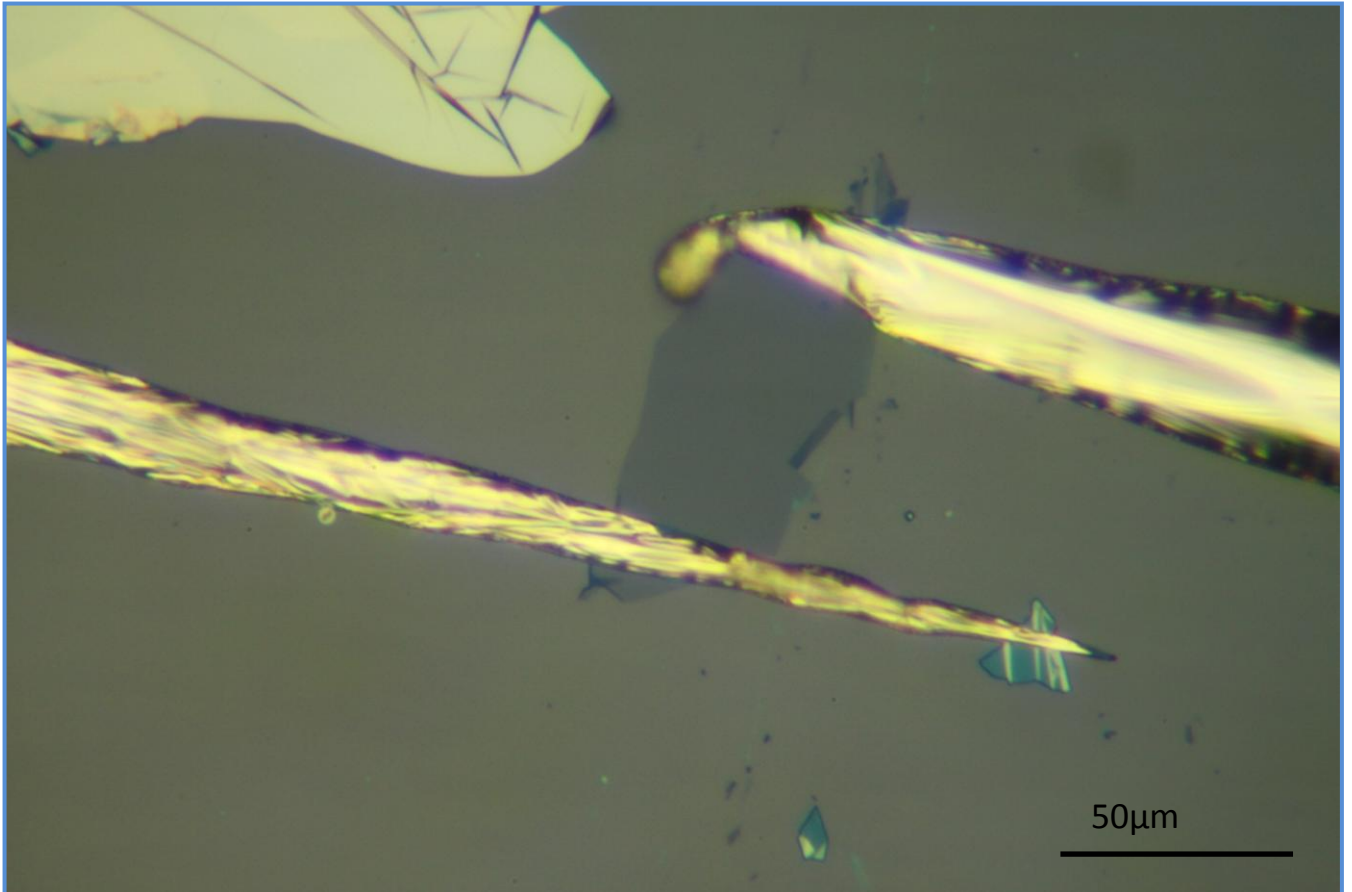


Production and Characterization of Graphene Devices



A EUCYS-project by
Luca Banszerus & Michael Schmitz

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Table of contents

1. Abstract

2. Objective of the project

3. Introduction

4. Graphene

4.1 Properties of Graphene

4.2 Production of Graphene

4.3 Application of electrical contacts on Graphene

4.4 Monolayer Verification

4.5 Graphene-FET

4.6 Sensor Applications

4.7 Large Area Synthesis of Graphene using CVD

5. Conclusion

6. Prospect

7. Acknowledgement

8. Reference

1. Abstract

Since the discovery of graphene in 2004 by a British team of researchers, it has been attracting great interest. By now it is one of the most current topics of solid state physics and nanotechnology. Graphene is a mono-atomic honeycomb-lattice of sp^2 -hybridized carbon; it is exactly one layer of graphite. Because of its huge surface area and its extremely high carrier mobility graphene qualifies for very precise sensor applications in the physical, chemical and biological sector. During our project we were able to produce multiple graphene monolayers with lengths of more than $100\mu\text{m}$ on a Si/SiO_2 substrate. Additionally we developed a technique to apply electrical contacts on our graphene flakes at school without relying on optical lithography and Lift-off, which can't be conducted at school. Moreover we invented a method to optically determine the number of layers in mono- and few-layer-graphene. After we successfully deposited electrical contacts on our graphene we built multiple devices, such as different gas sensors and field-effect-transistors.

2. Objective of the Project

The objective of our project is to produce well working graphene FETs and sensors using only methods available at school. However the quality of our devices should be comparable to devices created with high-tech methods. Thereby we would create an opportunity for almost every school to participate in up-to-date research. Additionally we want to implement new applications of graphene.

3. Introduction

The discovery of new carbon allotropes often caused sensations in the world of solid state physics and nanotechnology. After the discovery of the carbon nanotubes in 1993 many scientist predicted that CNTs would soon replace the silicon technology. However CNT technology is still in the basic research stage today. The major problems using CNT technology is applying electrical contacts to the nanotubes on an industrial scale. Even though graphene is a carbon nanoparticle, it often has an area of several thousand μm^2 . With state of art lithography, contacts can easily be applied on this scale. Researchers recently developed a method to synthesize large area graphene on metal catalysts that also serve as substrates. The ability to pattern and contact graphene on an industrial scale makes an emergence of carbon electronics possible. Graphene has very advantageous electrical properties that would make carbon based electronics superior to conventional silicon technology. The mean free path of an electron in graphene is approximately 400nm , the carrier mobility is more than $20,000\text{ cm}^2/\text{Vs}$. In Silicon electrons have a mean free path of just a few nanometers and a mobility of roughly $1,000\text{ cm}^2/\text{Vs}$ depending on the doping. By now there are several graphene devices being developed such as gas sensors and a graphene MOSFET.

4. Graphene

4.1 Properties of Graphene

The properties of graphite are very anisotropic. Within a basal plane graphite conducts heat as well as electricity very well. However, perpendicular to the basal plane graphite has insulating properties. The anisotropic properties of graphite can be explained by analyzing the atomic structure. Within the basal plane, the sp^2 hybridized carbon atoms are covalently bound to each other. The discrete basal planes or graphene layers are bound to each other by very weak Van-der-Waals-Forces. Because of the huge discrepancies between the bond energies (Van-der-Waals-Forces: 0,07eV, covalent bonds: 4,3eV), graphene layers can be mechanically isolated from a graphite crystal using the “Scotch-tape-method”. Analyzing the atomic structure of graphite can’t explain the unique electrical properties of graphene. In order to fully understand phenomena such as the long mean free path and the high carrier mobility it is necessary to take remaining pz-orbitals into account. Analog to benzene there are two possible configurations of three double bonds in a graphene hexagon, which are energetically equivalent. Therefore resonance occurs and a delocalized π -molecular orbital forms. Since graphene consists out of multiple carbon hexagons, the π -molecular orbital spreads throughout the whole graphene flake. The high potential for sensor applications can be explained considering that every atom in a graphene crystal is a surface atom. Even very small

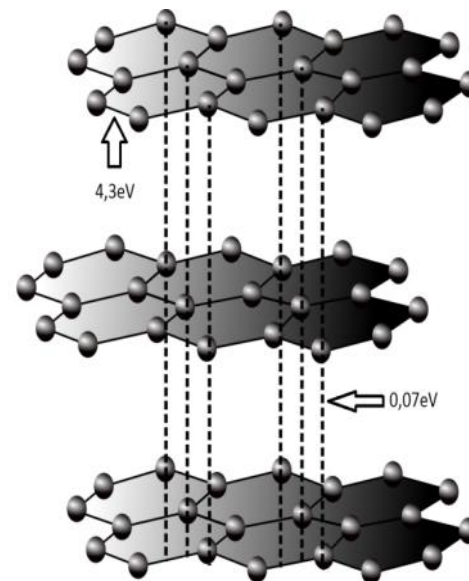


Fig. 4.1.1 Bond Energies in Graphite
Source: Wikipedia

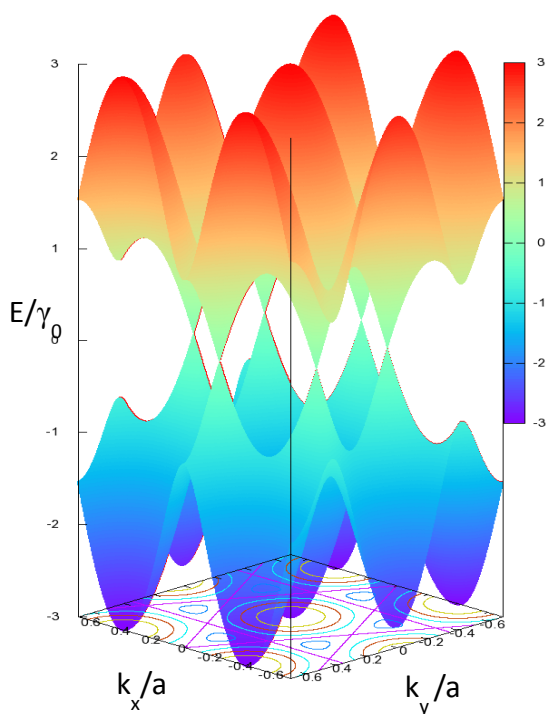


Fig. 4.1.2 Tight-Binding-Model of Graphene

concentrations of certain gases can shift the Fermi level in graphene and thereby alter the concentration of charge carriers. Since the valence band and the conduction band intersect in 6 discrete points, graphene is a semimetal, therefore it is not suited for semiconductor applications; however, there are several approaches to create an artificial band gap in graphene. The Tight-Binding-Model of graphene (Fig. 4.1.2.) also shows that close to the zero band gap the energy of an electron is directly proportional to the momentum of the electron ($E(k) \sim p$). Because of this observation the Dirac-equation is used instead of the Schrödinger-equation to describe an electron in graphene.

4.2 Production of Graphene

The "scotch tape method" is the standard process to produce graphene. A natural graphite flake is placed on a piece of scotch tape. By folding and unfolding the scotch tape multiple times, the graphite is being exfoliated. After repeating the folding step about twenty times, the scotch tape is pressed on the desired substrate. We chose to use silicon wafers, which have a 90nm oxide layer on top (Si/SiO₂ wafer). Through destructive interference of the light that is reflected at the graphene and the silicon, even a graphene monolayer has a visible contrast to the regular wafer background. After transferring the graphene from the scotch tape to the new substrate, the wafer needs to be cleaned with acetone and IPA from residues of the adhesive tape. Now the wafer can be examined with a reflected light microscope. In order to produce large graphene flakes, it is useful to exfoliate graphite in an oxygen atmosphere. Oxygen intercalates between the basal planes of the graphite and weakens the Van-der-Waals-Forces, thereby the chance of producing larger graphene flakes increases. After trying different types of natural graphite and using oxygen, we increased the size of our graphene flakes from initially 20-30µm up to 110µm. Large graphene flakes are extremely important for us, because we don't have access to optical lithography and lift off. This means that we needed to find a method to apply metal contacts to our graphene at school.



Fig. 4.2.1 Natural Graphite Flakes

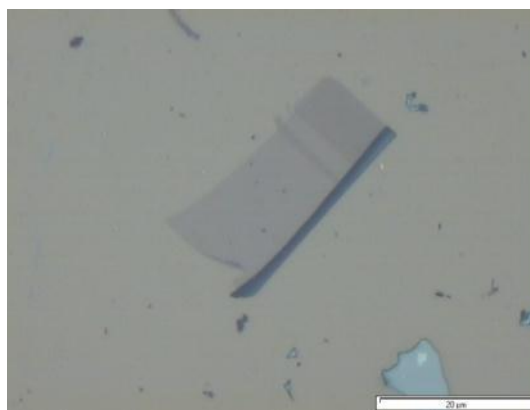


Fig. 4.2.2 In 2008 this was a good flake (Multilayer)



Fig. 4.2.3 monolayer produced in 2009

4.3 Application of electrical contacts on Graphene

In order to conduct independent research with graphene, we needed an autonomous and inexpensive method to electrically connect our graphene flakes. At the beginning of our work with graphene in 2008, we needed professionals to help us contact our flakes. A university offered to do optical lithography (Fig. 4.3.1) on one of our samples so we were able to start characterizing our graphene. Normally a micromanipulator with a tungsten tip is used to connect to the contact pads of a metal lithography. Such a probe station is too expensive for school research, so we built our own contact set up out of a microscope to observe the sample and two other microscopes that precisely drive needles that are attached to their moving stages in x, y, and z direction (Fig 4.3.2.). The problem of this setup was that the lithography was scratched easily and the contact was very unsteady. In order to contact graphene by ourselves, we first tried to use our contact apparatus to mark fine tracks out of conductive silver finish. However we soon realized that the solvent evaporated way to fast and that the traces showed a width of 40 μ m. With this approach, a two-sided contacting of one flake would be impossible.

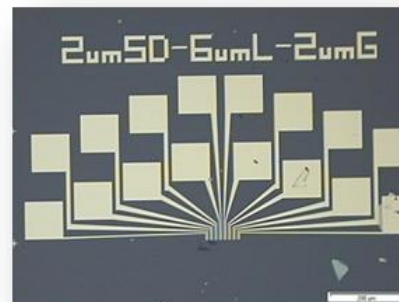
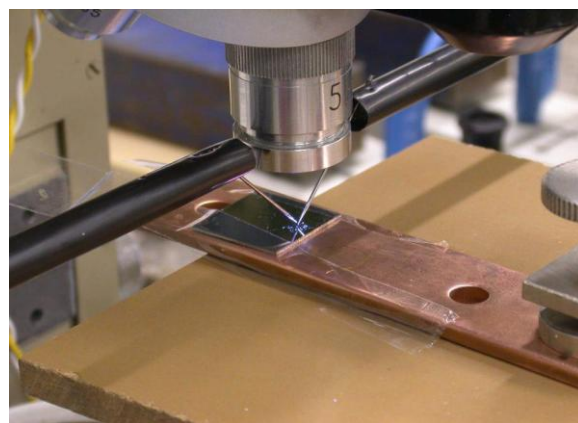


Fig.4.3.1 Lithography



Fig.4.3.2 Contact Setup



Another question we saw ourselves confronted with was, whether the conductive silver finish, consisting of many tiny silver particles, would be suitable for our purposes. Then, we asked ourselves an apparently “stupid” but essential question: Wouldn't it be possible to simply solder on the graphene? Of course, this wouldn't fit with a conventional soldering iron. But what about heating the samples under the microscope and using the needles as a soldering iron? So, simply using a bathroom tile and constantan wire, we constructed a sample heater. With the aid of a digital thermometer we could control the temperature. At first, we melted solder on a cover plate and tried to create paths with it. However, this attempt didn't work, because the

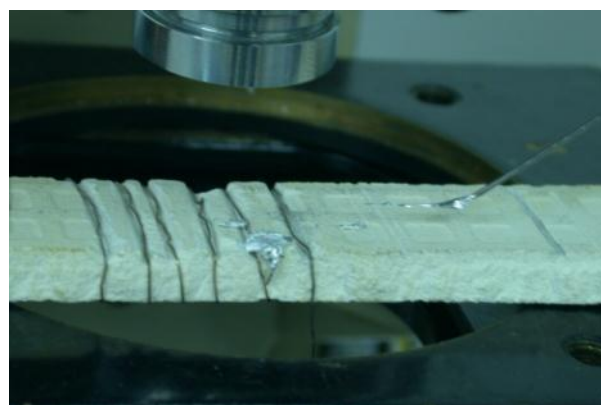


Fig. 4.3.3 Indium on our self-built heater

flux in the solder led to a formation of solder pellets. Besides, the solder melted at temperatures above 320°C, where graphene starts to decompose or roll up. Thus, it became clear that we needed a different material as solder. The requirements are a melting temperature of less than 200°C and a good adhesion on SiO₂. Tin and indium are two of the metals showing a comparatively low melting point. But as indium has the advantage to adhere on surfaces of glass and is already used in semiconductor technology to solder on glass, we decided to try soldering graphene with a piece of indium wire that was in our storage anyway. We melted down the wire on a glass support at 170°C until it became liquid. We first tried to draw conductive paths by manipulating the drop of Indium with our contact needle. The attempt failed, because the adhesion on glass was too good. However, by pulling the contact tip out of the indium again, a extremely fine indium tip was formed. By pulling slowly enough, it is possible to create tips with a length of several centimeters (Fig. 4.3.3). Now we were able to align the indium tips with a heated graphene sample and melt the tip onto the flake. The tips are fine enough to contact a large graphene flake at least twice (Fig. 4.3.4). With that, we actually achieved our goal! We had avoided the lithography and found a method, which enabled us to produce contacted graphene at school. The indium contacts offer an additional advantage: They have very thick ends, what makes it possible to contact these ends by soldering. Thus, we didn't even need our contact apparatus anymore, merely enabling a very instable contact on the lithographies two years ago.

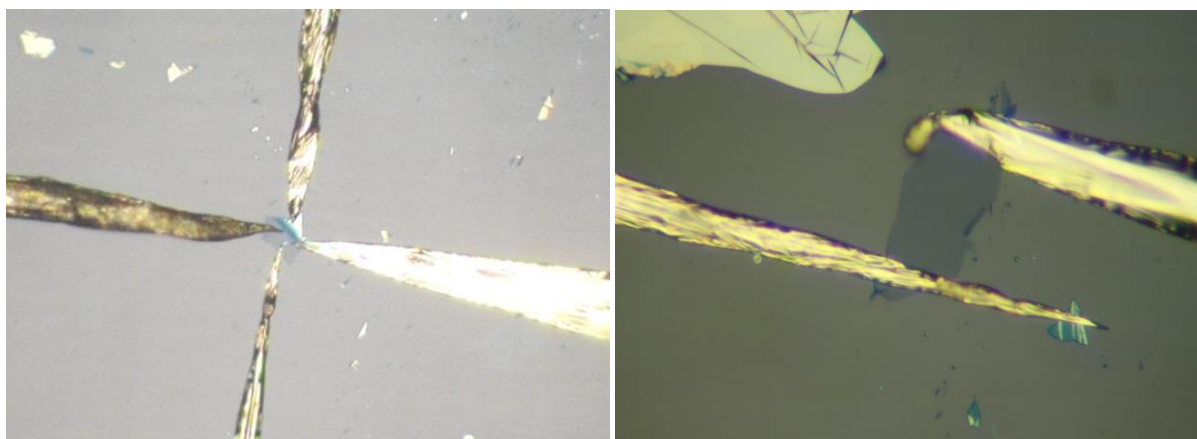


Fig. 4.3.4 Indium contacts on Graphene

As a result of our new contacting method, the idea of a completely new and simple contacting apparatus was born. The new equipment should be considerably smaller and should allow, contacting every sample as fast as possible without trouble. Furthermore, we wanted to avoid a wearing of the sample due to the contacting process. In our previous approach, we always had the problem, that the lithographies only could be used for a certain number of contacts until being scratched. The ideal solution for this problem would therefore be, to create the contact not on the sample but on wear-free material. We created a circuit board, to be used as sample carrier. We fixed the wafer in the middle on a big copper surface which serves as a back gate contact for the FET at the same time. Now we simply needed to solder from the indium to the contact pads on our circuit board. With this method, every sample is fixed on an own sample carrier, thus eliminating wear of graphene or indium contacts. The contact pads on the sample holder can be easily connected with screws.

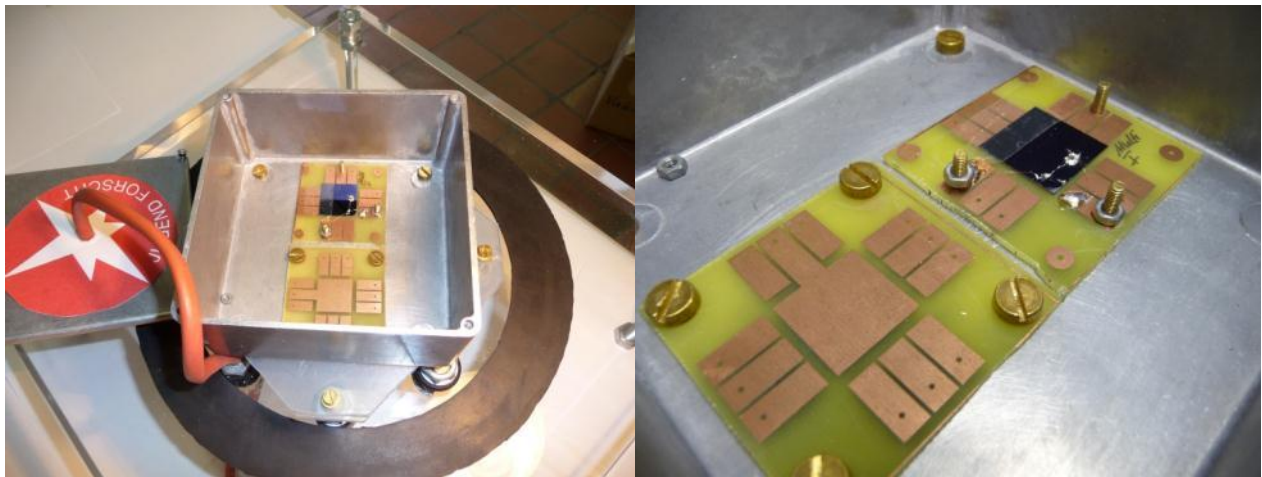
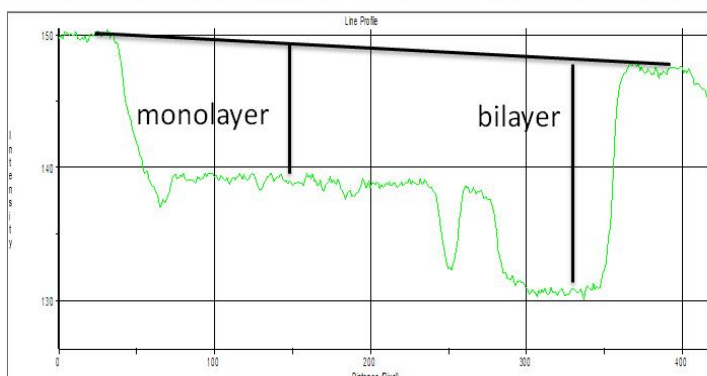


Fig. 4.3.5 Measuring arrangement and contact masks

The size of the measuring equipment could thus be minimized and it was now possible to establish an extremely stable electrical contact, so that the vibration absorbing table, we had to use before, wouldn't be needed anymore (Fig. 4.3.5). So we managed to optimize the whole production and contacting process so that it can be easily used in school laboratories. Thereby we achieved our goal to make graphene applicable for being used as an example for up to date research at school. Now, we could finally apply ourselves to the research of the electrical properties of graphene.

4.4 Monolayer Verification

With the aid of a good microscope and some experience, it is not too difficult to identify monolayers optically. Nevertheless it is necessary to have an objective measure to determine the number of layers. Graphene can be visualized on the wafers by an interference of the waves, being reflected on graphene, SiO₂ and silicon. The resulting contrast mainly depends on the thickness of the SiO₂ layer and the number of graphene layers. With the aid of image analyzing software we measured the intensity of the substrate and the flakes. The percentage divergence



of the intensity of our monolayers as measured on 90nm SiO₂ is about 5 and 8 percent. We compared this result with photos, we found on websites of companies selling graphene monolayers. It occurred, that the contrast of up to five layers is equal to the monolayer contrast multiplied by the number of layers. Thus, for bilayers, a contrast of about 10 and 16% - depending on the sample – can be expected. This is a free and easy method to prove monolayers without having to do an expensive Raman spectroscopy, which can also be used to determine the number of layers.

$$C = \frac{I_{\text{graphene}} - I_{\text{substrate}}}{I_{\text{substrate}}} \times 100$$

4.5 Graphene FET

The principle of a graphene field-effect-transistor consists of shifting the fermi level with an electric field and thereby changing the concentration of charge carriers. Since graphene is a semimetal, it is not possible to completely tune the FET to an insulating state. Nevertheless it is possible to change the resistance of such a device significantly. After subtracting a contact resistance of approximately $4\text{k}\Omega$ we estimated an intrinsic On-Off-ratio of about four for our graphene FET (Fig. 4.5.1).

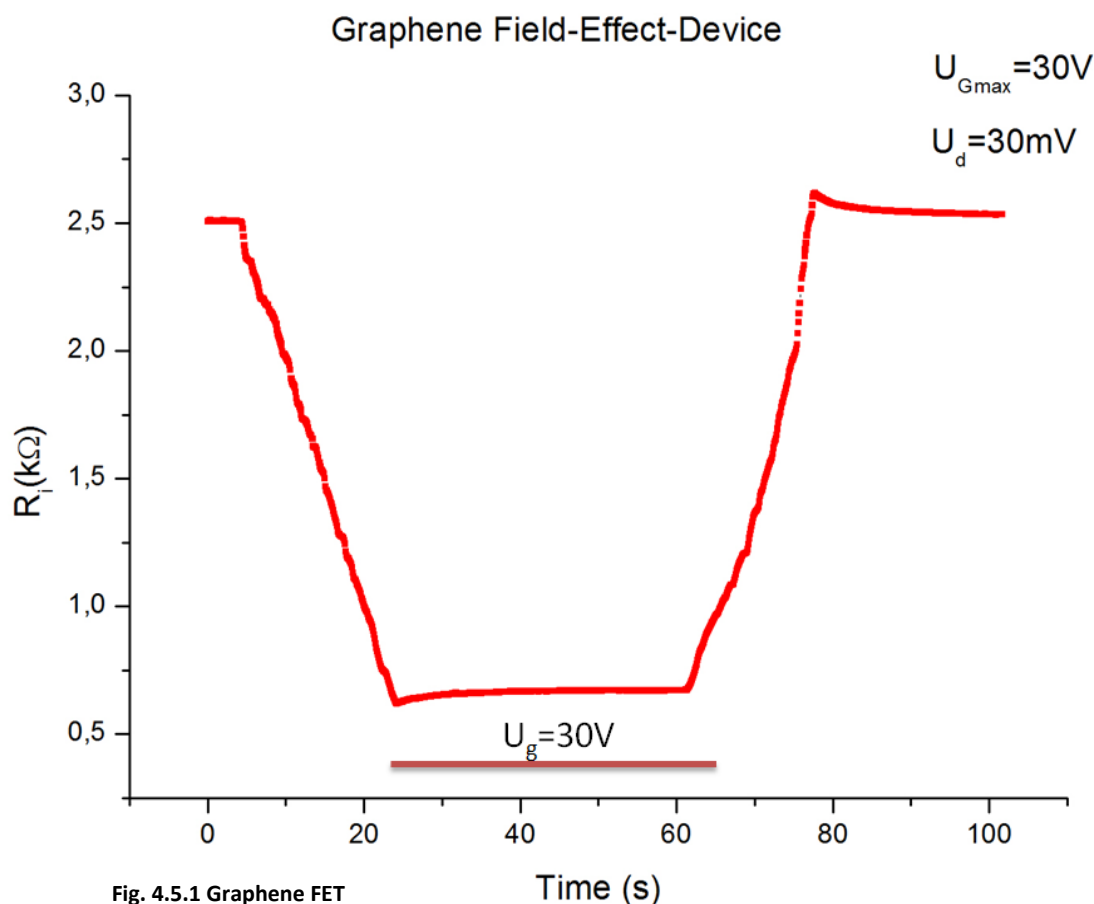


Fig. 4.5.1 Graphene FET

The measurement above does not only show a working graphene FET, it also demonstrates the quality of our Indium leads and our measurement setup. In order to improve our signal-to-noise-ratio and conduct measurements in a regulated atmosphere, we changed our setup and placed the graphene device in a faraday's cage inside a vacuum bell jar (Fig. 4.5.3). This greatly improved our measurements and allowed us to detect changes on the 10^{-8}A scale. Measuring in vacuum makes sure that adsorbates don't effect the measurement.

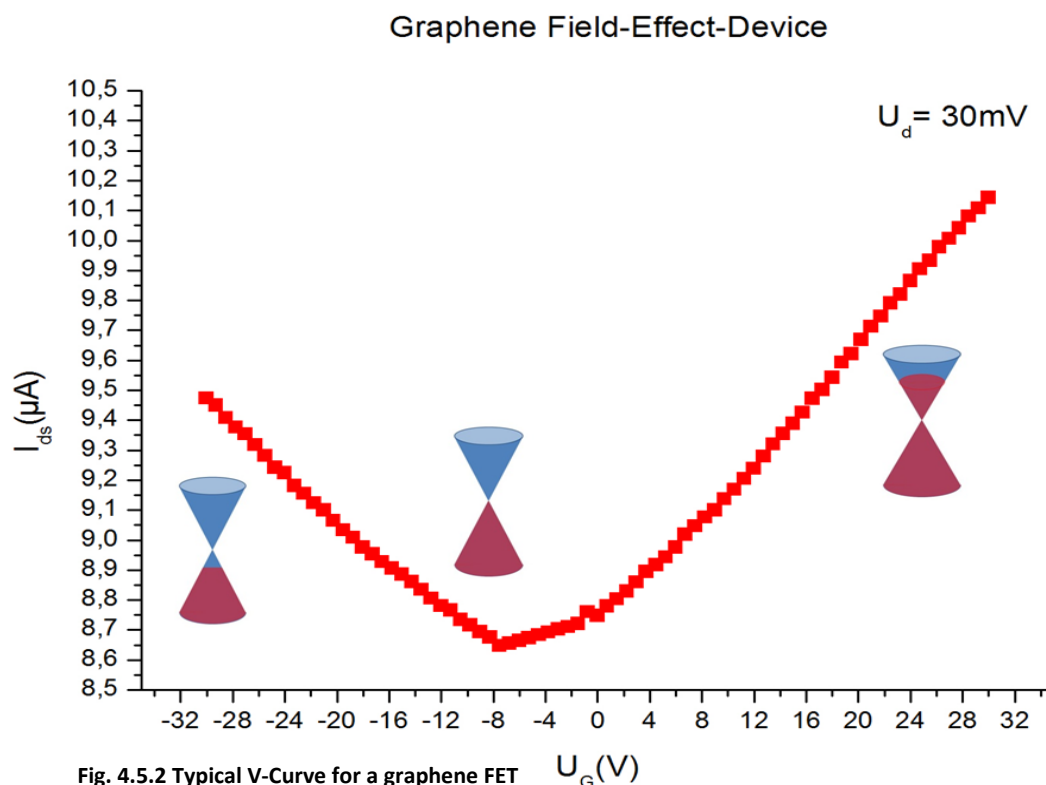


Fig. 4.5.2 Typical V-Curve for a graphene FET

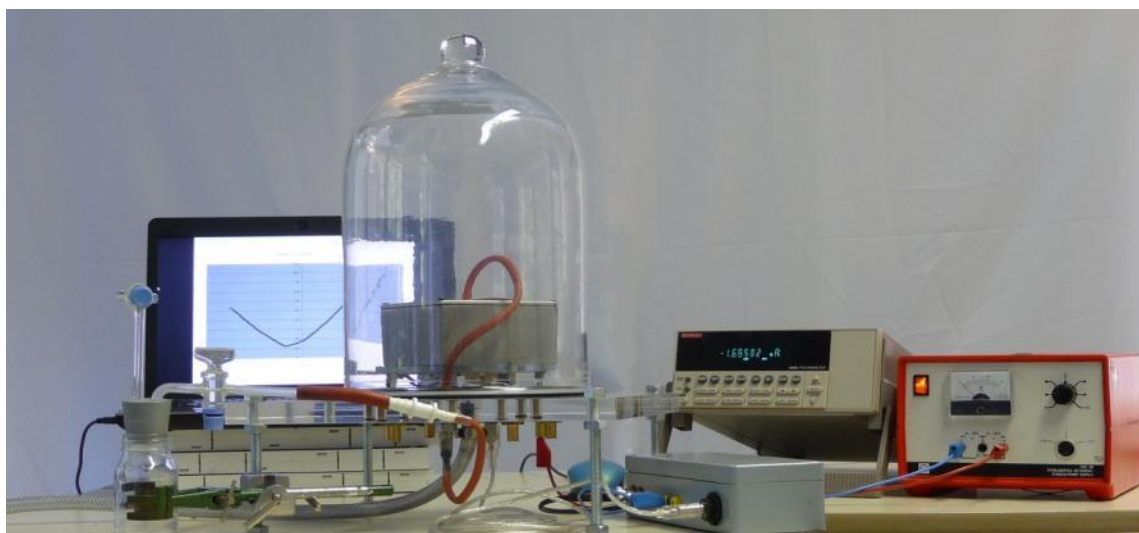


Fig. 4.5.3 experimental setup

In order to use graphene as a semiconducting material, several approaches to create an artificial band gap up to 0.5eV in graphene have been developed. One of them is to produce graphene nano ribbons (GNRs), which are essentially sub 10nm ribbons of graphene. Creating and contacting GNRs usually needs high-tech equipment such as e-beam lithography to define the ribbon and the leads. Recently a method that includes the electrochemical etching of GNRs with an STM was discovered. Since we had the opportunity to use an STM at a university, we tried to etch a GNR out of a HOPG crystal. In order to etch graphene or graphite with an STM, 2.5V tip voltage should be applied, and the tip velocity should be about 5nm/s. After optimizing our etching parameters we were able to etch a 7nm wide ribbon into the HOPG crystal Fig. 4.5.3. However, etching graphene is still a problem, since the STM tip would be driven into the insulating substrate, as soon as the conducting graphene is etched.

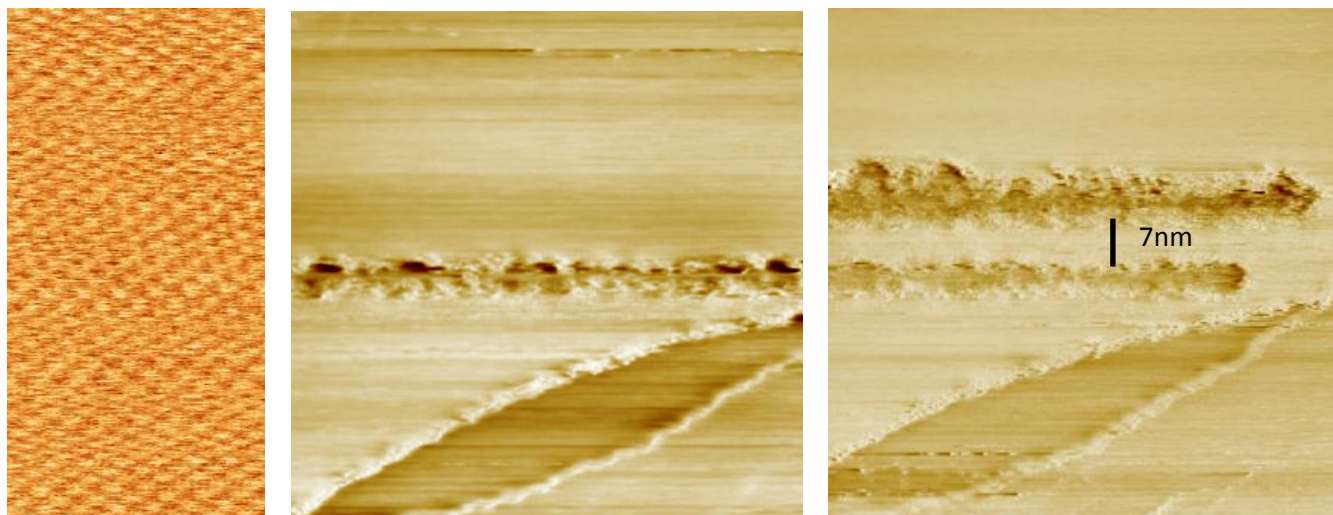


Fig. 4.5.4 STM image of HOPG: atomic resolution and etched structures in HOPG respectively

Another method to improve the FET is to apply a second gate on top of the graphene. The second gate amplifies the change in carrier concentration, when a gate voltage is applied. Since a school doesn't have the equipment to simply sputter a second gate dielectric onto the graphene, we decided to spin coat a polymer onto the graphene, using a magnetic stirrer. On top of the thin polymer film the top gate electrode was applied (Fig. 4.5.5.). Using the top gate instead of the back gate we were able to show a very weak field effect. Since our polymer film is at least several μm thick, the electric field is much weaker than the field of the back gate, which has a just 90nm thick gate dielectric. We were able to demonstrate a proof of principle with our top gate FET, but with methods available to a school it isn't possible to develop a high performance top gate FET.

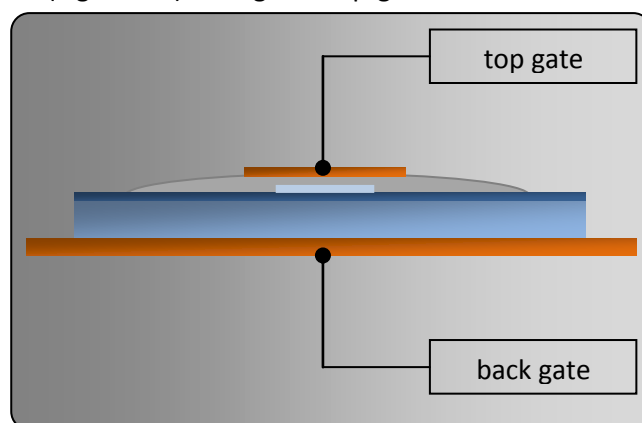


Fig. 4.5.5 Double gated FET

4.6 Sensor Applications

Because of the very low intrinsic noise and the fact that every atom in graphene is a surface atom, graphene is particularly suited for sensor applications, even for the detection of single gas molecules. The objective of our science project is to study our self-build graphene sensors with methods applicable at school. In order to gain experience in sensor applications of graphene, we decided to reproduce certain graphene based gas sensors that were already known for showing an effect before investigating on new effects. First we built a graphene based sensor for ammonia. The ammonia molecules are adsorbing on the graphene and thereby changing the carrier concentration and the resistance. After conducting measurements in a vacuum bell jar, we were able to demonstrate a strong effect of ammonia on the Fermi level in graphene (Fig. 4.6.1). The graph shows ammonia adsorbing on graphene (blue phase), and afterwards desorption phases in vacuum and under ambient conditions (beige and orange phase respectively). This measurement already shows the potential of graphene for sensor applications. A strong effect, even of small ammonia concentrations, as well as the fact that the current dropped back to the initial value after desorbing are very advantageous qualities of a sensor.

By now we built several additional gas sensors and we were able to detect small concentrations of NO_2 , CH_4 and H_2O (g). However, hydrogen gas and ammonia proved to show by far the strongest effect on graphene (Fig. 4.6.2).

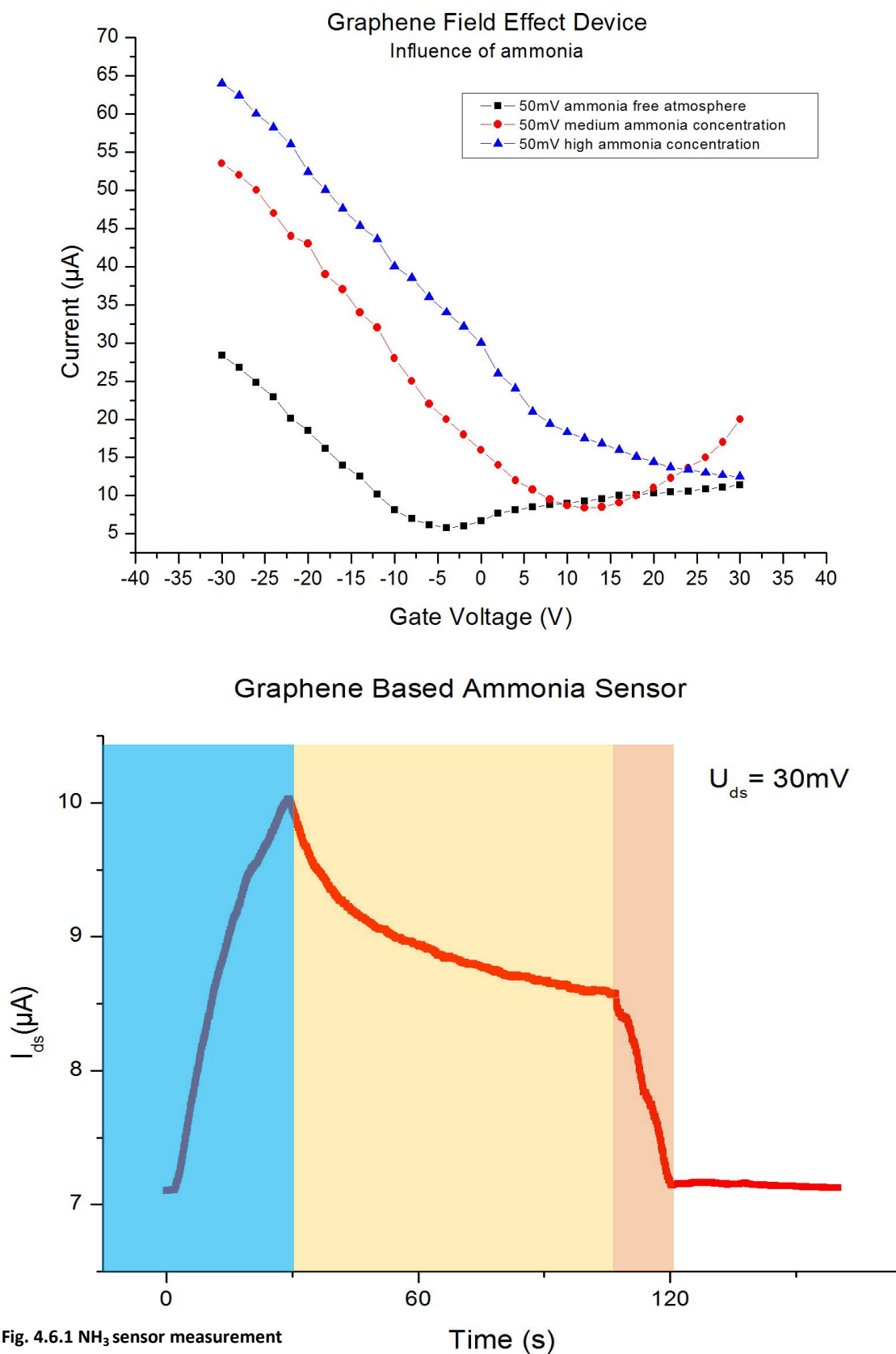
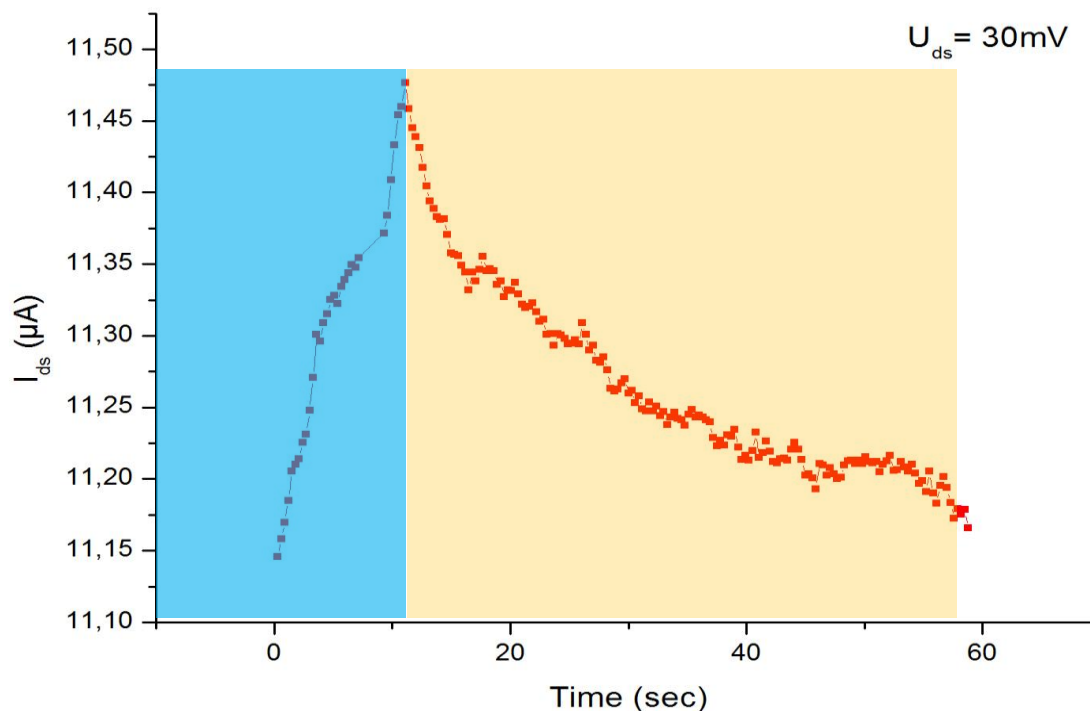


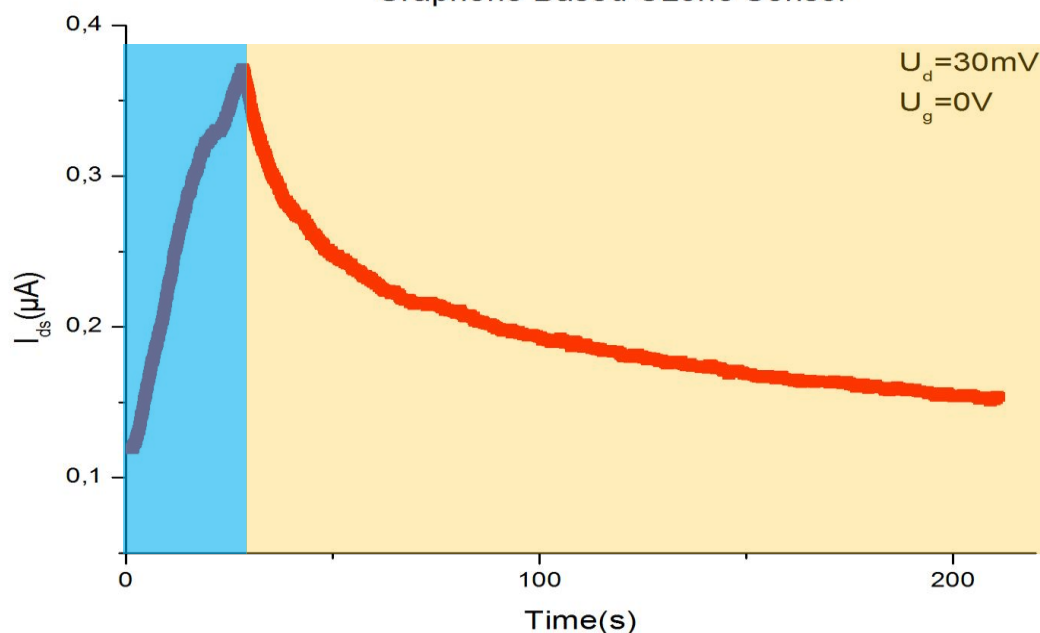
Fig. 4.6.1 NH_3 sensor measurement

Graphene Based Hydrogen Sensor



We discovered an interesting effect, when we studied the effect of light on graphene. When irradiating a graphene device with short UV wavelengths (centered around 254nm) we noticed a continuous increase of the current, after turning the UV light off, the current slowly dropped back to the initial value. Because of the slow desorption phase that was similar to a gas desorption, we concluded that the effect couldn't be caused by the UV-light directly (Fig. 4.6.3). Instead we assume that the UV-light caused oxygen to form ozone which adsorbed on our graphene device and changed the carrier concentration. In order to proof this hypothesis, we want to irradiate the graphene with UV light in an inert gas atmosphere. Since the UV light is not passing through the glass of our vacuum bell jar, a change in our setup is necessary.

Graphene Based Ozone Sensor



4.7 Large Area Synthesis of Graphene using CVD

In order for graphene to make the step out of basic research and into industrial applications, it is necessary to move from applying electrical contacts on flakes randomly produced by mechanical exfoliation to synthesizing large area graphene in a top-down approach, which can be patterned afterwards. Large area synthesis of graphene is being realized by chemical vapor deposition (CVD) on metal substrates that serve as catalysts. Experience has proofed that thin copper foil is particularly suited for synthesizing graphene monolayers. Since the carbon solubility in copper is low and the reaction is surface catalyzed by the copper substrate the reaction stops as soon as one layer of graphene is deposited. Similar to the CNT synthesis, a mixture of methane, hydrogen and an inert gas is streaming through a heated (approximately 1000°C) quartz reactor in order to synthesize graphene. Because of the high temperatures the methane decomposes to carbon, which is deposited as graphene on the substrate and hydrogen, which reduces oxides on the copper. The inert gas just serves as diluent gas for the hydrogen and the methane, so that the reaction can occur at ambient pressure. Our setup consisted of a quartz tube that served as reactor and which was heated with a standard Bunsen burner. Since our school doesn't have any flow meters, we had to mix the gases in the correct ratio ($\text{Ar:H}_2\text{:CH}_4 \approx 93:2:5$) in a glass cylinder. We used a glass displacement vessel in order to build up enough pressure to drive the gas through the reactor. Even though this setup didn't allow us to precisely control the gas flow velocity as well as the temperature, the CVD process was successful due to the strong catalytic impact of the metal substrate. However, even a small contamination with oxygen, caused by the dead volume in a gas syringe will react with the graphene to CO_2 . After we optimized our setup and determined the correct ratio of reaction gases, we successfully produced monolayer graphene on a centimeter scale. In order to check whether the CVD process was successful, we put our sample together with a regular piece of copper foil on a hot plate. After a few minutes the regular piece of copper turned its color due to oxidation, whereas our sample stayed shiny. This indicates that we deposited graphene, which serves as oxidation protection onto our sample (Fig. 4.7.1). In order to electrically characterize our CVD graphene, it is necessary to remove the conducting copper foil and transport the graphene to an insulating substrate. Using our Si/SiO_2 wafers as the new substrate is ideal, because we are able to actually visualize the graphene and we also would have a back gate for FET applications. Graphene can be transported by coating it with a polymer and etching the copper with an Fe(III)Cl solution (fig. 4.7.2). After the etching process, the graphene is attached to the polymer. The polymer is now rinsed in DI water and then baked onto a Si/SiO_2 substrate. Afterwards the polymer is dissolved in acetone and the transfer is completed. Now it is possible to optically characterize the graphene. Even with the naked eye, the graphene is visible on the wafer substrate (Fig. 4.7.3). Using a reflected light microscope, one can see that the graphene is not lying flat on the substrate, instead it is wrinkled and has several cracks close to the edges, which is probably due to the different thermal expansion coefficients of graphene and copper, as well as the fact that the graphene was synthesized on a rough copper foil and then transferred to a much flatter surface.

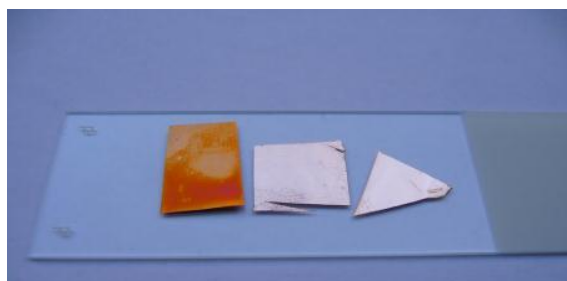


Fig. 4.7.1 oxidation test: oxidized piece of copper, CVD-Graphene, reference piece of copper respectively.

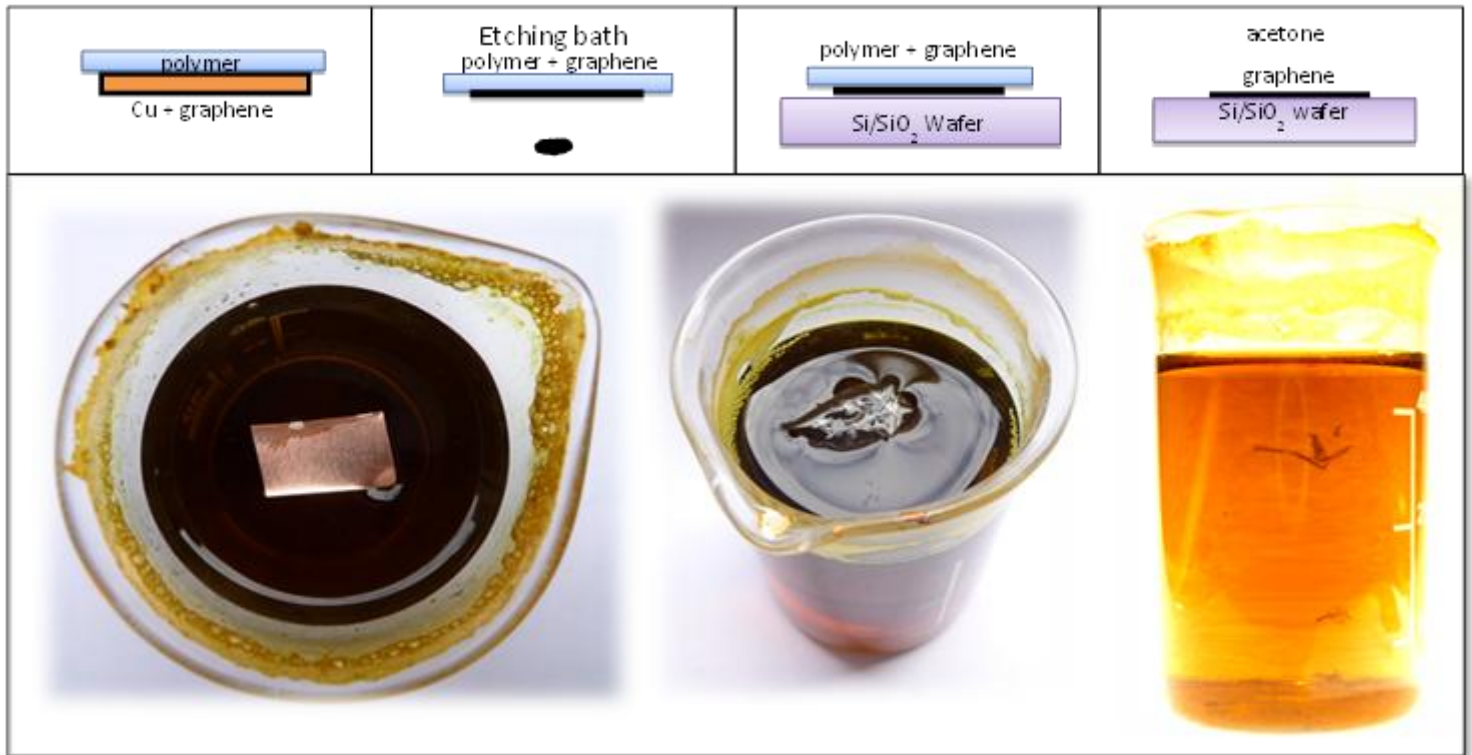


Fig. 4.7.2 schematic diagram of CVD-graphene

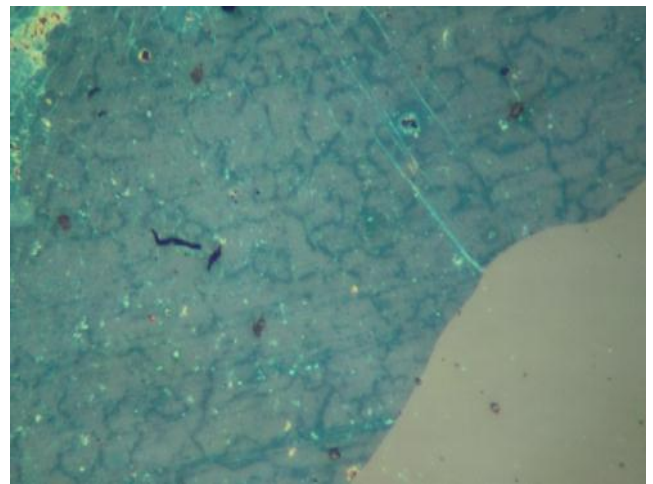
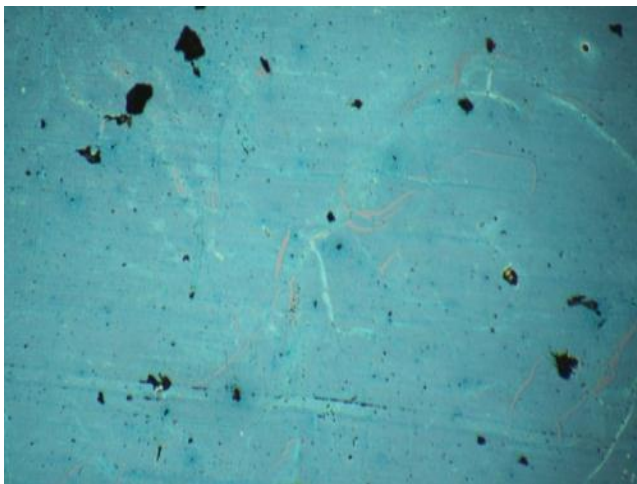
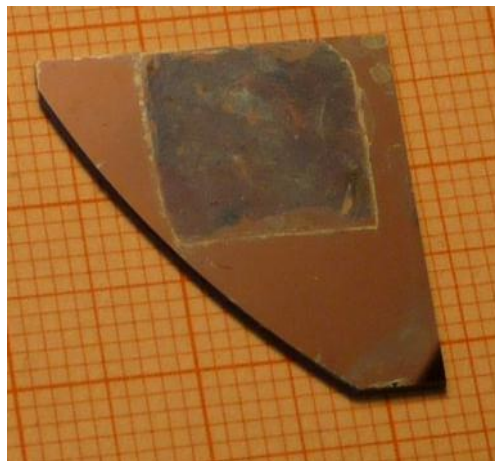


Fig. 4.7.3 CVD-Graphene with naked eye and under light microscope

In order to proof our assumption that we synthesized and transferred graphene, we asked the RTHW Aachen University to record SEM images and a Raman spectrum of our sample. With this data, we can be very certain that we achieved our goal of synthesizing graphene. The SEM images (Fig. 4.7.4) clearly show that there is a wrinkled layer like structure.

We were able to show a transition of the D-peak in the Raman spectrum (Fig. 4.7.5), which is a measure of lattice defects in graphene, from very high at the beginning to moderate by now. There is a discrete G-peak, which proofs that the layer consists of sp^2 hybridized carbon. Unfortunately the 2D-peak is very small, so we can't determine the number of layers from the Raman spectrum. Finally we deposited contacts onto our CVD graphene and build a well working sensor for ammonia (Fig. 4.7.6).

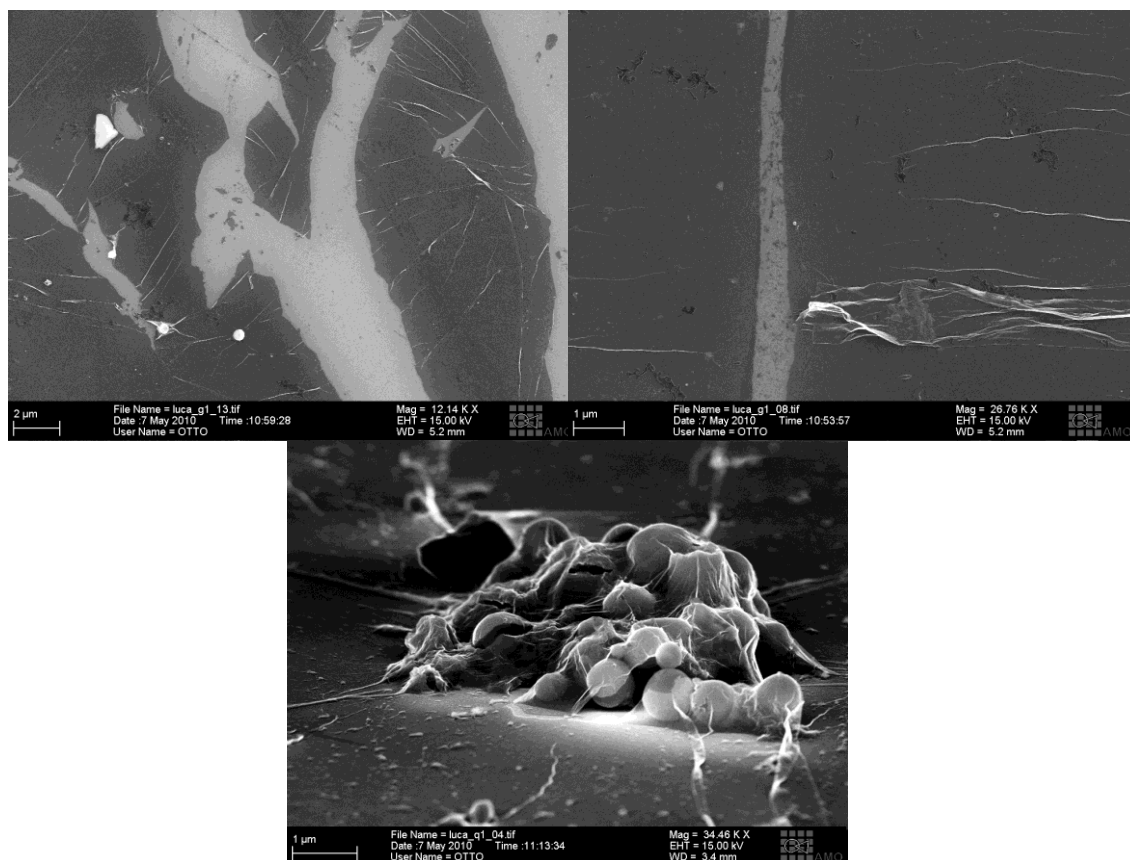


Fig. 4.7.4 SEM images of CVD-graphene on a Si/SiO₂ Wafer:

1. Wrinkles in graphene
2. Enlarged crack & wrinkle
3. Fe(III)Cl residue under a graphene layer

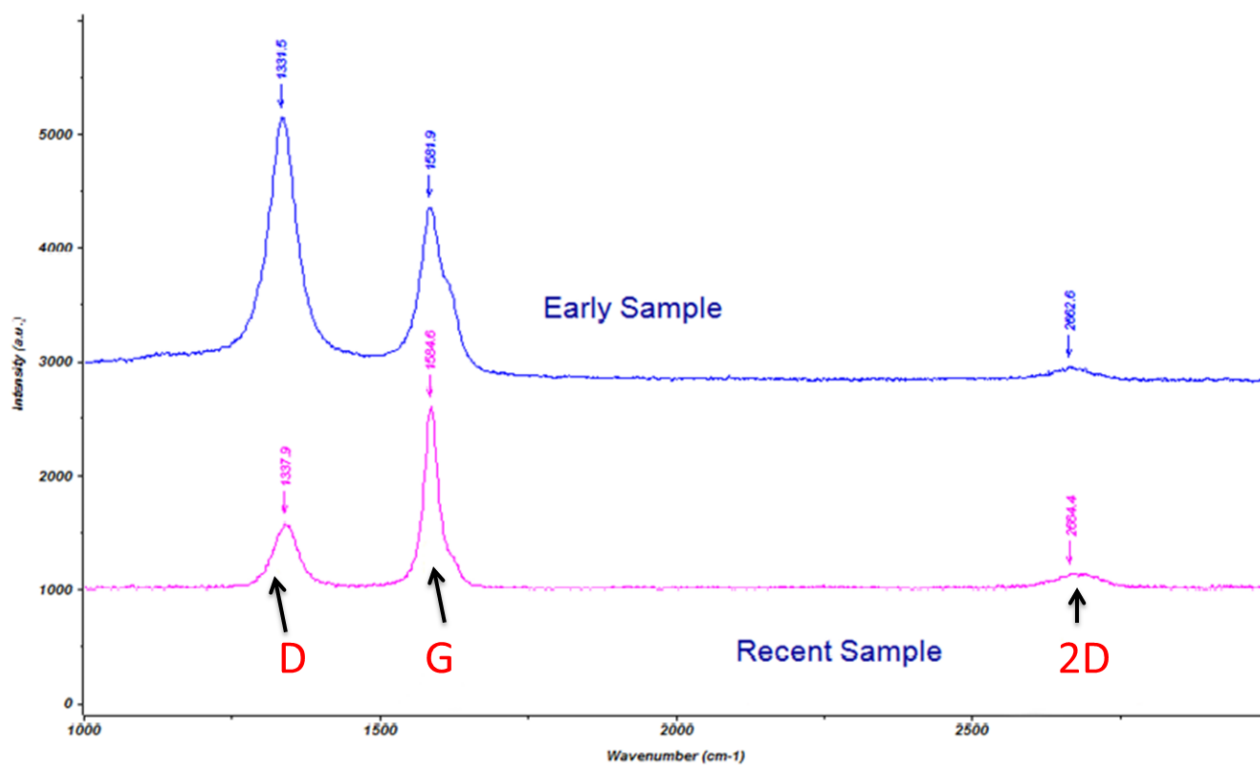


Fig. 4.7.5 Raman spectrum of the CVD graphene

CVD-graphene based ammonia sensor

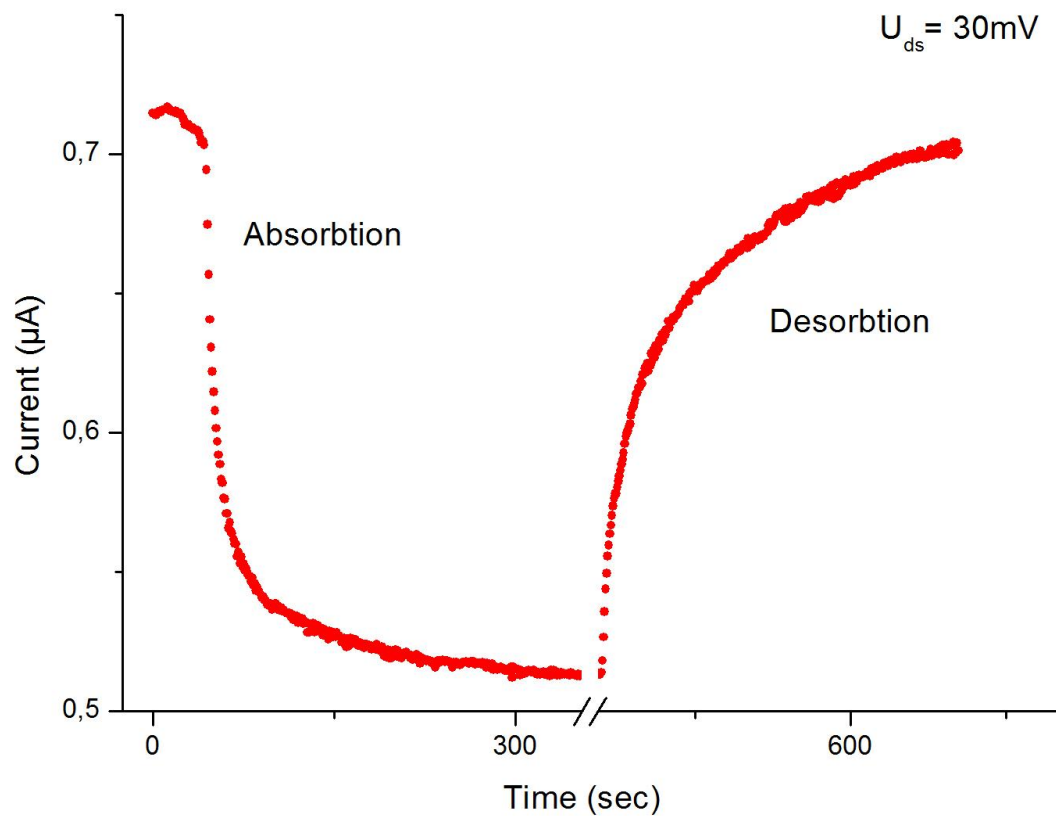


Fig. 4.5.7 CVD graphene based NH₃ sensor

5. Conclusion

We achieved our major goal to produce, contact and characterize multiple graphene devices with methods that are available at school. We found a method to replace optical lithography and Lift-off with a simple method that allows applying contacts to multiple flakes on one sample. Our experimental setup shows a high reliability and a great signal to noise ratio. We created known as well as new graphene devices in a quality that is comparable with devices produced by professional R&D scientists. The method to determine the number of layers in a graphene flake optically is extremely advantageous, because it allows us to differentiate between monolayers and fewlayers before we electrically connect them. Synthesizing graphene on a large scale enables us to conduct research for other applications of graphene e.g. oxidation protection, as a coating for electrochemical electrodes and as transparent electrode.

6. Prospect

Until we present our project to the jury, we want to increase the quality of our CVD graphene, by using thinner and flatter copper foils as well as optimizing the process parameters, such as temperature and gas flow velocity. Eventually we will be able to improve the transfer of graphene from one substrate to another as well. This would allow us to investigate material science applications of graphene such as oxidation protection and coatings for electrochemical electrodes.

7. Acknowledgement

We want to thank our teacher Walter Stein, who motivated and supported us whenever we needed his help. Thanks to Dr. Ingo Braun, who provided us with an reflective light microscope. Without him we wouldn't have been able to see our graphene. We thank Tobias Plötzing and Christopher Matheisen from the Institute of Semiconductor Electronics of the RWTH Aachen, who offered us to use their STM. We want to thank Martin Otto from AMO Aachen Ltd. for taking SEM pictures and a Raman spectrum of our CVD graphene. Finally we thank Egbert Hiemann from the Institute of Semiconductor and Microsystems Technology of TU Dresden.

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