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**The role of oxidation treatments before and after CVD
synthesis of graphene on copper catalytic surface**

Bachelor's thesis and research
project
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Abstract

Graphene is a sheet of honeycomb bonded carbon, that is only one atom thick. Aside from its remarkable strength, graphene has great conducting and photochemical properties. Due to its unique properties, it can be used as viable option for rare metals in circuits and in new type of measuring components. To express these properties at their best, graphene should be single crystal and as clean as possible.

In this bachelor thesis, different treatment options for catalytic metal surface for graphene synthesis are studied in chemical vapor deposition growth. Different options to treat the catalytic metal layer were studied, such as changes in gas compositions in annealing process, electropolishing, plasma and UV-light treatment. All the processes effect the oxidation level of the surface. Different catalytic metals can also lead to higher quality graphene. Synthesised graphene can be cleaned from amorphous carbon by treating it with carbon dioxide or changing the carbon precursor for the chemical vapor deposition process.

In the experimental part, the effects of higher concentration of hydrogen during synthesis was studied. Higher concentration of hydrogen led to lower nucleation density of graphene, but the catalytic copper surface was damaged in these processes. After synthesis, annealing under carbon dioxide flow was studied as a means of cleaning the surface. It was found to reduce amorphous carbon in the product but it increased the manifestation of double layers.

Prologue

This bachelor thesis and research project were done to the department of chemistry and the nanoscience center of university of Jyväskylä. The thesis and research project were done during the spring of 2021. Project was performed mainly in the nanoscience center clean room and atomic force microscope. Also Raman spectrum of the department of chemistry was used in the project. Research was mainly done by using google scholar and JYK.doc services. Supervision of the work was done by senior researcher Andreas Johansson.

I would like to thank Andreas Johansson for great guidance during this project and for the opportunity work with an interesting and topical project. I would also like to thank postdoctoral researcher Erich See for the training for the atomic force microscope. I would like to present my greatest gratitude to laboratory technician Olli Rissanen, who single handily taught me the copper chip synthesis, the growth process, transfer process and use of the Raman spectroscope, as well as provided me with data from the laboratory.

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Abbreviations and terms

Abbreviation	Meaning
CVD	chemical vapor deposition
nm	nanometers
PMMA	Poly(methyl methacrylate)
sccm	standard cubic centimeters per minute
α -Al ₂ O ₃ (001)	Alpha aluminium oxide
GCD	Graphene crystal domain
UV	Ultra violet light

1 Introduction

Among the elements in periodic table, you can argue that carbon might be the most important element, when talking about the planet that we live on and its history. The basis of life on this planet resides in the organic compounds that are capable to form and function because of the unique properties of carbon. Carbon is present in all natural biological reactions and lifeforms. Our current world is depending on carbon as much as ever. Aside from the fossil fuels that are used to power our everyday life, carbon is also studied in many forms. For example, in medical field, many medicine and vaccines have carbon based carrier molecules and new treatments to diseases are developed using nano-scale structures that utilize carbon. Carbon can also be used in circuits, where the most common use is the one molecule thin sheet, graphene.

Graphene is a sheet of carbon that is bounded in honey comb formation, and it has a thickness of one atom. Graphene has great fracture strength compared to its simple structure. However, pure and clean graphene is very hard to synthesize. Common synthesis methods struggle with the problem of polycrystalline graphene formation, where the graphene is formed from multiple crystal domains.¹ Theoretical calculations show, that single crystalline graphene has higher fracture strength than polycrystalline graphene. Creating larger and fewer crystal domains increases the fracture strength of a single graphene sheet.^{1,2}

A commonly used method of graphene synthesis is chemical vapor disposition (CVD). In CVD synthesis, 2D materials are synthesised in well controlled and pressurized atmosphere. Major factors in CVD include the temperature and pressure of the synthesis, the precursor and the carrier gases of the synthesis and the catalyzing substrate.³ In graphene CVD synthesis, most commonly used catalytic substrate is copper (Cu) due to the carbons low solubility to Cu.^{3,4,5} This study was done to find methods to increase large grain growth on the catalyzing Cu surface via oxidation and to study alternative methods of Cu preparation and improvements to graphene quality.

Literature part

2 CVD growth of graphene on Cu

Catalytic Cu surface has two roles in the CVD graphene synthesis. First, it reacts with the precursor gas in the CVD process without mixing with it, making it a good catalytic substrate. Second is the control of crystal-domain formation on its surface.³ Cu functions as a good base due to its low carbon solubility of about 7 ppm at 1050 °C.⁴ Favourable compositions of Cu for graphene synthesis is Cu(111) that provides a hexagonal growth template to the graphene.⁵ Using oxidation treatment, the roughness of the Cu films can be reduced to 1.3-3.8 nm which allows better single crystal formation of graphene.⁴

2.1 Cu catalyst film with large grain sizes

The following method is described in the article "Giant secondary grain growth in Cu films on sapphire" by David L. Miller.⁵ A Cu surface is created on top of α -Al₂O₃(0001) surface. α -Al₂O₃(0001) is annealed at 1100 °C in O₂ atmosphere in atmospheric pressure for 24 h to create a clean and flat surface to attach the Cu film. After treatment, α -Al₂O₃(0001) wafers are mounted on above a heated Cu puck and placed in a vacuum sputter deposition system. Films are coated using 99.999 % of pure Cu. Average thickness of the films was between 430 nm and 500 nm. Depending on the temperature, different films are treated in different ways. Films that have temperature below 500 °C, are deposited in a turbopumped chamber, that has base pressure of 2×10^{-9} mbar and sputtering power of 100 W in 1.7×10^{-3} mbar of Ar. Films that have temperature equal or higher than 500 °C, are deposited in a cryopumped bell-jar-style chamber, with base pressure of 2×10^{-8} mbar and sputtering power of 200W in 6.7×10^{-3} mbar of Ar. Deposition temperatures are reported using a thermometer contacted to a sample puck. After deposition, each wafer is coated with Poly(methyl methacrylate) (PMMA) and diced to 5mm x 6mm chips. The chips are stripped from PMMA and cleaned using ultrasonic agitation in acetone and isopropanol before characterization and annealing. Annealing is performed in a hot-wall tube furnace with a base pressure of 6.7×10^{-3} mbar at temperatures between 950 °C and 1050 °C for 40 min. To suppress Cu sublimation, total pressure of 53 mbar is maintained while flowing 500 sccm 99.999 percent pure Ar and 11 sccm of 0.2% H₂ in Ar, yielding a H₂ partial pressure of 2.3×10^{-3} mbar. Graphene is synthesised from mixture of AR and methane (CH₄) that has flow rate of 14 sccm, making the partial pressure of CH₄

2.8×10^{-3} mbar. Graphene growth is performed in temperature of 1055 °C for 40 min. All gasses are filtered to avoid O_2 and H_2O contamination. The product of this method can be seen in figure 1.

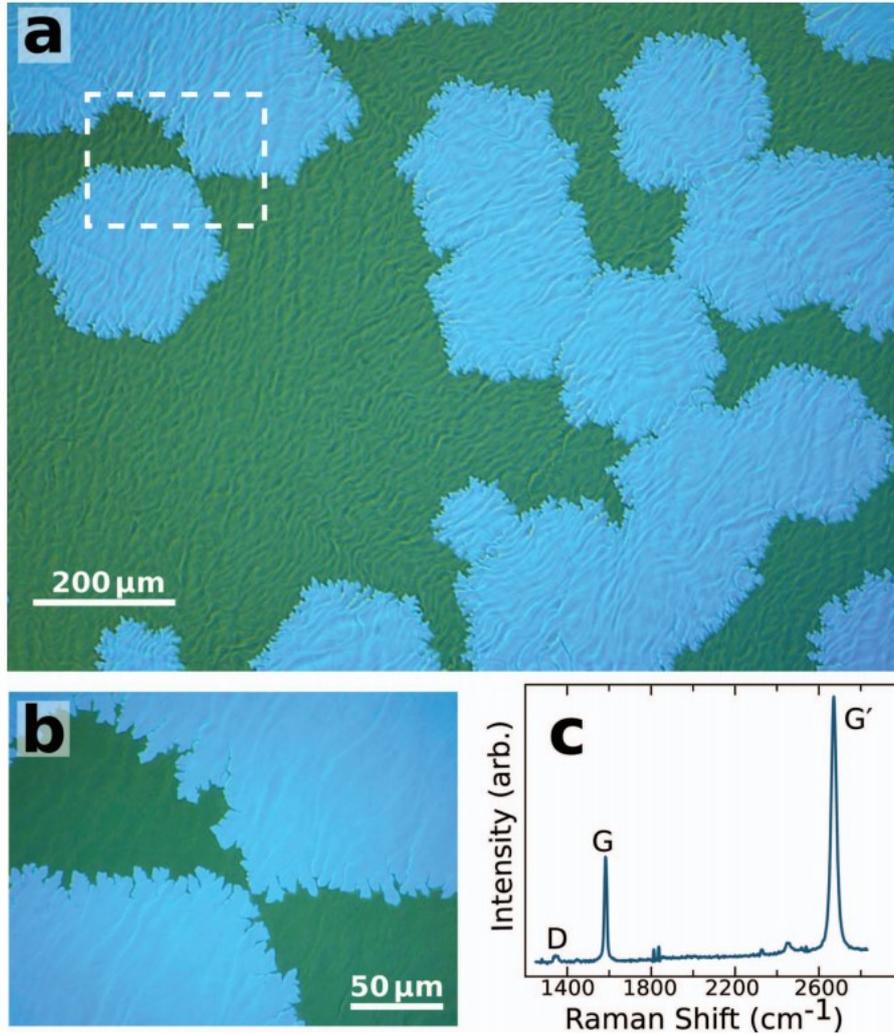


Figure 1. Graphene growth on giant-grain Cu(111) films. (a) Optical image using differential interference contrast of graphene on Cu after oxidation. Oxidized Cu appears darker than regions covered by graphene. (b) Higher magnification image of the region of (a) in the dashed box. (c) Raman spectrum of graphene after transfer to SiO₂ substrate. Taken from ref. 5.⁵

2.2 The role of oxygen in graphene synthesis

Formation of the graphene from precursor CH_4 is based on the dehydrogenation of the carbon atom. When a high amount of oxygen is present on the surface of the Cu film, the reaction on the Cu surface starts to change to opposite direction. This causes the

oxygen to react with the most favourable substance.⁶ In our case, this means the hydrogen that is bonded to the CH₄ molecules. The reaction equation for this phenomenon goes as follows:⁶



In the equation, $x = 1-4$ hydrogen atoms. A highly oxidised Cu surface helps to lower the attachment energy of the graphene during the formation and reduce the nucleation density.⁷ Higher amount of oxygen in the Cu also speeds up the nucleation rate.⁷ The oxygen concentration influences the shape of the forming graphene. Higher concentration of oxygen leads to formation of more complex graphene crystals, which are shaped like snowflakes.⁷ This can be compensated by control of the deposition flux. Lower deposition flux can help to create complex graphene crystals and in the opposite, the higher deposition flux can create more round shaped domains.⁷ The last major factor in the synthesis is surface diffusivity. Diffusivity is dependent on the temperature of the synthesis. Decreasing diffusivity factor creates more snowflake like irregular crystals.⁷ Careful balancing between these three oxygen factors is key to create wanted hexagonal shaped graphene crystals.⁷

Oxygen is also used to clean impurities from the synthesized graphene sheet. When carbon impurities, which may form on top of the graphene during the synthesis, are treated with atomic oxygen, the bonds to this waste creating more easily cleanable waste molecules are created, for example epoxies, carbonyls and lactones.^{7,8}

3 Effect of gas composition changes to oxidation

In CVD, the environment of the synthesis can be easily controlled in order to change the different components and factors of the reaction. One way is to change the atmospheric compositions by changing the partial pressures of used gasses. In our method, the gasses used in CVD-synthesis are argon (Ar), hydrogen(H₂) and methane (CH₄).⁴

3.1 The role of Ar during Cu annealing

Ar is the main atmospheric gas in the synthesis, thus its partial pressure is preferable to be kept stable for most of the reactions.^{4,5} In the annealing process, the temperature of the Cu substrate gets very high, up to over 1000 °C, and the surface of the Cu becomes more reactive as it reaches close to its melting point of 1084 °C.⁴ Annealing in a reactive gas field causes the Cu surface to oxidize. Cu starts to react with the atmosphere before it reaches the annealing point, causing premature oxidation. This can be avoided by heating the Cu in inert Ar atmosphere, thus preventing any substances to react with Cu before the annealing process. This decreases the density of graphene crystal-domains, allowing more room to grow larger crystals.^{5,9} The duration of the annealing process is a major factor in the synthesis. Longer annealing time decreases the nucleation density of the graphene. This phenomenon is caused by the formation of Cu₂O on top of the Cu surface during the annealing. The oxidation reaction that happens on the surface is an equilibrium reaction[1].^{6,9}



This reaction is pushed towards the Cu₂O by increasing the Ar gas pressure. Equilibrium state for this reaction at 1035 °C when oxygen partial pressure is 0.001 mbar.⁹ When Cu is annealed in higher temperature and under Ar atmosphere, the balance of the reaction tilts to the right side of the equation, thus preventing the reduction of the surface. Annealing the Cu in pure Ar atmosphere lowers the domain sizes of the Cu, thus making less favourable positions for graphene to form.⁹ The best result for the annealing process is achieved when H₂ gas is introduced to the process.^{9,10} Ar atmosphere is crucial in the heating of the Cu to the annealing temperature, as it prevents unwanted Cu surface reactions.⁹

3.2 The effect of adding H₂ during annealing of Cu

Controlling the flow rate and partial pressure of H₂ has an effect on the oxidation of Cu surface during the annealing process. H₂ has two roles during the graphene synthesis. It

activates the surface bonding carbon that leads to monolayer growth and helps to control the size and morphology of the formed graphene.¹⁰ Used H₂ gas must be very pure, because oxidizing compounds mixed in the gas can lead to unwanted surface oxidation and unfavourable grain growth.⁹ By applying a H₂ partial pressure below 1.5 mbar, H₂ molecules help O₂ molecules to bond to the surface.^{9,10,11} A major difference is experienced when the partial pressure of H₂ is raised during the annealing process. With partial pressure of 60 mbar and flow rate of 200 sccm, H₂ reduces the Cu surface.¹⁰ This impacts the reactivity of the Cu surface greatly and makes it cleaner by removing impurities.^{10,11} The reaction on the surface happen according to the following equation:¹¹



High H₂ pressure and flow rate are not suitable for graphene growth.^{10,11} This is, because high pressure of H₂ gas prevents the spontaneous formation of the graphene and high flow rate destroys the forming domains before they are able to grow.¹⁰ The solution is, to perform the annealing and graphene synthesis in different H₂ environments. Notable difference in the nucleation density is experienced, when Cu foil is treated with two different H₂ environments. During the annealing process, Cu is treated with higher partial pressure and flow rate of H₂. This causes the oxidation level to decrease, due to the supersaturation of the Cu film.^{10,11} After annealing, the pressure of H₂ is lowered to less than 2 mbar and flow rate is lowered to be less than 1:10 of the Ar flow. This makes the surface of the Cu highly susceptible to oxidation and oxidized peaks on graphene become main point of graphene crystal growth.^{10,11} The nucleation density of graphene decreases up to 62 %.¹⁰

3.3 CH₄ as precursor for CVD of graphene

Graphene is synthesized from CH₄ gas with a partial pressure of 3x10⁻³ mbar.⁴ Growth of single crystal graphene correlates positively to the partial pressure of the CH₄ gas. Higher partial pressure increases the crystal size of graphene. Increase in partial pressure forces larger amounts of CH₄ to react on the Cu and form graphene crystals faster. Higher growth pressure also decreases the nucleation density of the graphene. This can positively effect

the formation of larger graphene crystals.^{12,13,14} This growth pressure must be achieved with balance between H₂ and CH₄ gasses. A study shows, that the H₂/CH₄ ratio should be on the large. When turned into numbers, the high ratio of 8 is more suitable to graphene growth than 0.125.¹⁴ This is supported by the fact that higher H₂ concentration can prevent and etch away small graphene formations, that don't have enough binding energy to sustain large crystal, thus decreasing the nucleation density of graphene.¹⁰

4 Electropolishing coupled with oxidation

4.1 Basics of electropolishing

Electropolishing is used to polish metal surfaces by running current between two electrodes. Between the electrodes, there is the metal film and a small amount of liquid electrolyte, for example an acidic compound. The voltage from electrodes causes the electrolyte to react with the metal surface and grab ions, especially from the protrusions in the surface, thus polishing and smoothing it in the process.^{15,16} (Figure 2) When treating a Cu surface with electropolishing, the treatment works best with low viscosity acidic solutions and with short treatment times.¹⁵ One suitable solution is for example phosphoric acid.¹⁶ Smoothness is also effected by the voltage, that should be about 8 V, and electric current, that should be 0.40-0.45 A/cm². Optimal time for the electropolishing is about 120 s. Using this method, it is possible to reduce the surface roughness up to 99.3 percent.¹⁵

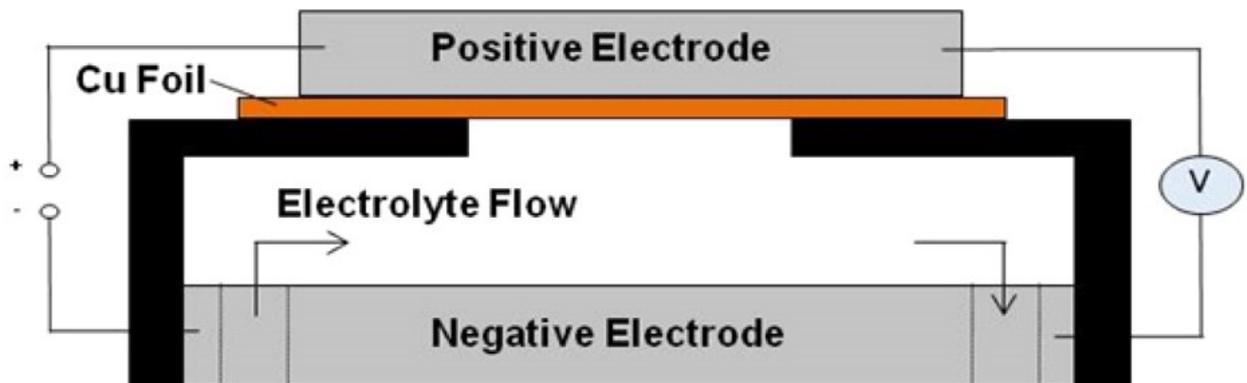


Figure 2. The schematic of basic electropolishing system. Reprinted (adapted) with permission from riep, M. H., Sandoz-Rosado, E., Tumlin, T. M. and Wetzel, E., Enhanced Graphene Mechanical Properties through Ultrasooth Copper Growth Substrates, *Nano Letters*, 2016, 16, 1657–1662. Copyright 2016 American Chemical Society.¹⁵

4.2 Benefits of electropolishing and oxidation combination

Electropolishing is a good way to reduce nucleation density in the synthesis by eliminating surface roughness.^{15,16} This does effect the formation of the crystal-domain but the formation of graphene still has high nucleation density.¹⁶ The main advantage of oxidation of the surface of Cu, is to create stable growth domains and reduce unwanted crystal-domain formation.⁶ By combining electropolishing and surface oxidation, the problems that occur in both methods, could be fixed. The polished surface would allow greater area of oxidation of the Cu and this would reduce the nucleation density.^{6,16} The major draw back, of the oxidation reaction is the surface roughening of the Cu. Oxidation of the surface causes deformation on the Cu surface with the formation of Cu_2O . However, this does not effect the entire grain size negatively. On average, surface oxidation and electropolishing produce larger grain sizes of graphene than electropolishing treatment alone. This comes at a cost, with longer growth time of the graphene crystals, but at the same time the nucleation density drops significantly.

5 Plasma treatment

5.1 Bases of plasma treatment

Plasma treatment is an optional method of Cu film preparation for the CVD synthesis of graphene. In plasma treatments, the Cu film is exposed to an intensive plasma at low pressures and the Cu surface react with the plasma.^{17,18,19} Depending on the pressure, pretreatment and the used plasma, different surface conformations can be achieved.^{17,18}

5.2 Pre synthesis plasma oxidation

An optional method for Cu surface oxidation is plasma treatment. The plasma treatment is performed in two stages. The first stage is treating the surface with O₂ plasma. This causes supersturation of O₂ at the surface and oxidation starts to occur.¹⁷ In the second stage, the surface is treated with another type of plasma that favourably consists of a noble gas, such as helium or argon, and the Cu is cooled in same atmosphere. This causes the oxidation levels to stabilize and prevents further oxidation.^{17,18} The plasma treatment increases the oxidation on the Cu surface with Cu₂O domains. The size of the Cu₂O domains is affected by the time under plasma treatment. Longer time under the effects of plasma increase the area of the domains.¹⁸ Major difference of the oxidation with plasma is the higher surface roughness. The roughness of the surface can increase up to 430 nm and if substrate is not properly treated, the roughness can be in the scale of micrometers.¹⁷

5.3 Pre synthesis plasma deoxidation

Plasma treatment can produce a deoxidized surface with the right kind of treatment.¹⁹ The Cu foil is favourable to be pre-treated to reduce the roughness of the surface. This can be achieved for example with electropolishing.^{12,15} The Cu film is then exposed to plasma in low pressure environment (4-5 mbar) for 40 min. This causes the surface to deoxidize and form CuO domains. After the plasma treatment, Cu is annealed in Ar and H₂ atmosphere with temperature of 1000 °C for 30 min. This produces a very low oxidized Cu film. The graphene synthesis on top of the film is faster than common methods, with growth time of 2 h and forming maximum grain size of 5 μm.¹⁹

5.4 After synthesis plasma treatment

Plasma treatment with O₂ plasma can be applied after the graphene synthesis. Graphene is synthesised using CVD and the Cu and the graphene are moved to a plasma cleaning system after the synthesis. Graphene is treated with O₂ plasma etching under low pressure environment. The plasma affects first on the surface of the graphene oxidizing it. Oxidizing the graphene causes the edges of the crystal-domains to go through hybridization from

sp^2 to sp^3 . When domain edges are oxidized enough, plasma moves through the edges under the graphene and to the catalytic Cu surface. When Cu oxidization reaches certain point, the amount of sp^3 has risen enough, that the graphene starts to detach from the Cu surface. The Cu surface interactions with O_2 causes the graphene to have sp^3 hybridized edges that have less bonds than their hybridized levels allows. This causes the edges of the crystal-domains to bridge with each other, creating more monolithic graphene sheet.²⁰ This mechanic is illustrated in figure 4.

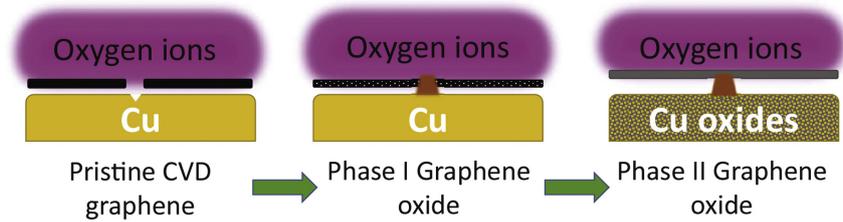


Figure 4. Schematic presentation of graphene oxide formation from CVD synthesized graphene on Cu via oxygen plasma etching. From before the etching (left) to when edging is started and plasma oxidizes the defect sites (middle). Final stage, where oxidized Cu and graphene bridging occurs. From ref. 20.²⁰

6 Photocatalytic oxidation

In photocatalytic oxidation, wavelenghts of UV and visible light are used.^{21,22} The reaction is performed under a light source and oxidizing environment, like liquid mixture of TiO_2 or atmosphere of O_2 . The deoxidation reaction is illustrated in figure 4. Depending on the environment, different wavelenghts of light are used.^{21,22}

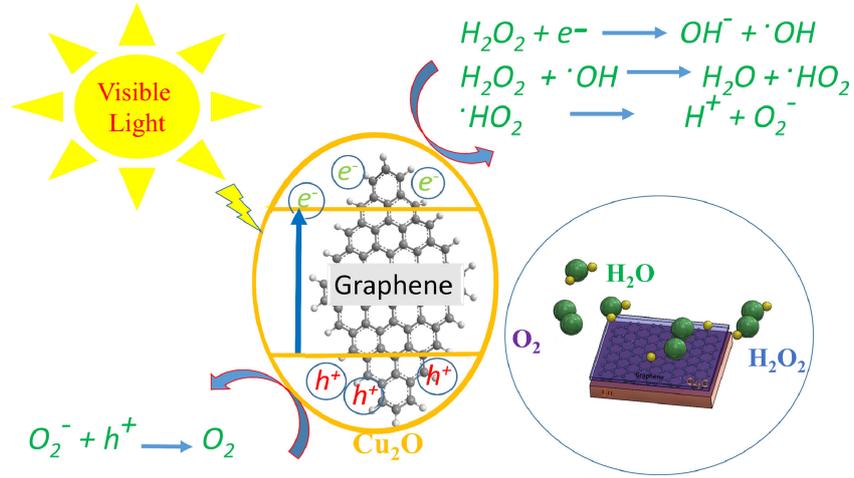


Figure 4. Photocatalytic oxygen formation mechanism from hydrogen peroxide. Taken from ref. 22²²

Cu is treated by illuminating it through graphene. The purpose of this treatment, is to prevent the oxidation of the graphene by preventing the Cu surface to deoxidize from Cu_2O to CuO .²² The Graphene and Cu sample absorbs highest amount of light between 480-650 nm meaning that photochemical catalysis is most active at this wavelength.²² Photocatalytic reactions cause the graphene sheet to bridge the gap between edges of the crystal domains. This leads to the formation of a more monolithic graphene sheet.^{21,22} Photocatalytic oxidation helps to observe graphene grain size and growth without risking the quality of the graphene.²¹ Due to the conducting characteristics of graphene, band gap energy can be calculated to study the conductivity of graphene when it is exposed to light source. The band gap energy of the catalytic reaction can be calculated by using the Kubelka Munk function ($f(r)$):²²

$$f((r)hv)^{1/n} = A(E_g - hv) = k/s = (1 - R)^2/2R \quad (1)$$

Where the E_g is the gap energy, A is the area of the gap, h is Plancks constant, s is scattering factor, R is the reflectance and n varies according to the semiconductor of being indirect or direct band gap. Using this formula, the band gap energy of the catalyst can be calculated and parameters can be altered to gain the wanted energy outcome.²²

7 Removing amorphous carbon

During the synthesis of graphene with CVD, most common contamination comes with the formation of amorphous carbon. Amorphous carbon is formed, when excess amount of graphene precursor, in our case methane (CH_4), is introduced to the surface.^{23,24,25} Amorphous carbon is formed from CH_4 , due to unwanted reactions of the graphene surface and dehydrogenated forms CH_3 , CH_2 and CH .²⁴ Amorphous carbon forms on the top of the synthesized graphene as chunks of carbon, that are 0.3-3 nm thick.^{23,25} Amorphous carbon has internal bond lengths between 0.09-0.22 nm and bond angles range between 90-150 degrees. Compared to the hexagonal bonding of carbon in graphene, with bond length of 0.142 nm and angle 120 degrees, the structure makes amorphous carbon very reactive. Amorphous carbon can induce unfavourable reactions on top of the graphene, like reduction reaction, thus it must be removed for the graphene to be clean.²³

7.1 Cleaning with CO_2

One way to clean the graphene of amorphous carbon is using carbon dioxide (CO_2) gas. By oxidizing the amorphous carbon, CO_2 can break down the contaminated carbon and edge it off from the surface.²³ Treatment is performed in the CVD chamber at a temperature of 500 °C.^{23,25} This cleaning method is based on the lower reaction barrier of the CO_2 , which is at about 2.52 eV, compared to the graphenes at 4.76 eV. Because of this difference, amorphous carbon and CO_2 react with each other easier than they would react with graphene.²³ The oxidation reaction on top of the graphene goes as follows:²³



The quality of CO_2 treatment can be examined by exposing the cleaned graphene surface to titanium tetrachloride (TiCl_4) in a humid air. With well cleaned graphene, none or very few titanium dioxide (TiO_2) particles are formed and bound to contaminated regions.^{23,24} Optimal temperature for CO_2 treatment is between 400-550 °C in which the amorphous

carbon can be etched without major damage to the graphene surface. This can be examined by calculating the dissociation rate for CO₂ using the Arrhenius equation:^{23,24}

$$k = Ae^{(-E_a)/RT} \quad (2)$$

Where the k is the dissociation rate constant, A is the pre-exponential factor, E_a is the calculated reaction barrier, R is the universal gas constant and T is the temperature. The removal of surface contaminations using CO₂ improves the optical and electrical properties of the graphene.²³

7.2 Changing the precursor of graphene

Another route of reducing amorphous carbon is to use a different precursor of graphene than methane. One alternative is cupric acetate (Cu(OAc)₂). Cu(OAc)₂ is decomposed at 189 °C and 1.22 mbar before exposed to the Cu surface.^{24,25} Applying continuous flow of Cu(OAc)₂ introduces constant Cu supply to the boundary layer during the synthesis. This will prevent formation of amorphous carbon by increasing the dehydrogenation in the gas phase. This effect can not be achieved if only pure Cu-vapor is used. This is because the saturated vapor pressure of Cu in the synthesis conditions of high temperature (950 K) is less than 3×10^{-4} mbar.^{5,24} The concentration of Cu-vapor would also decrease because of the surface-mediated growth mechanism.²⁴ Applying the Cu in to the reaction via precursor also reduces the reaction energy barrier. For example, the formation of CH₃ from CH₄ has an energy requirement of 1.29 eV, but with Cu catalysis this drops to -0.4 eV.²⁴ Also the low solubility between copper and carbon prevents unwanted reactions in the gas phase.⁴ Using Cu(OAc)₂ reduces significantly the amorphous carbon on the surface, meaning that gas phase reactions have a great effect on the surface contamination in graphene formation.²⁴

8 Different metal catalyzis options

8.1 Titanium based catalyzis

Even though, most graphene CVD synthesis techniques use Cu as the cathalytic surface, other metals might also be reliable options in this process. One of these optional metals is titanium (Ti). One major advantage to Cu, is that Ti can naturally oxidize to titanium dioxide (TiO_2) when it's exposed to air.²⁶ This lessens the need for long oxidation processes that need to be done with Cu to achieve the optimal composition and oxygen concentration. Unfortunately the presence of TiO_2 effects negatively to the formation of single layer graphene. The formation energy, E_{form} , is about 0.22 eV/nm^2 when TiO_2 is present at the surface. Positive E_{form} value means that the formation of the graphene is not spontaneous.²⁶ This means that the Ti must be deoxidized before the synthesis. This can be done with for example hydrogen treatments.^{10,26} The rest of the process can be carried out as if the graphene would be synthesized on Cu. The annealing point does not go that high because of two reasons. The melting point of Ti is about $1651 \text{ }^\circ\text{C}$ and graphene synthesis works best at lower temperatures due to the high oxidation tendency of Ti. Graphene can be synthesized at temperatures between $150\text{-}800 \text{ }^\circ\text{C}$ and also the working pressure for the synthesis can be as low as $0.006\text{-}0.25 \text{ mbar}$.^{26,27} Graphene can be synthesized with these parameters without any defect in surface or the properties of the product.(Figure 5)²⁶

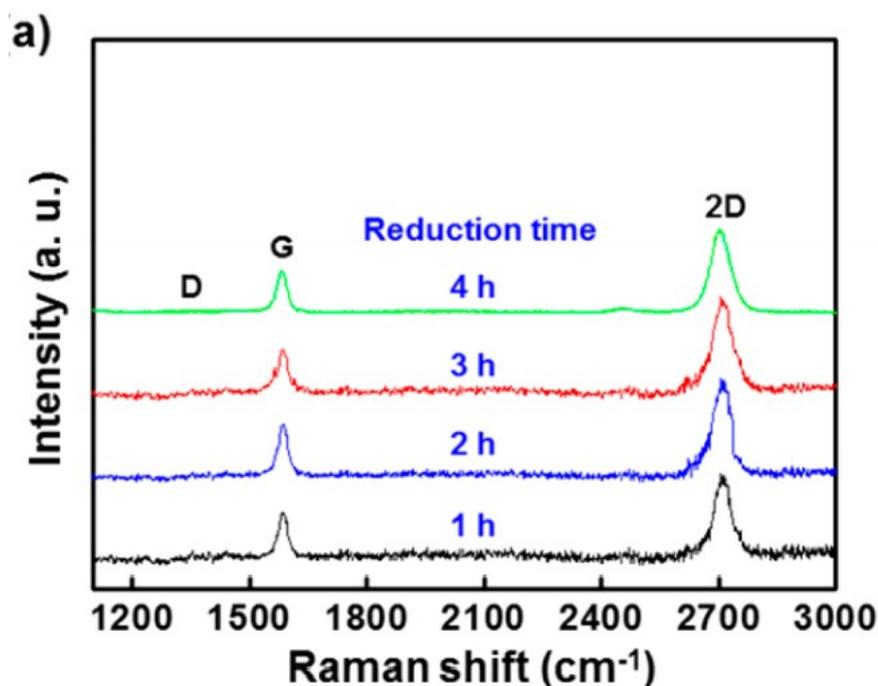


Figure 5. Raman spectra of graphene synthesized at 150 °C on a 10 nm thick Ti layer reduced for different reduction times under hydrogen treatment. Reprinted (adapted) with permission from Park, B. J., Choi, J. S., Eom, J. H., Ha, H., Kim, H. Y., Lee, S., Shin, H. and Yoon, S. G., Defect-Free Graphene Synthesized Directly at 150 °C via Chemical Vapor Deposition with No Transfer, *ACS Nano*, 2018, 12, 2008–2016.

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8.2 Germanium based catalysis

One viable option to Cu is germanium (Ge). Graphene can be synthesised with very similar methods on top of Ge as for Cu with lower temperatures that are below 1 000 °C. The H₂/CH₄ ratio can be as high as 20 but with the longer process time of 100 min.^{5,28} A notable difference in Ge pretreatment is that it can be done with one treatment step. One of the options is to treat the surface with acidic solution before the synthesis. The treatment consists of 1 min hydrogen flourine bath and then 5 minutes of deionized water bath.²⁸ Another option is to treat the Ge with ultrasonic isopropyl bath.²⁹ These treatments lead to light surface oxidation that helps the graphene grow on top of Ge.^{28,29} After graphene synthesis, the synthesized graphene sheet is treated in hydrogen halide bath for 1 min and then again to deionized water for 5 min. The most suitable candidate

to the hydrogen halide acid bath is hydrogen bromide (HBr), which produces a grain size of 22.6 ± 2.9 nm. The hydrogen halide bath is used to clean native oxides and suboxides.²⁸

Experimental part

9 Experimental questions

Goal of this bachelor thesis experimental work was to study ways to improve the graphene growth process used at the university of Jyväskylä. The method is based on the method published by David L. Miller.⁵ The main study area on the experiment was to examine effects of different gas compositions and environments on the synthesis.

The First experiment focused on the effects of H₂ gas on the graphene growth. In the experiment, annealing of the sample was done at higher hydrogen concentration and partial pressure than the growth phase. Due to the unique graphene growth technique, the results of this experiment could not have been accurately predicted, because the effects of oxidation or reduction of the thin Cu surface has not been studied in this method. Therefore, the predictions are done based on the literature. Effects of H₂ pressure increase in the experiment could produce lower nucleation density and more unified and clean graphene.^{9,10,11,14}

The Second experiment studied the effects of carbon dioxide treatment after the synthesis. Carbon dioxide treatment was applied directly after graphene growth. This experiment was predicted to produce cleaner graphene that would contain less amorphous carbon and other impurities on the graphene surface.^{23,24}

10 Methods

10.1 Production of Cu films

Sample Cu films were prepared using a modified method, which is based on the method described in the article "Giant secondary grain growth in Cu films on sapphire" by David L. Miller.⁵ Sample Cu films were synthesized on top of 5x5 mm α -Al₂O₃(0001) sapphire substrates. The sapphire was annealed at 1100 °C in O₂ atmosphere, using Eurotherm 3216 PID oxidizing furnace, for 24 hours. This treatment polished the sapphire and removed surface contamination and smoothing it in the process. Substrates were checked on quality and then moved to a vacuum thin film deposition system. The chips were attached on a Cu puck and placed on the BAL-TEC BAE 250 coating system. Sapphire chips were left to the coating for 20 minutes. Cu coating on top of the sapphire was 400-500 nm thick. The Chips were cooled down and then moved to the graphene synthesis. The samples were prepared by laboratory technician Olli Rissanen.

10.2 Control synthesis

All synthesizes were performed in GLS-1100Z MTI corporation graphene furnace, seen in image 1, that was self rebuilt. Control samples were annealed in tube furnace for 15 minutes under atmosphere of 470 sccm of Ar (partial pressure of 1145,1 mbar) and 27-30 sccm of hydrogen (partial pressure of 67,6 mbar). Growth was performed under 4,7 sccm of 99% Ar and 1% CH₄ atmosphere (methane partial pressure of 11,3 mbar) for 15 minutes. Treatments were done under temperature 1050-1060 °C. Samples were cooled in the tube furnace for 10 minutes before removing them from the furnace.

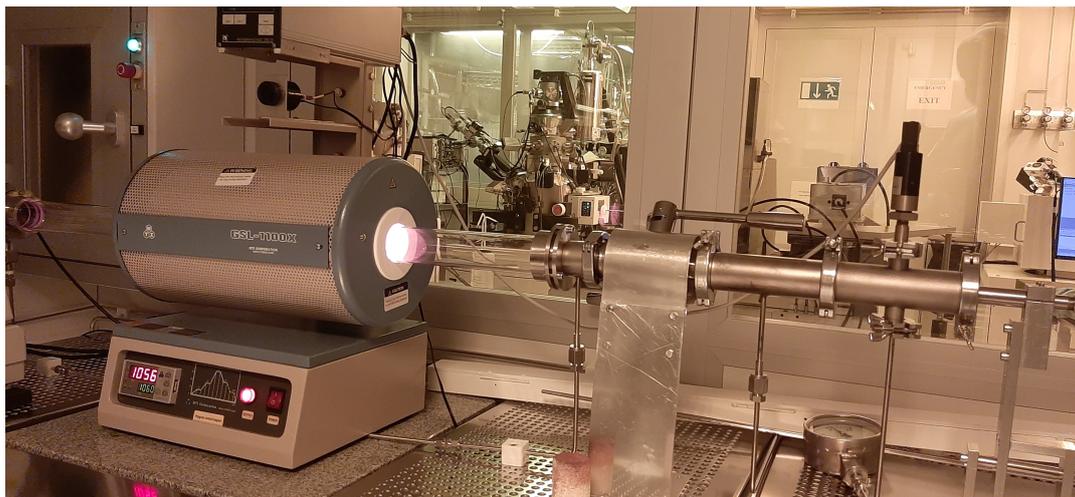


Image 1: Home built GLS-1100Z MTI corporation graphene furnace

10.3 Increase in hydrogen flow

The effect of deoxidation of Cu was studied by performing the annealing at high flow rate of hydrogen and then lowering the flow rate for the growth. Cu was annealed for 5, 10 and 15 minutes in 470 sccm Argon (partial pressure of 1098,6 mbar) and 44 sccm hydrogen (partial pressure of 104,6 mbar) and for the last 5 minutes of annealing, the hydrogen flow was dropped down to 24 sccm. Graphene growth was performed for 15 minutes in 7,8-8 sccm Argon/methane mixture and 24 sccm hydrogen at temperature of 1050-1060°C (partial pressure for argon was 1155,1 mbar, to hydrogen 57,6 mbar and to methane 11,4 mbar).

10.4 CO₂ treatment

The effect of CO₂ gas on grown graphene was studied by treating the graphene with CO₂ gas in the furnace after the synthesis. Synthesised graphene was pulled out about 1 cm from the furnace and left to the tube to cool down for five minutes. Temperature in this position was measured to be about 500 °C. After cool down, the graphene was treated in argon flow of 470 sccm (partial pressure of 1163,2 mbar) with 20,24 sccm of CO₂ for 5 and 10 minutes (partial pressure of 50,1 mbar). Graphene was then cooled to room temperature before removing from the furnace. Cleaning position is shown in image 2.

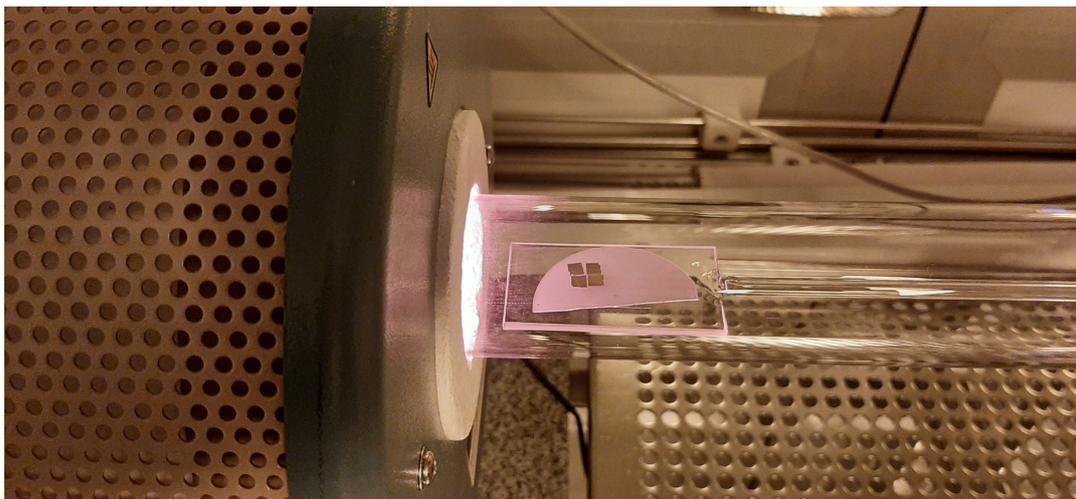


Image 2: CO₂ treatment position.

10.5 Characterisation

Samples were studied first with optical microscope Olympus BX51M (2008/2008), to make sure the purity of the sample and condition of the Cu chips after synthesis. Then samples were studied using Raman spectrometer Thermo Fisher DXR Raman microscope with excitation wavelength of 532 nm. Half of the samples were analysed using Raman spectroscopy to analyse the purity and possible contamination of the graphene. Graphene was removed from the Cu chips to oxidized silicon (Si). Transfer was done by spinning Cu chips in PMMA and chips were left in a ammonium persulfate to edge away the Cu overnight. After the Cu layer had been etched away, the PMMA layers with the graphene were washed twice with deionized water, hydrochloric acid and then again twice with water before being transferred to silicon chips. Surface of the sample was studied using atomic force microscope Bruker Dimension Icon (2016/2016).

11 Results and discussion

11.1 H₂ annealing experiment

All samples were analysed using an optical microscope to detect the condition of the Cu layer and to identify direct contamination or damage on it.

In the increased H₂ annealing, the condition of the Cu suffered notably. The annealing in high H₂ flow damaged the structure of the Cu surface, causing multiple defects to the samples surface. Annealing for 5 minutes caused the damage to the Cu surface, making multiple defect spots and cracks to the chip. The 10 min annealing caused less defects to the surface, but still noticeable more than in the control. The most devastated sample was the one annealed in high H₂ flow rate for 15 minutes. In all of these samples, the surface was completely cracked at the centre and the edges were notably damaged. The cracks also were similar in all of the samples, by going through the sample in the direction of the gas flow in the furnace. Difference in the samples is seen in figure 1, where the images are chosen as the medium representative of the sample condition. Each sample patch had 4 samples, except the 5 minute anneal, which consisted of 3 samples.

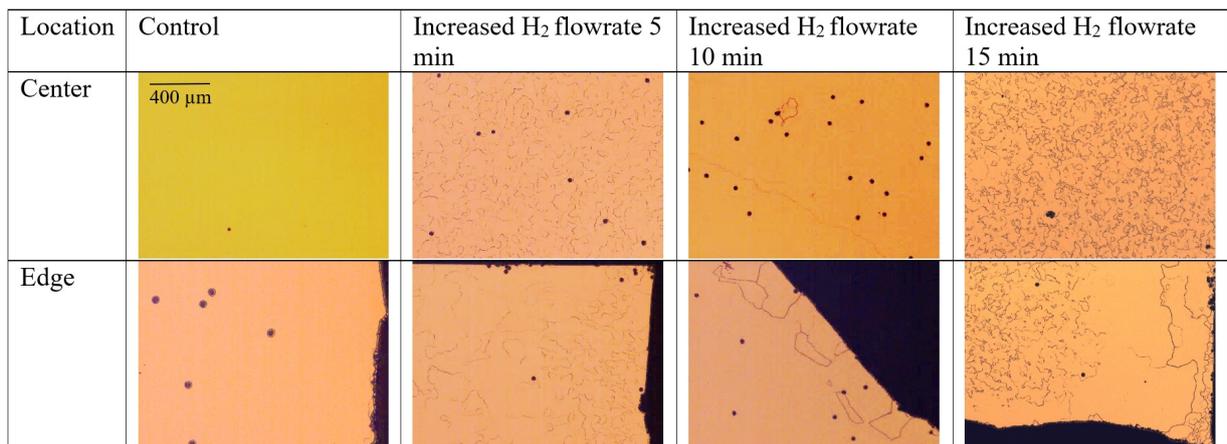


Figure 6: The Cu surface study under a optical microscope 5x magnification.

From figure 6, it can be deduced that the increased H₂ flow rate does not effect favourably to the Cu surface. All the samples, that are annealed at higher H₂ flow rate, have visible cracks in them. Notable difference between the samples was that the 10 min increased annealing samples were the least damaged of all the samples but had major

increase in the amount of dewetting spots. This could mean that the 10 min annealing experiment samples could have been contaminated or the sample preparation was done slightly differently. The surface of the 15 min annealing sample was cracked but it can also be seen to be edging away, as seen in figure 7.

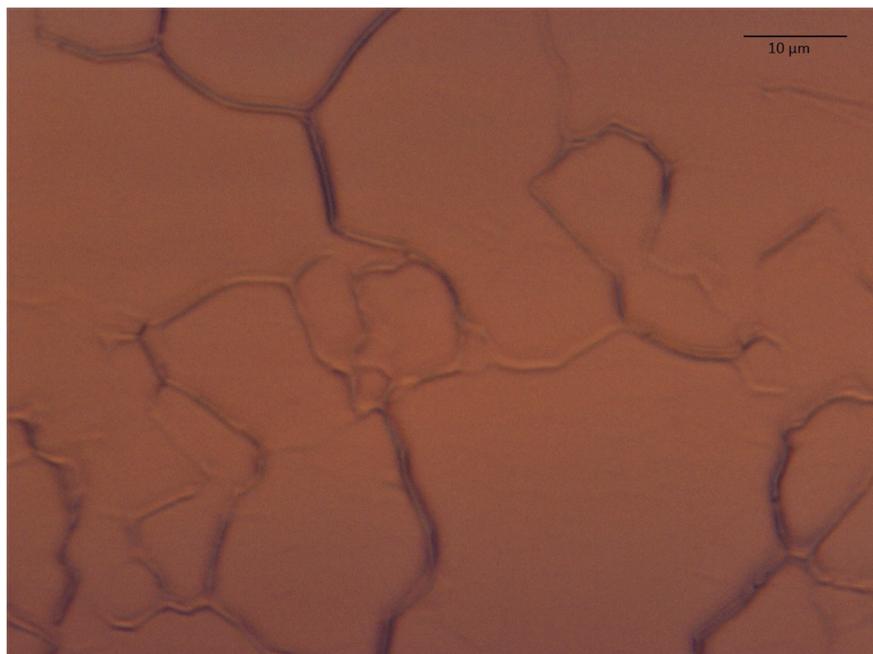


Figure 7: Close up capture of the H₂ sample annealed for 15 minutes in 100x magnification.

The 15 min sample Cu surface had clear grooves that had been carved during the process. When compared to the 5 min samples, the cracks were full and went deep into the Cu layer. This observation can lead to following deduction about the annealing reaction: The high levels of H₂ may cause the surface to reduce rapidly and this may damage the Cu surface. Too long annealing and reduction could cause the Cu to edge of and cause defects on the surface.

The samples were studied by atomic force microscopy from areas of 50x50 micrometres. The data was examined with data-analysis program Gwyddion. The main data to identify impurities and crystal size was the height and adhesion of the samples. In figure 8, the height and the adhesion data of the control samples can be seen. Height data was used to detect abnormalities, defects, and contamination. Adhesion data was used to analyse the grain size and detect double layers, grain boundaries and other contamination.

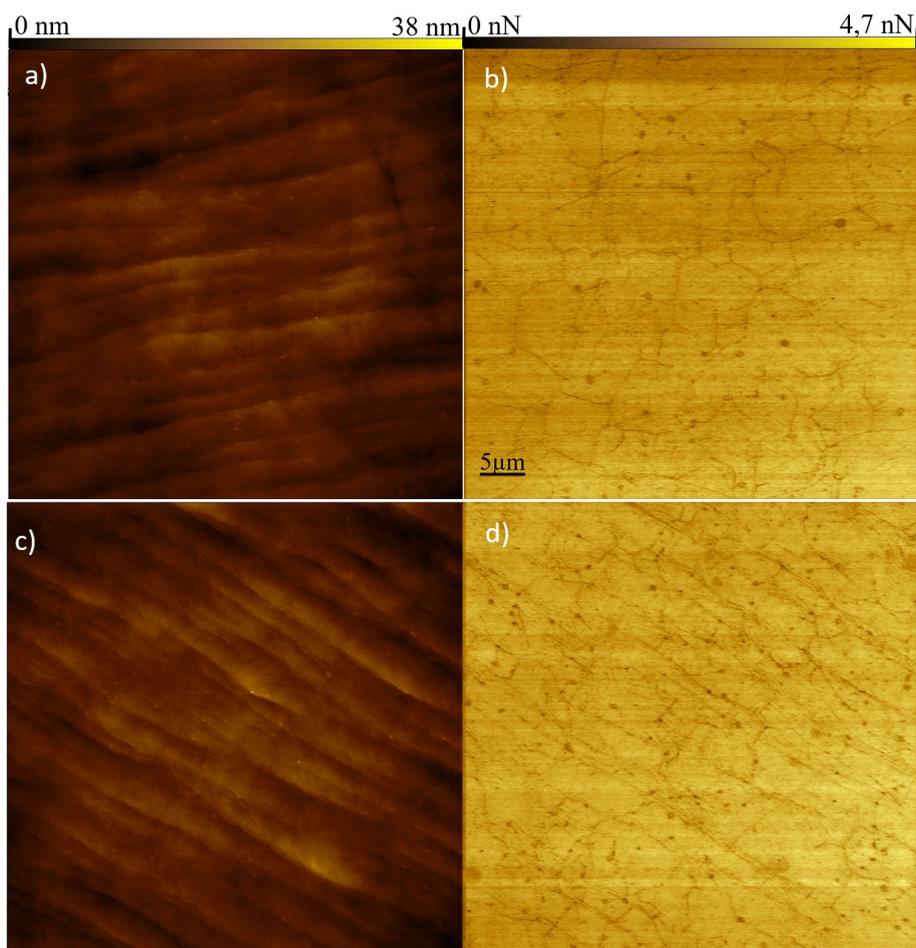


Figure 8: The control sample 1 a) height data and b) adhesion data and control sample 2 c) height data and d) adhesion data.

The control synthesis produced very clean and unifying graphene. The graphene crystal size is very large, as can be seen in adhesion data, and some double layers are visible in both samples.

The H₂ samples were studied under atomic force microscope. The 5 min annealing samples had the least contamination and defects on them compared to other samples. The 10- and 15-min annealing samples had more defects on them. After studying the 10 min annealing sample with the program's height profile expression tool, the white spots on the sample were deduced to be holes that had small graphene crystals in the middle of them. The 10 min sample was most defected out of all the samples, with clear crystal domain edges visible in the measurement and many impurities and deformations. The 15 min sample had very few visible graphene grain boundaries. The graphene had multiple small holes and defect spots that were identified as amorphous carbon. The condition of graphene in 5 min and 15 min samples was good inside the Cu grains that are visible

on optical microscopy. The grain boundaries in Cu caused the graphene to not grow smoothly across the surface and the grooves on the Cu surface cause the graphene to grow into them, covering the grooves in graphene. Comparisons of the graphene surfaces of the H₂ samples can be seen in figure 9.

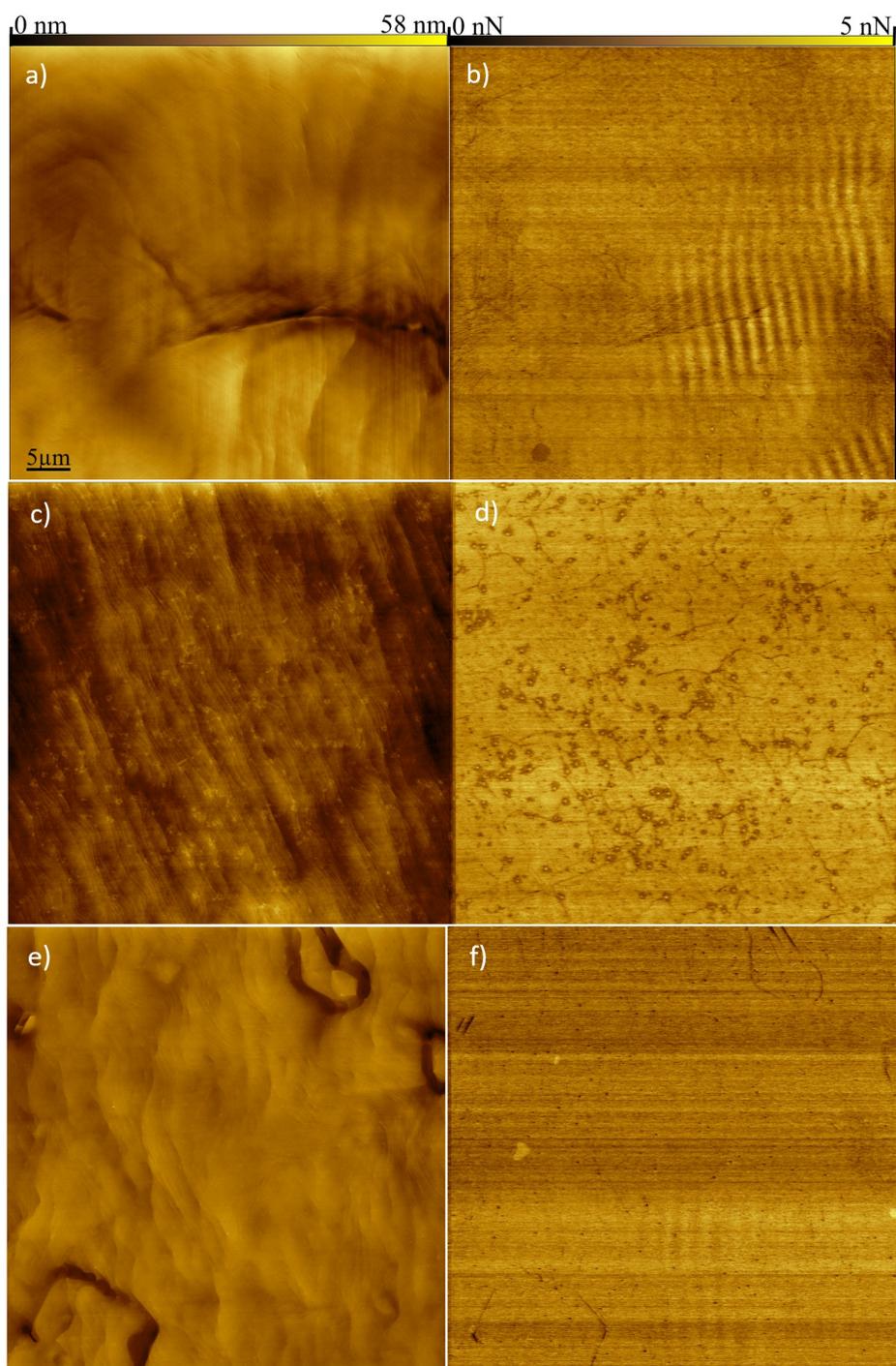


Figure 9: Graphene surfaces of the H₂ samples with height sensor data on left column and adhesion data on the right column. Top images (a, b) are 5 min annealing samples, centre (c, d) are 10 min annealing and bottom (e, f) are 15 min annealing.

Raman spectra of the H₂ annealing samples are represented in figure 10. When examining the spectra of different anneal times, we can see that the longer annealing time causes the G and 2D bands to reach the same intensities and the D-band starts to become sharper. This leads to conclusion, that produced graphene is clean and does not have major impurities, such as defects and amorphous carbon, until you get to the 15 min samples. This helps to confirm that oxidation levels effect the graphene synthesis and that high reduction to Cu surface produces lower quality graphene.

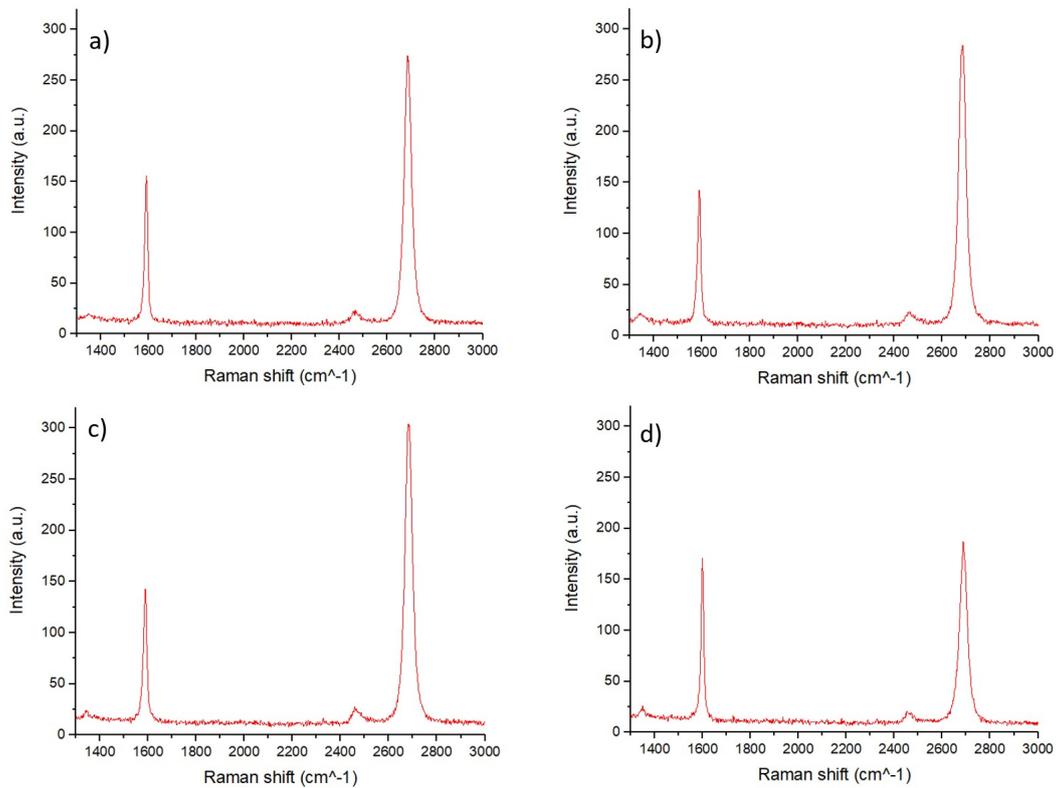


Figure 10: Raman spectra of a) control sample, b) 5 minute H₂ annealing sample, c) 10 minute H₂ annealing sample and d) 15 minute H₂ annealing sample.

When the Cu cracks were analysed using the AFM, the effects of broken Cu surface can be seen. As presented in figure 11, from the adhesion the grooves in the Cu surface do have graphene. The graphene was synthesised along the surface of the Cu and so the grooves are coated with graphene. This breaks the otherwise united and smooth graphene surface and is more likely to induce more defects.

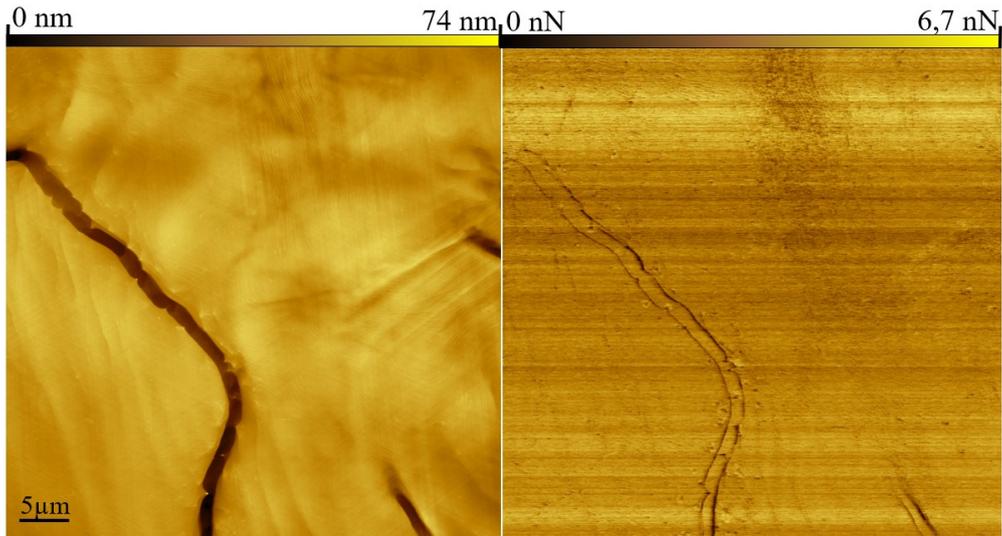


Figure 11: 5 minute H_2 sample crack height data on the right and adhesion data on the left.

All samples had areas of clear graphene and multiple contamination areas. The contamination could have been formed during the synthesis or during the transferring process. The contaminations were identified from the Raman spectra as holes, amorphous carbon, doped single layer graphene, and double layers. Examples of each contamination spectrum is represented in figure 12.

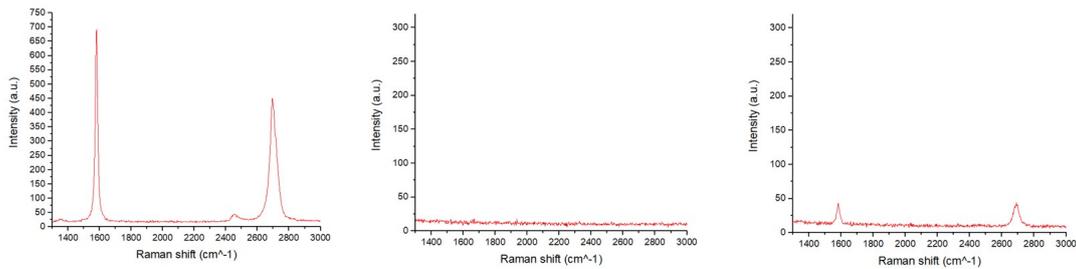


Figure 12: Collected Raman spectrums of the contamination detected in the samples. Doped single layer graphene on left, holes in the graphene in the centre and graphite on the right.

11.2 CO_2 treatment

CO_2 samples were grown using the same parameters as in the control synthesis and in the optical microscopy the Cu surface looked like the control synthesis. Difference of the samples was that the presence of amorphous carbon was clearly reduced when samples

were examined in optical microscopy, AFM and Raman spectroscopy. In the AFM images, the double layering of the samples had been increased and Raman spectroscopy gave similar data. Difference of the 5 min treatment and 10 min treatment was clear: longer treatment time caused more contamination on top of graphene. These layers can be interpreted as double layers from the adhesion data. This could mean that the CO₂ does etch of the amorphous carbon but it also increases and grows the double layers on top of the clean graphene. This is illustrated in figure 13, where the AFM topography of both samples is presented.

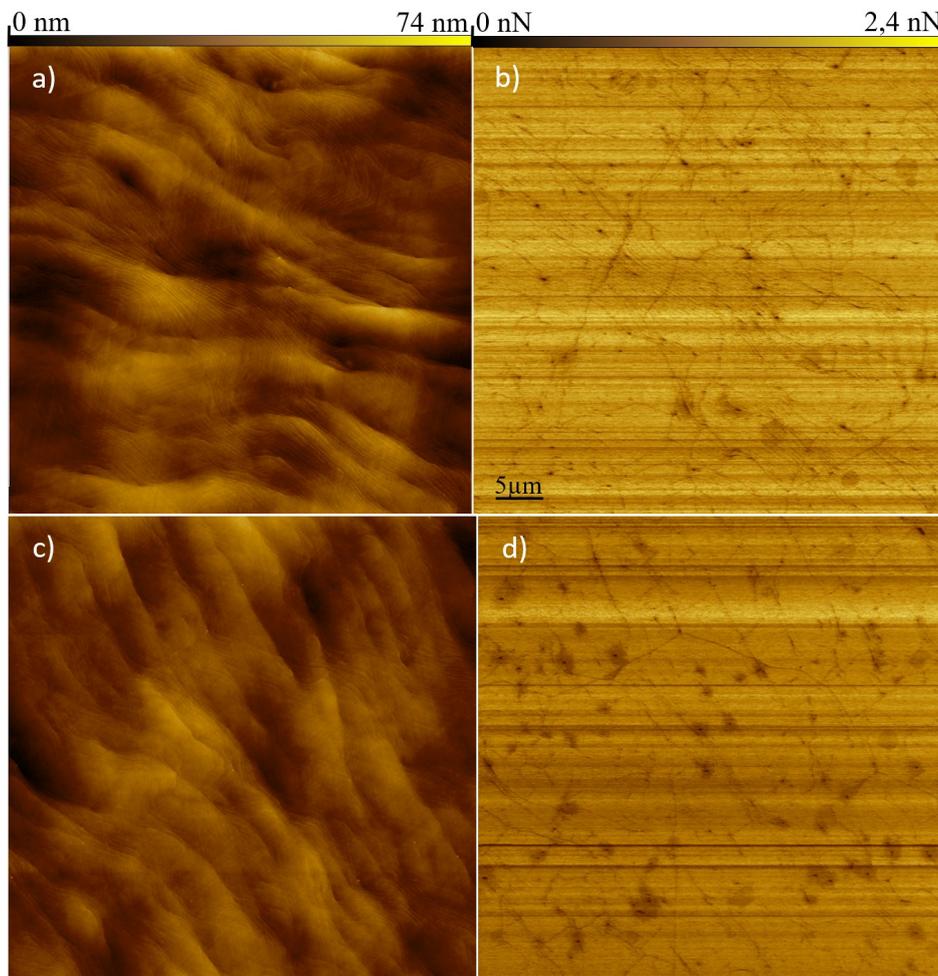


Figure 13: AFM height (a and c) and adhesion (b and d) data of CO₂ treated graphene. 5 min treatment (a and b) and 10 min treatment (c and d)

The Raman spectrum of the samples is consistent with the observations made from the AFM images. The double-layering can be seen in the spectrum from the sizes of G and 2D bands, as they are closing on each other in height. Also, the D-band from the gets

sharper in the 10 min experiment, meaning that the sample has more defects in it. From this data, it can be said that the CO₂ treatment does reduce the amount of growth face amorphous carbon in the sample, but it crates and grows existing double layers in the sample. Raman spectrums of the CO₂ samples are represented in figure 14.

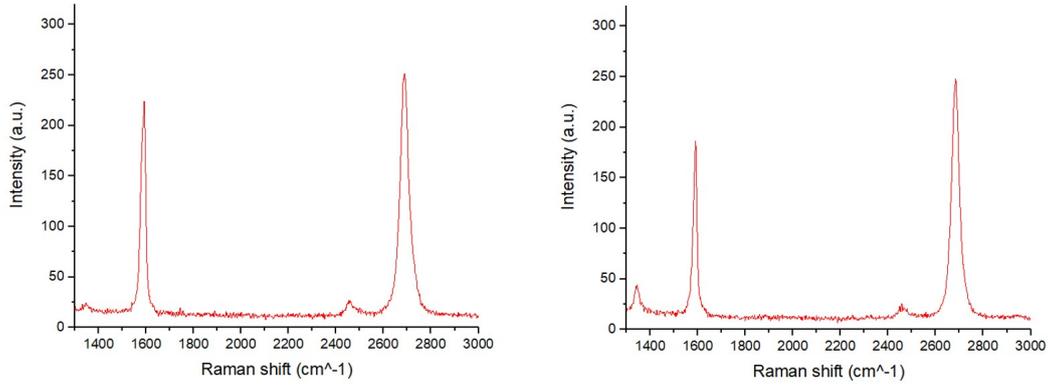


Figure 14: Raman spectrums of the CO₂ samples. 5 minute treatment on left and 10 minute treatment on right.

12 Conclusion

In conclusion, the experimental work was success and results were reliable, because they are supported bu the literature. Major contamination of the samples did not happen in the experiment and data was consistent and led to logical conclusions about the process that happens in the graphene growth. Both experiments were performed under very extreme conditions to get clear results of the used techniques.

The effects of reduction of the catalytic Cu surface was studied by examining the effect of different hydrogen gas compositions during the annealing of the sample. The results of this experiment lead to the conclusion, that reduction of the oxidation level on the Cu surface can be used to produce higher purity graphene, as seen from the samples that were annealed in higher hydrogen pressure. However, there is a limit when reduction is no longer favourable, as seen from the samples that were annealed over 5 minutes in high hydrogen flow. If reduction is used as a preparation method in the future, the ideal annealing time to higher gas compositions should be determined.

The possibility of using carbon dioxide to clean the surface from amorphous carbon after synthesis of the graphene was studied by exposing the synthesised graphene to carbon dioxide gas directly after the growth in the furnace. Carbon dioxide did remove major amounts of amorphous carbon from the surface of the sample. As a downside, carbon dioxide may promote the growth of double layers on the graphene and longer exposure increased the amount and the size of the double layers in the graphene. If carbon dioxide is used to clean the samples in the future, lower flow rates or treatment times might be favourable.

Contamination of the control sample and 5- and 10-minute hydrogen annealing samples could have affected the results of this experiment. The contamination in these samples could have occurred because they were removed from storage cabinets mostly and experienced the most environmental changes because they were used as training samples in the AFM and Raman-spectrum training. Possible contamination to the samples that were transferred to the silicon oxide could have come from the transfer process. This

phenomenon was common according to the instructors.

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