Graphene and Permalloy Integration in Functional Fluidic and Solid-state Devices

Wesley van den Beld

GRAPHENE AND PERMALLOY
INTEGRATION IN FUNCTIONAL FLUIDIC
AND SOLID-STATE DEVICES

Wesley van den Beld

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Introduction

The aim of the work of this thesis is to develop novel technologies for functional micro- and nanofluidic devices, as well as exploring the functionality of first examples of such devices. The research thereby is mainly centered around graphene, and involved its synthesis, device fabrication, Raman spectroelectrochemistry and transmembrane transport experiments. As such, this work represents a step in the development of real-life applications of this unique material. In addition, the use of magnetic materials is explored for functional lab-on-a-chip systems. In both cases the use of cleanroom technology is indispensable for the developments.

1.1 Graphene introduction

Figure 1.1 Overview of several carbon structures. Benzene (a) serves as a building block for the three subsequent sp^2 carbon structures (b-d). Buckminsterfullerene (b), carbon nanotubes (c) and graphene (d) represent zero, one, and two dimensional allotropic carbon structures. For simplicity only the carbon atoms are drawn.

Carbon is an interesting material in nature that appears in many different forms. Three sp^2 carbon allotropes that received much attention in the last decades are buckminsterfullerene, carbon nanotubes and graphene (shown in Figure 1.1) that all have outstanding physical properties^[1,2]. The most recent discovered was graphene and it has received much attention because of its unique properties such as mechanical strength and impermeability to gasses.^[1,3–6] In Figure 1.2 it is schematically shown that a pencil is composed mainly out the bulk material graphite, a single carbon layer of which is called graphene^[7,8]. The first method that was successfully used to isolate a single layer of graphene was exfoliation of highly ordered pyrolytic graphite (HOPG) on silicon dioxide^[8]. The novel carbon material proved to be interesting for a wide range of applications^[6,9,10]. Graphene can be used in novel ultra-thin nanopore devices because of its atomic thickness of

Figure 1.2 Schematic showing a pencil and the structure of graphite (multilayer) and graphene (single layer). A pencil core exists, among other components as clay, for the larger part out of graphite. Graphite is composed out of many weakly coupled layers of carbon. An isolated single layer of this carbon honeycomb lattice is graphene.

only ~ 0.37 nm and mechanical strength^[5,11], theoretically enabling highly optimized sensing and filtration processes^[12–15]. Also, graphene is particularly interesting for electrochemistry and energy storage applications^[16] because of its high surface area^[17], high conductivity^[1,17] and low interfacial capacitance^[18]. Finally, the graphene Fermi level can be probed by its strong Raman signal, giving information about the graphene doping^[19–22].

1.2 Graphene technology

Instead of exfoliation, graphene synthesis by chemical vapor deposition (CVD) is also possible. In the research reported in this thesis, CVD on copper was used, resulting in large area single layer graphene. This graphene then has to be transferred from the copper catalyst to a substrate using a manual transfer protocol. As an alternative therefore, a method for direct graphene synthesis on silicon dioxide would much simplify the procedure and such a method was investigated in this thesis.

The Dirac-cone band structure of graphene, together with the absence of bulk (and thus an extremely large surface area) make graphene an outstanding candidate for sensing applications^[23]. In Raman spectroelectrochemistry experiments we employed these properties, by performing electrochemical experiments and simultaneously recording the graphene Raman spectrum.

Single layer defect-free graphene is an excellent barrier material, since it is impermeable for all gasses and offers a high energy barrier for ionic transport^[5,24–27]. Nanopores in graphene however allow transport of ions and small molecules. In combination with its atomic thickness and mechanical strength, graphene with nanopores offers a potential high transmembrane transport rate for sensing and filtration processes^[5,11–15].

Raman spectroscopy is a fast technique to obtain information about carbon materials such as graphene^[28–30]. In Figure 1.3 the Jablonski diagram is shown that illustrates elastic and inelastic scattering phenomena. When a sample is exposed to monochromatic light with wavelength λ_0 , most of the light is scattered elastically with the same wavelength as the excitation source (Rayleigh Scattering).

Figure 1.3 Jablonski diagram illustrating Rayleigh scattering (elastic), Stokes and anti-Stokes Raman scattering (inelastic) for an excitation wavelength λ_0 .

In Raman microscopy, most of this elastically scattered light is filtered out with a dichroic mirror (beam splitter) and what remains is the weak Raman scattering signal with a shifted wavelength λ_1 , composed of photons that are inelastically scattered^[31]. The resulting Raman spectrum is usually displayed as function of the shift in wave numbers Δw . To calculate the shift in wave number Δw [cm^{-1}] from the excitation wavelength λ_0 [nm] and resulting Raman wavelength λ_1 [nm], the following equation can be used:

$$\Delta w = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \times 10^7 \quad (1.1)$$

The peak pattern in the Raman spectrum is symmetric around $\Delta w = 0$ and the intensity ratio between the Stokes ($\Delta w > 0$) and anti-Stokes ($\Delta w < 0$) scattering peaks depends on the temperature. The Stokes Raman signal is typically used since it has a higher intensity than the anti-Stokes signal. A shift to a higher wave number is called a red-shift (towards the red wavelength) and to a lower wave number a blue-shift (towards the blue wavelength).

In Figure 1.4 a typical Raman spectrum of single layer graphene is shown, in which three characteristic peaks (resonant frequencies) are found. The D-peak (1350cm^{-1}) indicates disorder in the graphene crystal (defects and discontinuities such as grain boundaries and edges) in the graphene crystal, the G-peak (1590cm^{-1}) is probing the in-plane bond stretching mode and the 2D-peak (2677cm^{-1}) holds information regarding the stacking orders^[28,29]. In a good quality single layer graphene crystal, no defects are present (low D to G-peak intensity ratio I_D/I_G) and the 2D-peak is narrow (low full width half maximum of the 2D-peak G_{FWHM})^[29,32]. The positions, widths and intensity ratios are analyzed for characterizing and studying the graphene, e.g. its doping^[33].

Figure 1.4 Typical measured Raman spectrum of single layer graphene on silicon dioxide containing three characteristic peaks: the D-peak (indicating discontinuities), the G-peak (from the in-plane bond stretching mode) and the 2D-peak (indicating stacking orders).

1.3 Lab-on-a-chip technology

Lab-on-a-chip technology involves the development of miniaturized on-chip systems for biomedical and environmental applications, integrating analytical laboratory functions on chip. The development started with miniaturized chemical analysis systems, μ TAS in short, as a branch of micro-electro-mechanical systems (MEMS). Later the field further developed when the μ TAS technology was not only used for analysis purposes, but also for other applications such as (integrated) microfluidics and nanofluidics, microreactors, manipulation of cells, organisms and organs on chip. As a generic name then the term lab-on-a-chip was introduced. The technology creates new opportunities for life-science applications: faster and compacter analyses while using less sample, amongst others making use of the higher surface to volume ratio compared to larger systems.

The fabrication of such lab-on-a-chip systems started off with glass/glass and silicon/glass chips in which microchannels were fabricated using wet (hydrogen fluoride) and dry (plasma based) etching techniques. Later polymer based devices became more popular, because they are cheaper since only little or no cleanroom technology is required. Polydimethylsiloxane (PDMS) has been used massively for (bio)medical applications, but also epoxy-based photoresists such as SU-8 are popular for lab-on-a-chip device fabrication. At present, novel rapid prototyping techniques are rising like 3D printing, that enable fast testing of microfluidic designs.

Lab on a chip systems are typically comprised of microchannels, microchambers, integrated sensors/heaters (e.g. graphene^[34]) and fluidic components such as pumps, mixers and valves. Pumps make active transport of (sample) liquid through microchannels possible, which is generally essential in such devices. In closed systems (such as circular channels), pumping using external pressure or electroosmotic flow is not possible, since these techniques are actuated from the outside world. Pumping in closed microfluidic systems has been studied previously using optical, electrical and magnetic methods that each have limitations such as

pumping in only one direction, requirement of a large setup or necessitating a large chip footprint^[35,35–37]. In the research reported in this thesis, a compact magnetic actuation method is investigated using rotating magnetic microspheres around magnetic microdisks, enabling locally controllable transport on-chip in combination with mixing.

1.4 Thesis outline

In the work represented in this thesis, graphene technology was studied involving its synthesis, device fabrication, Raman spectroelectrochemistry and transmembrane transport experiments. In addition, the use of magnetic materials was investigated for pumping in lab-on-a-chip systems. In Chapter 2 graphene chemical vapor deposition synthesis on copper foil is discussed accompanied by a characterization of the synthesized graphene. In addition, the graphene transfer process from the copper foil to a substrate is described and critical steps are identified and improved, resulting in an increased graphene transfer yield. In Chapter 3 an alternative graphene synthesis method is reported, that is based on the dewetting of copper on a grooved substrate, making the manual transfer steps redundant. In Chapter 4 adsorption of reactive species on graphene is investigated by Raman spectroelectrochemistry for three species with different electrode interaction mechanisms. In Chapter 5 the ionic transport through suspended graphene membranes is investigated under an applied electrical field in a case by case analysis of the devices, showing possible detachment of graphene from the silicon nitride support during the transmembrane experiments. In Chapter 6 a novel method for pumping liquid through microchannels is presented that makes use of rotating magnetic microspheres around magnetic disks. Chapter 7 finally presents a summary with suggestions for further research.

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1. INTRODUCTION

2

Synthesis, transfer and characterization of graphene

In this chapter the chemical vapor deposition (CVD) synthesis method of graphene on copper foil as well as the protocol that was developed to transfer the graphene are reported. The graphene quality is characterized by using Raman spectroscopy. The method resulted in monolayer graphene synthesized on copper foil. CVD synthesized graphene was transferred from its catalyst (copper foil) to a substrate (silicon dioxide or silicon nitride membranes) using a manual process. In this process a polymer support layer was employed, and wet etching was used to remove the back-side graphene and copper. After a thorough rinsing step, the floating polymer-graphene sample was scooped by a substrate. The device assembly was finalized by dissolving the supporting polymer. Transferred graphene has been characterized by optical microscopy and Raman spectroscopy, giving insight in important graphene parameters. Delamination from the substrate, improper back-side graphene removal and graphene wrinkles were optically imaged. To circumvent debris from back-side graphene and have proper adhesion, a nitric acid etch and a proper PMMA bake proved to be necessary.

2.1 Introduction

In this thesis two methods for graphene synthesis are discussed: one on a copper foil and one by thin film dewetting. In this chapter synthesis by the first method is reported, which encompasses graphene synthesis on copper foil and a transfer procedure onto a desired substrate. This method is most commonly used for fabricating functional graphene devices. The graphene sensing and membrane devices fabricated using this method are further discussed in Chapter 4 and 5. In the schematic overview of this method presented in Figure 2.1, it can be seen that the method includes several manual steps such as cutting of foil and scooping of a floating sample. Since this makes the method labor intensive and cumbersome, the second method was developed for direct synthesis of graphene on silicon dioxide by controlled copper dewetting. More information on this method can be found in Chapter 3. Using a grooved substrate and thin film copper deposition at an angle, here graphene is selectively deposited during copper dewetting as schematically shown in Figure 2.2. This method has the advantage that it is automated, thus does not require manual steps as in the conventional method.

Figure 2.1 Schematic overview of the graphene synthesis on copper foil and transfer process to a substrate. As a substrate a copper foil is used, on which a pre-clean is preformed to obtain a better catalytic surface (a) after which the foil is annealed and graphene is synthesized (b). This synthesized graphene is coated by a polymer (c). This polymer serves as a support in the subsequent steps. Next the sample is cut (d) and the graphene which was deposited on the other side is etched (e). Next the copper is removed by a wet etching (f). After the graphene polymer stack was rinsed, it is scooped with a substrate (g) and baked to let the polymer conform to the substrate (h). Finally the support polymer is dissolved (i) resulting in a substrate with a graphene layer.

Figure 2.2 Schematic overview of graphene synthesis directly on silicon dioxide by thin film copper dewetting. A silicon wafer with crystal orientation $\langle 100 \rangle$ (a) is processed by oxidation, conventional lithography, dry etching, wet etching to form grooves (b). To form a barrier for copper, the silicon is oxidized. Copper is deposited by evaporation at an angle to the substrate (c). The graphene synthesis takes place in a chemical vapor deposition (CVD) process where the copper dewets into the grooves and a layer of graphene stays on the mesas (between the grooves) (d).

2.2 Graphene synthesis

Single layer graphene (SLG) has unique electric and mechanical properties as it is extremely thin (essentially no bulk), has a potentially high in-plane electron mobility and could enable selective trans-membrane transport of protons^[1–7]. The synthesis of SLG and measurement of its properties is therefore one of the central aims of this thesis. Historically, exfoliation of highly ordered pyrolytic graphite (HOPG) on silicon dioxide was the first method used to successfully isolate SLG^[8]. Although this results in high quality graphene, it offers only a low yield and is troublesome to integrate in practical devices. A reproducible technique resulting in large area graphene is synthesis by chemical vapor deposition (CVD) on metals such as copper or nickel^[9–11]. Unfortunately, the quality is inferior to exfoliated graphene, since CVD graphene is polycrystalline and contains therefore imperfections e.g. at the grain boundaries. The carbon solubility in copper is very low, therefore synthesis on copper typically results in SLG^[12]. Also when using copper, the resulting graphene is not dependent on the heating or cooling ramp in contrast to nickel^[13]. In addition, in contrast to other metals which can serve as a catalyst material, copper has the advantage of being inexpensive and amenable to etching without damaging the graphene^[10,14]. Thus copper is suited for SLG synthesis with the possibility of transferring the graphene to a substrate using a transfer protocol (see Section 2.3).

The CVD graphene synthesis is schematically shown in Figure 2.3. A commercial copper foil is pre-cleaned to remove surface contamination, yielding a clean surface which can be loaded into the CVD furnace. In this furnace the foil is annealed at high temperature (close to the melting point of copper) with hydrogen to reduce the copper oxide. Subsequently the sample is exposed to a gaseous carbon source (often methane), which starts the nucleation of graphene islands. At longer exposure these graphene domains grow until domains coalesce, which results in stitching and the formation of a continuous layer.

The graphene domain size is dependent on the density of nucleation points

Figure 2.3 A detailed schematic of the graphene synthesis process. On a commercial copper foil (a) a pre-cleaning treatment is performed to remove contamination such as organics (e.g. from its packaging) or coatings (chromium oxide) (b). The cleaned foil is annealed at $\sim 1000^\circ\text{C}$ with hydrogen to reduce the copper oxide (c). Subsequently a gaseous alkane (commonly methane) stream is added to the process chamber (d). Nucleation of graphene islands starts at irregularities or impurities with different crystal orientations. After further exposure to this carbon containing stream the domains will further grow (e). The domain shape is mainly dependent on the process pressure. Where coalescence of the domains occurs, they will be stitched by pentagons and heptagons. Finally by further domain growth a fully continuous layer is obtained (f).

on the copper foil^[15,16]. By the catalytic action of the copper to dissociate the methane, the graphene domains will grow, where the domain shape is dependent on the CVD process parameters^[11]. For SLG growth hydrogen is essential, since it serves the role of activating the surface-bound carbon^[17]. Hydrogen must also be present during the synthesis process to prevent re-oxidation of the copper by potential impurities in the reactive gasses, since the presence of oxidizing impurities will lead to the amorphization or etching of graphene at elevated temperatures^[18,19]. At temperatures close to the melting temperature of copper, and especially at low pressures, copper evaporation is furthermore significant. Copper covered by graphene will be passivated and evaporation is locally terminated^[20]. Therefore a lower process pressure will result in rougher surfaces.

Several types of defects are usually found in CVD graphene: dislocations in the crystal (pentagons and heptagons also known as Stone-Wales defects)^[21,22], point defects in the graphene (one or more missing carbon atoms)^[22,23] and stitching

Figure 2.4 Schematic showing three types of defects which usually occur in CVD graphene: Stone-Wales (a, dislocation in the crystal), single vacancy (b, missing carbon atom(s)) and grain boundary defects (c, caused by difference in crystal angle, in the image 24°).

defects at grain boundaries (differences in crystal angle will create pentagons and heptagons)^[15,24] as shown in Figure 2.4. The point defects can be caused by impurities on the copper surface, and have a diameter in the range of $0.5 - 2\text{ nm}$ with an average spacing in the order of 70 nm ^[23]. Defects can affect the unique properties of SLG and will lower the transport barrier for e.g. protons and lithium ions^[7,22] and gasses^[25] through the graphene basal plane. To compensate for the imperfections caused by defects (introducing e.g. a lower electron mobility or electron scattering), metal or insulating material can be applied selectively e.g. on line defects (on domain edges) by atomic layer deposition (ALD)^[26,27]. Efforts have been made to seal all the graphene defects using ALD (for nanoscale defects $< \text{approx. } 10\text{ nm}$) and interfacial polymerization (for large defects such as cracks $> \text{approx. } 1\text{ }\mu\text{m}$), but even this combination fails for the intermediate size range of defects^[27].

2.2.1 Experimental

Two copper foils have been tested for graphene synthesis: 99.8% Alfa Aesar no. 13382 (coated by a thin film of chromium oxide) and 99.8% Alfa Aesar no. 46986 (uncoated). These polycrystalline copper foils were cut and folded into a small tray of $5 \times 2\text{ cm}$, which is loaded on a quartz boat into the CVD furnace (Figure 2.5). On the entire surface that is exposed to the reactive gasses, graphene will deposit in the CVD process. This graphene on the inside of the copper tray is commonly used, since here better quality graphene is found than on the outside. A cause for this could be that inside the tray an increased copper vapor pressure is present, leading to copper redeposition on the surface, resulting in a smoother surface and therefore improving the deposited graphene^[20].

Cleaning of the copper foil prior to loading in the CVD furnace improves the graphene quality. When using organic solvents, most of the organic contamination is dissolved. More destructive cleaning protocols etch the copper and remove all surface contamination by lift-off^[28]. Drawback of this more destructive cleaning is the increased roughness, but annealing will again smoothen the surface^[28].

In Figure 2.5 the CVD furnace is shown which is developed by the Plasma & Materials Processing (PMP) department of Eindhoven University of Technology. The system consists of a furnace on a slider which can be placed manually over the

Figure 2.5 Chemical vapor deposition system for graphene synthesis located in the PMP department of Eindhoven University of Technology. An overview of the system (a) consisting of: on the left a door to load the copper sample and on the right the sliding furnace enabling rapid heating and cooling. The copper tray in the quartz tube furnace on a boat(b).

quartz tube, enabling rapid heating and cooling of the sample. Using mass flow controllers and a pump the methane, hydrogen and argon inflow is regulated at sub-atmospheric pressures. This low pressure chemical vapor deposition (LPCVD) has the advantage over atmospheric pressure chemical vapor deposition (APCVD) that it has a self-limiting graphene synthesis^[12].

Prior to loading, the copper trays are first pre-cleaned with organic solvents (acetone, ethanol and isopropanol), rinsed, and subsequently etched using nitric acid (1M HNO_3 for 30sec). After this pre-clean, the copper trays are loaded into the tube furnace as shown in Figure 2.5b. The tube furnace is pumped down to $\sim 5 \times 10^{-3}$ mbar, and then for 5 minutes flushed with hydrogen at ~ 0.5 mbar. The sample is annealed at 1020°C (monitored by a thermocouple) with 10sccm hydrogen and 500sccm argon at 0.46 mbar for 30 min, mainly to remove impurities and reduce copper oxide. This high temperature anneal will also smoothen the surface, since the copper becomes more mobile^[29]. Subsequently, graphene is synthesized at 6sccm hydrogen, 100sccm methane, 500sccm argon at 0.51 mbar for 20 min. Then the sample is cooled down to less than 300°C in about 4 min. The tube is further cooled by purging nitrogen and at a temperature of about 100°C the sample is unloaded.

2.2.2 Characterization

On both copper foils long lines can be observed as shown in the white light interferometric recording in Figure 2.6a, which originate from the rolling of the copper foil in the fabrication process^[30]. Along these rolling lines more impurities can be found causing preferred graphene nucleation along these lines^[9,28]. The copper crystal size is ranging from approximately 10 to $250\mu\text{m}$.

To obtain a closed graphene layer a synthesis time of 20 min proved necessary. When the synthesis time was shorter, the layer was not completely closed as can be seen in Figure 2.7, showing flower shaped domains during the synthesis. This domain shape is expected for the low pressure chemical vapor deposition (LPCVD) process as used in our experiment (0.51 mbar)^[17]. Based on Figure 2.7a a rough estimation of the density of nucleation points, and thus the obtained graphene

Figure 2.6 Recordings of copper foil after graphene synthesis showing a periodic roughness of around $60\mu\text{m}$ and an amplitude of $0.5\mu\text{m}$ (recorded with Bruker white light interferometer Contour GT-I).

Figure 2.7 SEM images of the copper sample after the CVD process with 10 min (a) and 20 min (b) of methane exposure. The darker areas correspond to synthesized graphene and the lighter to bare copper foil. For a closed graphene layer a minimum synthesis time of 20 min was required.

domain size is obtained in the order of $30\mu\text{m}$.

In Figure 2.8 the Raman spectra of graphene on copper foil are shown measured with a confocal Raman microscope (Renishaw inVia at lab located at Eindhoven University). Copper is causing a strong background signal, which is weaker for shorter Raman excitation wavelengths. The D-peak is lower than the noise level, which indicates good quality graphene without many discontinuities^[31]. Remarkable is the extremely sharp and symmetric 2D-peak, indicating SLG^[32].

2.3 Graphene transfer

The most common approach to fabricate devices using the CVD graphene on copper foils is by a transfer procedure using a supporting polymer^[33–36]. The transfer procedure is required to obtain a CVD graphene layer on an insulator. We will use this transfer approach in our study.

Figure 2.8 Raman spectrum of two graphene samples on copper foil measured using a 514nm laser. The raw spectra (a+c) are showing a strong background signal from the copper. After background subtraction the G- and 2D-peaks are fitted (b+d).

2.3.1 Experimental

In Section 2.2 the synthesis of graphene on copper foil was discussed. Here we continue our processing with transferring this graphene to a substrate. A schematic overview of the transfer procedure can be seen in Figure 2.1c-i. First the copper foil tray was unfolded, and taped by Kapton tape on a carrier support. When applying the tape extra force was applied at the edges to ensure proper sealing. The taped foil was then coated by supporting polymer (Figure 2.1c). The purpose of the coating is to make the graphene transfer easier to handle and increase the yield of the transfer process^[35,36]. Without a supporting polymer the process would in theory be simpler, however in practice it will result in more breaking, tearing and perforation of the graphene film^[36]. Two transfer polymers were tested: poly(methyl methacrylate) (PMMA) and poly(bisphenol A carbonate) (PC). Both proved to be able to serve as a graphene support during the transfer process. By ellipsometry it was furthermore found that both left a comparable amount of residue after dissolving. A drawback of PC however is occasional film breakage during the transfer procedure which therefore made it harder to handle. Also in view of the less hazardous chemicals involved in the PMMA process (for PMMA acetone and methoxybenzene are used for dissolution instead of chloroform for PC), PMMA was used as a support polymer. After spin coating 2% PMMA (950,000 molecular weight) in methoxybenzene at 1000rpm for 30sec the sample is pre-baked at 180°C for 3min to let the solvents evaporate, resulting

in a film thickness of approximately 100 nm^[37].

To define smaller graphene samples, the PMMA-graphene-copper-graphene stack was first cut (Figure 2.1d). In the synthesis process graphene has been deposited on both sides of the foil. The graphene on the back-side of the foil (the PMMA side of the foil is defined as front) can cause problems, since it can leave carbon deposits under the front graphene after the etching process as schematically shown in Figure 2.9. To remove this back-side graphene, either a dry or a wet etching process can be used. In case of dry etching, a light air plasma is used^[38], generated by a Plasma Cleaner (PDC-002, air plasma at 500 mTorr and ~ 25 W for 2 min). However, confirmation of the complete removal of the back-side graphene was hard to obtain, since no copper oxidation was observed. Furthermore, using this non-directional etching technique, the possibility existed of also etching the polymer support layer and even damaging the front graphene. For this reason the back-side graphene was removed by a wet etching process, where the sample is only modified where it is in contact with the liquid^[39]. The sample was exposed to a diluted solution of nitric acid (4 M HNO₃ for 1 min) (Figure 2.1e). The PMMA-graphene-copper-graphene sample was thereby floating on the solution due to the surface tension of the liquid and the high hydrophobicity of the PMMA^[40]. After this treatment the copper was found to be slightly etched, so it was concluded that the procedure was sufficient to remove the graphene. The samples were then thoroughly and carefully rinsed in demineralized water to remove any acid residue.

For the copper etching (Figure 2.1f) two chemicals are commonly used: ferric chloride (FeCl₃) or ammonium persulfate (APS, (NH₄)₂S₂O₈)^[41]. The ferric chloride etches fast, but has several disadvantages. The iron ions can adsorb to the graphene surface and introduce doping, necessitating one to remove these iron residues using a hydrogen chloride (HCl) treatment. In addition, this etchant can damage the graphene due to the formation of insoluble crystals^[42]. In this research we therefore chose for APS since it, in contrast to the iron based etchant, is free of metal ions which could adsorb to the graphene. The overall reaction for etching copper using APS is:

Figure 2.9 Schematic image of the influence of graphene back-side removal. On the left there is no removal, which could result in rolled up graphene. On the right the result with back-side graphene removal.

A drawback of this method is the potential of oxygen release^[43] during this reaction, which can form nanobubbles puncturing the graphene surface^[44] page 50. The formation of nanobubbles can be prevented by performing a long etching step with diluted solution, giving the produced gas time to dissolve in water. Therefore, the floating polymer-graphene-copper sample was etched in a low concentration APS (40mM etching for 8 – 9hour).

Prior to scooping the polymer-graphene sample with a substrate, it is crucial to properly rinse to remove the ions from the etching solution. In this way, an ion-free interface between the substrate and graphene is obtained. Trapped ions at the graphene substrate interface can degrade the electrical properties of the graphene, since they will introduce doping and scattering^[45]. Dedicated for this experiment therefore, we in-house developed and fabricated a rinsing setup, as shown in Figure 2.10. The sample was brought from the etching solution to this vortex-rinsing glass setup, still floating on the solution by surface tension. Two opposing inlets were connected to the supply of demineralized water, causing a circulating vortex flow by which is the sample is rinsed. The waste water is drained at the bottom, and its conductivity measured by a conductivity meter. The graphene polymer sample was rinsed until the conduction of the waste water was sufficiently low ($< 5 \mu\text{S}/\text{cm}$) to indicate a well-rinsed graphene layer which ensures a minimum amount of contamination. Substrates were also cleaned prior to scooping as will be discussed in the later experimental sections.

After this thorough rinsing step, the polymer-graphene sample is scooped by a substrate (graphene facing the substrate), as shown in Figure 2.1g). Silicon substrates with a 300nm silicon dioxide layer were used as a reference sample, which give maximum optical contrast with graphene^[46]. Using extra tweezers the polymer-graphene sample is positioned on the substrate^[47]. The sample is then dried to air to let the water evaporate. Subsequently the sample is baked

Figure 2.10 In-house developed vortex-rinsing glass setup for graphene rinsing prior to scooping with substrate. In the schematic of the rinsing setup (a) the dimensions, approximate level of demineralized water and the sample position are drawn. In the photograph (b) are the arrows indicating the direction of flow. Demineralized water is added which is rising the sample and waste water is drained at the bottom. The conductivity of the waste water is measured by a conductivity meter to ensure proper rinsing.

(Figure 2.1h) at 125°C overnight, so the PMMA will start to flow^[37], conform to the substrate and increase the adhesion between graphene and the substrate^[47]. This baking step proved to be crucial for adhesion between the graphene and the substrate. We found that when the baking was performed at too low a temperature or for too short a duration, delamination of the graphene was observed in the next step.

The final step of the transfer procedure is to dissolve the supporting PMMA layer in acetone (at room temperature for 1 hour). The samples are subsequently submerged in ethanol and then isopropyl alcohol (IPA) for 5 min. IPA is evaporated in air in order to dry the sample resulting in a substrate coated by graphene. For samples that are very sensitive to breakage induced by surface tension forces, as micrometer-sized-membranes, the use of a critical point dryer (CPD) is preferred^[48]. The CPD exchanges the polymer solution (acetone or ethanol) for liquid carbon dioxide (CO₂), after which it is brought to its critical point, resulting in drying of samples with virtually no surface tension forces occurring.

To completely remove the PMMA layer proved to be difficult, since typically polymer residues were found to be left on the graphene. These residues, often in the form of small islands, can only be removed using aggressive treatments which could damage the graphene^[34]. The PMMA residues will influence the electrical properties of the graphene as they introduce p-doping and scattering (reducing the graphene electron mobility)^[45] and reduce the effective accessible area of the graphene surface. The most effective treatment to remove the residues is by annealing in hydrogen at about 400°C. This treatment will reduce the residual PMMA^[49], but can introduce defects in the graphene^[45]. Even after annealing in ultra-high vacuum (UHV) it is very difficult to completely remove the residues, since this treatment still leaves carbon traces on the sample, as covalent bonds can form between the PMMA and the graphene^[50,51]. In this research it was chosen to not focus on the residue removal from the CVD graphene, since these residues are expected to have a negligible effect on our experiments.

2.3.2 Characterization

In the previous section the transfer of the graphene from the copper catalyst to a substrate was discussed. To characterize the coverage and morphology of the transferred graphene optical microscopy was used. Additionally, Raman spectra were recorded to probe the crystal quality, number of layers and the condition of the graphene.

When the baking step is not performed (only sample drying at 60°C for 10 min), the graphene will delaminate from the substrate and form rolled flakes (Figure 2.11a). A graphene transfer where the back-side graphene is treated by air plasma results in rolled graphene debris under the graphene sheet (Figure 2.11b). If a proper bake and graphene back-side removal were both performed, this resulted in a good coverage (Figure 2.11c). Based on these observations it can be concluded that for a good graphene transfer two experimental parameters are crucial: the back-side graphene removal and the post-bake after scooping.

Cracks can occasionally be found in the transferred graphene. Folded wrinkles are commonly present (Figure 2.11d), and are caused by the excess of graphene for surface coverage, stemming from the large-scale periodical roughness of the copper

Figure 2.11 Results of the graphene transfer showing the influence of two important transfer steps: the removal of the back-side graphene and the post-bake after scooping. After an insufficient post-bake the graphene delaminated (a). In addition, insufficient back-side graphene removal resulted in graphene debris (b). A proper post-bake and graphene back-side removal resulted in a good graphene coverage (with occasionally a crack in the layer) (c) a zoom in shows graphene wrinkles (d). The inset in (d) shows a cross-sectional schematic of a folded graphene wrinkle. Graphene was transferred to a silicon (a) and a 300nm SiO₂/Si substrate (b-d).

rolling lines (see Section 2.2.2). We hypothesize that the graphene wrinkles are folded as shown in the inset in Figure 2.11d^[52,53].

The Raman spectra of transferred graphene were recorded using a WITec alpha 300 system with a 532nm laser at 1mW using a 100x objective (0.9 NA). The spectra of the suspended graphene and the graphene on silicon dioxide are comparable to the spectra of graphene on copper, where the D-peak is still absent indicating a good transfer. The 2D-peak is wider when the graphene is transferred from copper ($2D_{FWHM} \approx 21 \text{ cm}^{-1}$) to silicon dioxide ($2D_{FWHM} \approx 30 \text{ cm}^{-1}$)^[54]. According to theory the 2D-peak position is at $\sim 2677 \text{ cm}^{-1}$ for a 532nm Raman laser^[55]. The G- and 2D-peak position are influenced by several factors: for fewer graphene layers the G-peak red-shifts (higher G_{pos})^[31], while graphene doping red-shifts the G-peak (higher G_{pos}) and blue- or red-shifts the 2D-peak (depending on the type of doping),^[56] and strain red-shifts the G- and 2D-peak positions (lower G_{pos} and $2D_{pos}$).^[57,58]

To measure trans-membrane transport of suspended graphene sheets, silicon nitride membranes have been fabricated. For details on this fabrication process see Section 5.3. Graphene is transferred to such a membrane with a pore of 2μm diameter as shown in Figure 2.12a. Silicon nitride is a very suitable material for

Figure 2.12 Analysis of graphene suspended over a micropore and on silicon dioxide. The micrograph shows the 2µm micropore (a). The Raman spectrum of the suspended silicon nitride membrane possesses a very large background (b), making it impossible to detect the graphene peaks. The fit of the G- and 2D-peak to suspended graphene (c) is similar to the fitted graphene spectrum of the graphene on silicon dioxide (d), both showing single layer graphene which was transferred in the same graphene batch (so possessing identical experimental parameters).

membrane fabrication, however for performing Raman spectra measurements of graphene it is unsuitable. Especially for graphene on silicon nitride membranes a large Raman background is observed as can be seen in Figure 2.12b. This background signal is much larger than for silicon nitride on silicon, due to the light which couples to the silicon nitride membrane as a waveguide. For graphene suspended over the silicon nitride micro-pore this background is not observed, since the confocal laser theoretical spot size ($\frac{1.22\lambda}{NA} = 0.72\mu\text{m}$) is smaller than the pore diameter. Therefore a clean graphene Raman spectrum could be obtained (Figure 2.12c) for this suspended graphene. This suspended graphene proved to be a monolayer (low $2D_{FWHM}$ and symmetrical 2D-peak), unstrained and undoped ($2D_{pos} \approx 2677\text{cm}^{-1}$). In the same graphene transfer batch graphene was also transferred to a reference sample (300nm SiO_2/Si substrate), which showed a comparable spectrum (Figure 2.12d). The graphene on the silicon dioxide appeared slightly n-doped (the G-peak red-shifted (higher position) and narrower and the 2D-peak blue-shifted (lower position))^[56], presumably caused by the adhesion interaction energy to the silicon dioxide substrate^[59].

Folded graphene wrinkles of the transferred graphene (see Figure 2.11d) show

Figure 2.13 The Raman spectrum of flat graphene (a) is different from a folded graphene wrinkle, where the latter shows a stronger D-peak, a shoulder next to the G-peak and larger FWHMs.

clearly a different Raman spectrum compared to flat SLG. As can be seen in Figure 2.13, the D-peak intensity is much higher, a shoulder peak appears next to the G-peak (D' at $\sim 1620\text{cm}^{-1}$) and the G- and 2D-peak are wider. These Raman features are caused by electrically decoupled disordered graphene multilayers (turbostratic graphite), in contrast to normal multilayer graphene which implies a stacking order between adjacent graphene layers (which will show a low D-peak)^[31,55,60,61]. This description based on the measured Raman spectrum coincides well with the (folded) graphene wrinkles.

The coated and uncoated foils were both tested for graphene synthesis with the standard graphene CVD recipe developed in the PMP group. In contrast to the coated copper foil (Alfa Aesar no. 13382), the uncoated copper foil (Alfa Aesar no. 46986) did not lead to proper graphene deposition. In Figure 2.14 the Raman spectrum analysis is shown for graphene synthesized using the uncoated foil and transferred to a silicon dioxide substrate. From this analysis it follows that the disordered carbon follows the copper lines, while in between those lines the spectrum indicates a better quality graphene. In the disordered graphene spectrum the sharp graphene features are not present and thus no proper carbon crystals have been synthesized. The spectrum is comparable to multilayer nanographite with a very low degree of crystallinity^[60,62]. The graphene synthesis could potentially be improved by a more thorough pre-cleaning (however introducing extra roughness) or longer hydrogen anneal (which may not be effective) to remove all impurities. In contrast, good quality SLG was synthesized on the coated copper foil. We explain this by assuming that the coating is etched off in the pre-cleaning process, leading to a clean un-oxidized catalytic surface. Therefore the coated copper foil was used in all subsequent graphene synthesis experiments.

2.4 Conclusion

Continuous graphene layers were synthesized on copper foil using a CVD process in a tube furnace. The finally obtained copper foil has a periodical roughness caused by the rolling process during the foil fabrication. The minimum time for synthesizing a closed graphene layer, covering the complete copper surface, was

Figure 2.14 Quality of the graphene synthesized on the uncoated foil showing the copper line pattern (green indicates better quality graphene). 2D-to-G-peak intensity ratio I_{2D}/I_G (a); this ratio gives a rough indication for the number of graphene layers. D-to-G-peak intensity ratio I_D/I_G (b); the lower this ratio, the less defects present in the graphene. Full width half maximum (FWHM) of the G-peak (c); a higher value more disorder in the crystal structure. The two crosses mark the locations of the displayed Raman spectra (d); the gray spectrum shows a disordered carbon deposited and the black spectrum shows graphene with defects. The spectra were measured using a 532nm laser and a 100x objective (0.9 NA) leading to a theoretical spot size of 0.72 μm.

investigated. Finally, the graphene quality and number of layers were analyzed on the copper by Raman spectroscopy. It was concluded that the coated copper foil (Alfa Aesar no. 13382) led to the best graphene deposition. CVD synthesized graphene was transferred from its catalyst (copper foil) to a substrate (silicon dioxide or silicon nitride membranes) using a manual process. In this process a polymer support layer was employed, and wet etching was used to remove the back-side graphene and copper. After a thorough rinsing step, the floating polymer-graphene sample was scooped by a substrate. The device assembly was finalized by dissolving the supporting polymer.

The graphene transfer protocol was improved by the identifying critical steps in the process. Delamination from the substrate, improper back-side graphene removal and graphene wrinkles were optically imaged. Graphene peaks in Raman spectra of graphene on silicon dioxide, suspended graphene and wrinkled graphene

were analyzed, and revealed the quality of the synthesized graphene. Our findings show that graphene transfer yield is increased by a nitric acid etch and a proper PMMA baking step. The first removed the back-side graphene to circumvent debris from back-side graphene. The latter caused the PMMA to conform to the substrate, increasing the adhesion between the graphene and the substrate. Furthermore, an in-house rinsing setup was build that reduced the number of manual PMMA/graphene rinsing steps to just one and the setup also enabled live monitoring of the rinsing water conductivity providing a proper rinsed graphene surface.

2.5 References

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3

Graphene synthesis by directional copper dewetting*

In this chapter a method for the spatial control of direct graphene synthesis onto silicon dioxide by controlled dewetting is presented. The dewetting process is controlled by combination of a grooved substrate with copper deposition at an angle. The substrate is then treated by a typical graphene chemical vapor deposition synthesis process at elevated temperature during which directional dewetting of the copper into the grooves occurs while graphene is deposited at the mesas in between the grooves. The dewetting process and the synthesized graphene layer are characterized. The method is a non-manual, controllable and wafer scale process, and therefore opens new possibilities for the construction of functional devices as e.g. transistors. Additional material on this chapter is available in Appendix A.

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3.1 Introduction

Since its discovery in 2004 as functional material, there has been ever growing attention for graphene, owing to its unique electronic and mechanical properties^[1–5]. For most practical devices, such as transistors, it is essential to be able to synthesize a single layer of graphene on a dielectric surface^[4,6,7]. The first method successfully used to isolate a single layer of graphene was exfoliation of highly ordered pyrolytic graphite (HOPG) on silicon dioxide^[8]. Although this method results in high quality graphene, it is labor intensive, offers only a low yield and is therefore not useful for mass production. Another route to isolate graphene is by dissolving graphite in an oxidizing solution in combination with a drying procedure^[9–11]. Such chemical methods typically result in a large spread in the number of graphene layers^[12]. As an alternative, chemical vapor deposition (CVD) processes enable large area single layer graphene production. Usually, transition metals (copper, nickel etc.) are used as catalysts for the decomposition of gaseous alkanes (methane, ethane)^[13]. To release the CVD graphene from the metal substrate however, a manual transfer protocol is required, which makes the process again labor intensive and hard to automate. Therefore a direct synthesis process on dielectric substrates is seen to be crucial for future proper integration of graphene into practical devices. The possibility of graphene synthesis on copper oxide where copper oxide is also the catalyst material has been demonstrated^[14]. However, the electrical properties of copper oxide make it unsuitable for device applications^[15]. Other research has shown that direct graphene synthesis is possible by dewetting of thin copper films on silica substrates using a CVD protocol^[16]. A disadvantage of this route is that dewetting copper on a flat substrate results in a randomly distributed patchy graphene pattern^[16–20]. Furthermore, the remaining copper particles will not fully evaporate, even after long annealing^[16,18]. When very long process times are used, the remaining copper particles can eventually even sink into the silica substrate^[21].

In this chapter a solution for this random copper dewetting consisting of an improved method for direct and controlled graphene synthesis on silicon dioxide using controlled dewetting and evaporation of copper is reported. The dewetting process is controlled by combination of a grooved substrate with copper deposition at an angle. Areas for graphene deposition are defined as mesas in between grooves produced using a potassium hydroxide (KOH) wet etching process of a silicon substrate. Subsequently the wafer is oxidized to form a layer of silicon dioxide (SiO_2), and a layer of copper (Cu) is deposited on the wafer. There are several advantages of using a grooved substrate over e.g. copper strips. The copper dewets to a single direction which is defined by the copper deposition angle, making it possible to deposit a single graphene line on the mesa. In addition, minimum copper oxidation is occurring, since the last step prior to the graphene synthesis is the deposition of copper enabling a proper catalytic surface for graphene deposition. In this research copper was chosen, because of its excellent graphene synthesis catalyst properties, low carbon solubility and dewetting properties^[16,19,22]. For CVD graphene synthesis on thin copper films a lower temperature is required compared to copper foils^[23]. During the CVD process, graphene is continuously deposited directly onto the silicon dioxide mesa (the flat area between grooves as displayed in Figure 3.1a) while the copper is evaporating and dewetting into the silicon dioxide

grooves^[16,19]. The quality of the deposited graphene which stays directly on the silicon dioxide has been optimized by varying the partial pressures of the reactive gasses in the CVD process. The method does not require graphene transfer and therefore opens new ways for the implementation of automated wafer-scale graphene synthesis.

3.2 Theory

The design of the fabricated grooved substrate is shown in Figure 3.1a. The mesa widths m are ranging from $1\mu\text{m}$ to $10\mu\text{m}$ and the groove width w is set to $m/0.4$. The groove angle α_g is determined by the silicon $\langle 100 \rangle$ crystal orientation as 54.7° . The silicon substrate was oxidized, resulting in a silicon dioxide layer of 300nm serving as a copper diffusion barrier. Subsequently copper and graphene were deposited as schematically shown in Figure 3.1. The copper is deposited on the substrate at an angle α_{Cu} by e-beam evaporation. This results in a copper thickness on the mesa of $h = h_0 \cos(\alpha_{Cu})$, where the deposition thickness h_0 is set to 500nm . Subsequently, the substrate is treated by a CVD process at a temperature of 1000°C . In this process the copper conforms initially to the copper silicon dioxide contact angle, followed by dewetting which is driven by the gradient of the curvature in the copper landscape^[24,25]. During this dewetting process,

Figure 3.1 Design of the substrate with a groove width w and mesa width m which repeat in period P (a). The groove is etched at an angle α_g resulting in a groove depth d . Schematic of the method: copper deposition under an angle on the silicon dioxide/silicon substrate (b), conformation of the copper to the contact angle during heating up (c), propagation of the contact line by dewetting and evaporation of the copper during the CVD process leaving a graphene layer (d) and the final situation with copper in the groove and the mesa covered by graphene (e).

graphene is synthesized and left on the silicon dioxide surface by the retreating copper^[16,24–26]. Three phenomena can be observed in the dewetting process: conformation to the contact angle, propagation of the contact line and occasional film punch-through.

Firstly, to minimize surface energy, a fast rearrangement at the edge of the film will occur in the initial stage until the contact angle θ_c is obtained^[27]. This contact angle of the dewetted copper with the surface can be calculated using the Young's Equation

$$\gamma_i + \gamma_m \cos \theta_c = \gamma_s \quad (3.1)$$

The interface energy γ_i at the copper-silicon dioxide interface is 1.1 Jm^{-2} , the surface energy of copper γ_m is 1.3 Jm^{-2} and the silicon dioxide surface energy γ_s is about 0.3 Jm^{-2} close to the melting temperature of copper (1083°C), resulting in a contact angle of approximately 128° .^[28,29]

Secondly, after the fast initial conformation, copper evaporation and dewetting are driving the propagation of the contact line^[27,30]. The dewetting transport is dominated by surface diffusion of the copper (bulk transport can be neglected), minimizing the surface chemical potential and therefore smoothening the film over time^[27,31,32]. The chemical potential along a line profile $\mathbf{s}$ depends on its curvature $\mathbf{K}$ (in m^{-1}). Therefore the gradient of this curvature along a line $\left(\frac{\partial \mathbf{K}}{\partial \mathbf{s}}\right)$ leads to a metal flux $\mathbf{J}_m$ (assuming an isotropic surface energy) according to^[25]:

$$\mathbf{J}_m = \frac{-D_s \gamma_m N_s \Omega}{kT} \frac{\partial \mathbf{K}}{\partial \mathbf{s}} \quad (3.2)$$

where N_s the number of copper atoms per unit area, Ω the molecular volume of copper and kT the product of the Boltzmann constant and the temperature. The surface diffusion constant D_s is strongly temperature dependent as $D_s = D_0 e^{\frac{-Q_s}{kT N_a}}$ where N_a is Avogadro constant. For copper in a hydrogen environment at 1.0 mbar the surface diffusion pre-exponential is $D_0 = 1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and the activation energy $Q_s = 92 \text{ kJ/mol}$.^[33] The temperature dependence of this surface diffusion allows tuning of the retraction velocity of the contact line. For metal films on flat substrates, the contact line will propagate as a function of time in the form of $x_{cl} \sim t^{\alpha_{dw}}$, where α_{dw} is dependent on the geometrical film assumptions^[34]. In most studies an α_{dw} -factor of about $\frac{2}{5}$ is found, which is practically independent of the contact angle^[27,34,35]. The mechanism for graphene deposition proposed by Ismach et al.^[16] is that graphene is synthesized by the catalytic action of the copper. While the contact line is retracting, graphene is transferred from the copper to the silicon dioxide surface, resulting in an insulating surface covered by graphene.

The deposited copper film is conformal and will have a constant curvature at the mesa-groove corner prior to dewetting (see Figure 3.3a). To reduce the overall curvature of the copper surface, a dewetting flux will drive copper away from the mesa-groove corner as follows from Equation 3.2, resulting in local flattening of the surface^[31,36]. This process leads to a thinning of the copper film, eventually leading to a punch-through of the copper film by the mesa-groove corner.

3.3 Experimental

An oxidized $\langle 100 \rangle$ silicon wafer was patterned using conventional lithography with a line mask of 400 lines ranging from 1 μm to 10 μm width. After performing dry etching of the silicon dioxide, silicon was wet-etched anisotropically using 25% KOH at 75 °C to manufacture the grooves. Because of the crystal orientation of the wafer, a groove angle α_g of 54.7° is obtained. Subsequently, the grooved substrate was oxidized for 300 nm for optimal graphene visualization and to serve as a copper barrier at higher temperatures. Next, 500 nm of copper was deposited using e-beam evaporation at a controlled angle. Directly after this, the CVD process was performed in a cold-wall reaction chamber, which was purged with hydrogen prior to starting the process. While the substrate was heated to 1000 °C (ramping up and down at $\sim 60^\circ\text{C}/\text{min}$), the CVD-process was executed at a pressure of 10 mBar with a hydrogen flow of 50 sccm, methane flow of 50 sccm and argon flow of 700 sccm for 15 minutes, see Appendix A for the CVD log data. The Raman spectra are recorded using a WITec alpha 300 system with a 532 nm laser at 1 mW using a 100x objective (0.9 NA) leading a spot size of $\frac{1.22\lambda}{NA} = 0.72 \mu\text{m}$. For the fabrication of the graphene transistor device, gold contact pads were deposited by electron beam evaporation using a shadow mask, which were connected to a PCB by wire bonding. Subsequently, the gold pads and wire bonds were covered by epoxy (hysol), leaving the graphene area between the electrodes (5 mm) open. A droplet of 0.1 M KCl solution was applied on this area in which a silver/silver chloride electrode was inserted. Between the gold pads a voltage of 0.1 V was applied for measuring the in-plane conductance. The graphene was solution gated by connecting the silver/silver chloride electrode to a Biologic SP300 potentiostat.

3.4 Results and Discussion

To determine the copper silicon dioxide contact angle, a copper film of 500 nm was deposited on a flat substrate and processed in a CVD process at 1000 °C. By scanning electron microscopy (SEM) a contact angle of $131^\circ \pm 4^\circ$ was obtained, as shown in Figure 3.2, which is in agreement with the theoretical contact angle.

Figure 3.2 False colored cross-sectional SEM image of the dewetted copper film (orange) on silicon dioxide (blue) processed in a CVD process at 1000° for 30 min, showing a contact angle of about 131°.

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Figure 3.3 False colored SEM images of a cross section of the grooved substrate with 300nm silicon dioxide (blue) with 500nm of copper (orange) deposited at 35° prior to (a) and after the chemical vapor process showing full dewetting (b), partial dewetting (c) and punch-through (d) with mesa widths of 3.0μm, 4.1 μm and 5.0 μm, respectively.

Subsequently, the controlled dewetting on a grooved substrate was tested by depositing copper and applying the graphene CVD protocol. Three regimes could be distinguished in the resulting structures: fully dewetted, partially dewetted and punched-through, as can be observed in Figure 3.3. In the case of full dewetting, the copper has retracted into the groove. On the mesa (and in the groove) a layer of graphene was found to be deposited. Wider mesas became partially dewetted, with fingers of copper still remaining on the mesa. For even wider mesas punch-through of the copper film at the mesa-groove corner occurs, resulting in a remaining roll of copper.

The effect of the wafer cleaning procedure prior to the copper deposition was investigated by testing the following cases: 5 min UV-ozone, 5 min oxygen plasma, directly from oxidation oven and no pre-clean. No significant influence of this pre-cleaning protocol on the dewetted mesa area was found.

To further control directional dewetting, copper was deposited at an angle on the grooved substrate. A series of deposition angles α_{Cu} was tested to investigate its effect on the dewetted mesa area (see Appendix A for optical microscopy data). By image analysis of the dewetted surface the relative dewetted mesa areas as function of mesa widths and deposition angle were found as shown in Figure 3.4a. To the measurement data a logistic function was fitted in the form of

$$f(m) = L \left(1 - \frac{1}{1 + \exp(-k(m - m_{\text{mid}}))} \right) \quad (3.3)$$

where L , k and m_{mid} are fitting parameters. The fit parameter m_{mid} , the midpoint of the logistic curve, as function of deposition angle α_{Cu} is shown in Figure 3.4b. Since the groove angle α_g is 54.7°, the minimum deposition angle α_{Cu} for directional dewetting is 35°. The thickness of the copper film at the mesa-groove corner is increased by larger deposition angles α_{Cu} , delaying punch-through and allowing the full dewetting of wider mesas. However, if the deposition

Figure 3.4 The resulting dewetted mesa area as function of the total mesa width m for a series of deposition angles α_{Cu} (a), where the copper deposition thickness h_0 is set to 500nm. To these measurement data a logistic function is fitted. A dewetted mesa area of 100% corresponds to a fully dewetted mesa. The fit variable m_{mid} of the logistic fit function (see Equation 3.3) versus the copper deposition angle (b), showing an optimal deposition angle of 45° , the error bars show 95% fit confidence bounds.

angle α_{Cu} becomes too large, the mesa copper thickness h decreases rapidly. This thinner mesa copper film, in turn, breaks up into small structures^[24] (see also Appendix A), resulting in a larger transition region. Using a deposition angle of 45° the widest fully dewetted mesas were obtained.

To optimize the quality of the deposited graphene, several recipes were tested in which hydrogen and methane gas flows were varied. The total gas inflow was set to 800sccm using argon. The process pressure was set to 10mbar to prevent a too fast copper evaporation^[30]. The Raman spectra of the deposited graphene were subsequently recorded using a 532nm laser. The graphene spectrum shows three characteristic peaks: the D-peak (1350cm^{-1}) indicating defects and discontinuities (e.g. crystal boundaries) in the graphene crystal, the G-peak (1590cm^{-1}) probing the in-plane bond stretching mode and the 2D-peak (2700cm^{-1}) holding information regarding the stacking orders^[37,38]. To analyze the measured Raman spectra, Lorentzian peaks were fitted to the mapped Raman scan. A sharp (low FWHM) and symmetric 2D-peak indicates single layer graphene^[37]. Ideally no defects are present, thus the D-peak normalized to the G-peak intensity (I_D/I_G) should be low. Fewer graphene layers result in a higher G-peak position^[38,39], however doping will also increase this position^[40].

A series of recipes for graphene deposition was tested and Raman spectroscopy fitting results can be found in the Appendix A. The four most significant graphene quality indicators displayed are indicators for the number of layers and defect density (including grain size). In this process we aim at producing defect free, single layer graphene. When analyzing the graphene quality indicators discussed above, the recipe using 50sccm methane and 50sccm hydrogen was selected for the subsequent graphene deposition experiments.

The spatial distribution of the graphene quality was analyzed and can be found in Figure 3.5. Where the copper dewetting started, first no graphene is deposited. This is related to the high temperature required to synthesize graphene, which is

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Figure 3.5 Characterization of the deposited graphene on the mesa area, using the best CVD settings (hydrogen to 50sccm and methane to 50sccm). Raman spectra were recorded on the mesa (light blue) as indicated by the red box on the optical image, scale bar is 10 μ m (a). The colored crosses mark the locations of the displayed three Raman spectra (d). The dashed lines indicate the mesa edge in the mapped Raman scans, which reveal the graphene coverage on the mesa (b,c,e,f). The apparent noise in the right most spectrum (pink) is caused by the copper next to the mesa (d). The 2D- to G-peak intensity I_{2D}/I_G shows uniform quality over the sample (b). The D- to G-peak intensity I_D/I_G reveals more defects on the left edge of the mesa, where the copper dewetting had started (c). The 2D-peak sharpness is uniform over the sample, however next to the mesa the 2D-peak is sharper (e). The G-peak position is higher on the mesa than next to the mesa (suspended and on copper), which is probably caused by the difference in the substrate induced doping (f).

not yet reached when the copper starts dewetting. From this point on, the presence of a continuous layer of graphene was confirmed with Raman spectroscopy. The first deposited graphene possesses a higher D-peak compared to the rest of the mesa. We expect a variation in dewetting velocity to influence the quality of the deposited graphene. The dewetting velocity can be influenced by for example the process temperature. We therefore believe that it is possible to improve the graphene quality further by tuning the dewetting velocity.

After close inspection, the SEM images revealed ridging in the silicon dioxide as can be seen in Figure 3.6. By atomic force microscopy (AFM) the ridges were measured to have an average amplitude of 4nm and period of 47nm (see Appendix A for AFM data). The forming of ridges during the copper dewetting is explained by transport of silicon dioxide along the interface with copper to the triple point where process gasses, copper, and silicon dioxide meet. The silicon dioxide is transported by surface diffusion, which is inherent to metal ceramic systems at elevated temperatures^[21,41–43].

In the study of Ismach et al.^[16] these ridges are also observed, however here it was suggested that these ridges were wrinkles in the graphene. To conform that

Figure 3.6 False colored SEM image of the grooved substrate showing the fully dewetted mesa surface with silicon dioxide (blue) and the dewetted copper (orange). On the mesa surface ridges and graphene are found, which are both formed during the copper dewetting in the CVD process.

the ridges are in the silicon dioxide and not caused by e.g. graphene wrinkles, the sample was treated by an oxygen plasma to strip the graphene. AFM images before and after this treatment showed comparable roughness, from which we conclude that the silicon dioxide was ridged during the dewetting. The continuity of the graphene layer was investigated by a hydrofluoric acid (HF) treatment, since the graphene will protect the silicon dioxide against etching. After etching, the roughness was found to be comparable to the original sample, conforming that the graphene layer is continuous. In the AFM recordings nanoparticles of approximately 24 nm were observed on the sample surface. Analysis with energy selective backscattered (EsB) detector and energy-dispersive X-ray spectroscopy (EDX) showed that these nanoparticles are copper particles which must have pinched off during the dewetting process (see Appendix A for EsB data). The particles are most probably completely wrapped by graphene^[44].

Figure 3.7 The graphene in-plane conductance as a function of the gating voltage. The gating voltage was applied using a silver/silver chloride electrode in a 0.1 M potassium chloride solution. The length of error bars represent two standard deviation units of the measurement.

The deposited graphene could be used as a transistor channel, which was demonstrated by the construction of a device in which the graphene can be gated. The synthesized graphene was interfaced by gold electrodes and a well was made with epoxy resin which served as a reservoir for electrolyte solution. By solution gating a high gate capacitance is achieved, inducing high doping levels^[40,45]. In Figure 3.7 the rectifying behavior of the graphene as a function of gating voltage is shown, which is normally not present in single layer graphene field effect transistor devices^[46]. The curve we found indicates the presence of a band gap in the graphene^[47], which is useful for transistor devices.

In addition to this, the synthesized graphene could be exploited for other functional devices such as (bio)sensors, since the synthesized graphene layer consists of relatively small grains (nanocrystalline^[16]) and therefore possesses a relative high density of reactive grain boundaries. Another potential application for this graphene deposition method, after further optimization, would be the fabrication of graphene nanoribbons.

3.5 Conclusion

The presented method improved the direct synthesis process of graphene on silicon dioxide by controlling the location of the dewetted areas. For this purpose copper was deposited under an angle on a grooved substrate. The copper dewetted into the groove, leaving a layer of graphene on the flat part of the silicon dioxide surface. Optimization of the CVD process has been performed to obtain the best synthesized graphene. Analysis furthermore showed that the graphene layer is closed and the silicon dioxide surface was ridged after the dewetting process. This improved method opens new possibilities for wafer scale graphene synthesis directly on insulating surfaces.

3.6 References

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4

Raman spectroelectrochemistry on graphene*

In this chapter the electrochemistry at graphene is investigated using spectroelectrochemistry. The electrochemistry on graphene is of particular interest because of graphene's high surface area, high electrical conductivity and low interfacial capacitance. Because the graphene Fermi level can be probed by its strong Raman signal, information on the graphene doping can be obtained that is potentially caused by adsorbed atoms or molecules. The analysis was successfully performed using three electroactive substances with different electrode interaction mechanisms: hexaammineruthenium(III) chloride (RuHex), ferrocenemethanol (FcMeOH) and potassium ferricyanide/potassium ferrocyanide ($\text{Fe}(\text{CN})_6$). The adsorption state was probed by analyzing the G-peak position in the measured in-situ Raman spectrum during electrochemical experiments. Based on our findings we conclude that Raman spectroelectrochemistry on graphene is a tool to obtain in-situ information on adsorbed species on graphene, isolated from the rest of the electrochemical behavior, making graphene an even more interesting electrode material. We found indications that the adsorption of species for the larger part takes place on the less reactive basal plane, while local reactive sites determine the electrochemical behavior. We conclude that electrochemical Raman spectroscopy on graphene is a valuable tool to obtain in-situ information on adsorbed species on graphene, isolated from the rest of the electrochemical behavior.

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4.1 Introduction

Graphene has received much attention during the last decade because of its unique properties such as mechanical strength and impermeability to gasses.^[1–5]. Also the electrochemistry and energy storage on graphene is particularly interesting^[6] because of its high surface area^[7], high conductivity^[1,7] and low interfacial capacitance^[8]. Although graphene shows unique behavior as electrochemical interface^[9], the mechanism behind many of its specific properties is still not fully understood^[10–13]. Importantly, the graphene Fermi level can be probed by its strong Raman signal, giving information about the graphene doping that is potentially caused by adsorbed atoms or molecules^[14–16]. In Raman spectroelectrochemistry experiments, electrical and spectroscopic measurements are performed simultaneously, which gives real-time information about the graphene Fermi level during the electrochemical experiment^[17]. With this, a better understanding of adsorption at graphene surfaces can be acquired, which can be used to improve the performance of graphene for electrochemical applications and energy storage.

Here we will exploit the technique of Raman spectroelectrochemistry to obtain information about, among others, the reaction kinetics during Faradaic reactions on the surface of graphene. The results are obtained using chemical vapor deposited (CVD) graphene. In general, redox reactions at electrodes consists of different subsequent steps, such as mass transfer, chemical reactions (preceding or following the electron transfer), ad- and desorption (of the molecule to the electrode surface) and the electron transfer itself^[18]. Often the desorption phase is the rate-determining step in nano- and microfluidic systems, where mass transport by diffusion is relatively fast compared to large scale systems. E.g. in redox cycling experiments slow desorption results in a lower effective diffusion coefficient and thereby reduced signal levels^[19]. Our working hypothesis in this investigation is that adsorption of redox-active species on graphene can be measured by Raman spectroscopy. From this hypothesis follows our research question: can we find evidence for the adsorption state during redox reactions at graphene in the Raman spectrum? To investigate this, we measured the Raman spectra of graphene during electrochemical measurements of three electroactive substances. We thereby chose substances of which, according to literature, the adsorption differs. To explain redox reactions for complex molecules two mechanisms are recognized: inner-sphere and outer-sphere electrode reactions^[20]. In outer-sphere electrode reactions the reactant and the product do not require strong interaction with the electrode surface^[18]. Outer-sphere redox molecules that we use are RuHex (hexaammineruthenium(III) chloride)^[12,18] and FcMeOH (ferrocenemethanol)^[10]. Although FcMeOH is an outer-sphere redox molecule, it is known to adsorb (mostly) reversibly to the graphene surface with a desorption time constant of several minutes^[10,21]. After performing electrochemical experiments with FcMeOH a fraction of $\sim 1\%$ of a monolayer is permanently bound to the graphene surface, most probable at local defects sites for which the exact mechanism is unidentified^[10,22]. In contrast to outer-sphere molecules, species involved in inner-sphere electrode reactions require a strong interaction with the electrode surface in order to exchange electrons. Hereby the adsorption mechanism could be specific for an electrode material^[18]. In our investigation, the tested inner-sphere redox couple is $\text{Fe}(\text{CN})_6$ (potassium ferricyanide/potassium ferrocyanide), which is known to have different

reaction kinetics on monolayer graphene and pyrolytic graphite^[12]. For further interpretation of the voltammogram also the overpotential is of importance. For the redox molecules in our experiments (assuming symmetrical charge transfer coefficients), the distance between the oxidation and reduction peak in the voltammograms represents in approximation the required overpotential for the reversible reaction to occur. A higher required overpotential is related to a higher activation energy for the reaction to occur at the specific electrode^[18].

4.2 Theory

Whenever molecules adsorb to the graphene surface, the graphene Fermi level is shifted by local doping (changing the carrier concentration), which can be probed by Raman spectroscopy^[17,23]. The measured Raman spectrum S_m will be a superposition of two spectra: the graphene with adsorbed molecules S_{ad} and the bare graphene S_{gr} . For the ratio between both we define an occupation factor β as follows

$$S_m = S_{ad}\beta + S_{gr}(1 - \beta) \quad (4.1)$$

when this factor is low $\beta \approx 0$ solely the bare graphene spectrum is measured, indicating no interaction between the graphene and the molecules in solution. For a large factor $\beta \approx 1$ the graphene is entirely occupied by adsorbed molecules which interact with the graphene and therefore change the Raman spectrum. For calculating this β we model the adsorption of molecules as a continuous time-averaged molecular adsorption coverage. Our research question is, whether we can find evidence for the adsorbed state during the electrochemical reaction in the Raman spectrum. Making the basic assumptions that every molecule, inner- or outer-sphere, involved in a Faradaic reaction adsorbs and every molecule that adsorbs reacts Faradaically, we can define the following expression

$$\beta = \frac{J_m \tau_{ad} A_{ad}}{q_e} \quad (4.2)$$

where J_m is the current density of the Faradaic reaction at the graphene layer and q_e the elementary charge. τ_{ad} is the average adsorption time of a molecule to the graphene surface and A_{ad} is the graphene area affected by this adsorbed molecule and that shows as a consequence the spectrum of graphene with an adsorbed molecule S_{ad} instead of the bare graphene spectrum S_{gr} .

Using the parameters of our experiment, we can derive a lower limit for the adsorption time τ_{ad} assuming that a minimum β of 0.1 is required to obtain a measurable signal S_{ad} on top of the bare graphene signal S_{gr} . A typical current density J_m in our electrochemical experiments is $5 \mu A / (5 mm)^2 = 0.2 A / m^2$. Next we simply assume that the molecular size is approximately equal to the affected graphene area A_{ad} , which is $0.2 nm^2$ for a typical redox molecule in our experiment. This results in a minimum adsorption time τ_{ad} of about 0.4s needed to be able to obtain a measurable change ($\beta = 0.1$) in the graphene Raman spectrum.

In the measured Raman spectrum the G-peak position (in cm^{-1}) is analyzed, since this is the most sensitive indicator for the graphene Fermi level and therefore the adsorption level^[8,17]. When doping is induced in the graphene, this will cause two effects in the G-peak position curve. Firstly, doping will lead to a shift

in the charge neutrality point voltage V_{CNP} , which is the applied gate voltage corresponding to a minimum in the G-peak position curve, probing the graphene Fermi level. This will cause the valley to move horizontally (n-doping to more negative voltages, p-doping to more positive)^[14]. Secondly, the G-peak is known to shift position upon electrochemical doping^[8], resulting in a vertical shift of the curve. In addition to these two effects, the slope of this G-peak position curve is electrolyte concentration dependent: at lower ionic concentrations this slope is decreasing whenever species adsorb to the surface, indicating a decrease of electron and hole mobility^[14].

4.3 Experimental

The schematic of the fabrication and measurement setup of the graphene device are shown in Figure 4.1. Graphene is transferred to a silicon dioxide substrate using a procedure discussed in Chapter 2. Two gold electrical contacts are deposited on this graphene layer using a steel shadow mask and subsequently wire bonded

Figure 4.1 Schematic of the graphene device fabrication process for Raman spectroelectrochemistry. To a silicon substrate with 300nm of silicon dioxide (a) graphene is transferred (b). Two gold contact pads are evaporated by e-beam evaporation (c), and encapsulated by epoxy glue (Hysol) (d). Finally, a platinum wire is glued on top of the device (e). In the measurement setup, the wires bond to the graphene serve as the working electrode (WE), the platinum wire as the counter electrode (CE) and Ag/AgCl electrode as the reference electrode (RE), all contacting the liquid (light blue) (f). Using an immersion objective, the in-situ Raman spectra are recorded.

to a printed circuit board (PCB). The resistance between the contact pads was measured to be $1.6\text{ k}\Omega$, which is indicating a good contact to the graphene. Subsequently, the gold pads and the wire bonds were covered by epoxy (hysol), leaving a graphene area for contacting the solution open of approximately $5 \times 5\text{ mm}$.

The setup used in this experiment as shown schematically in Figure 4.1f and in Figure 4.2. It allows for simultaneous recording of the Raman spectrum while performing electrochemical experiments. Electrical potentials and currents are applied and measured using a Biologic SP300 potentiostat, always at a scan rate of 25 mV/s . To the background electrolyte, 0.1 M KNO_3 , the reactive species (RuHex , FcMeOH and Fe(CN)_6) were added in a concentration of 1 mM . Subsequently, $100\text{ }\mu\text{L}$ of solution was applied to the graphene device. All potentials were measured against an Ag/AgCl reference electrode (WPI Dri-Ref-450). The spectra are recorded using a WITec alpha 300 system with a 532 nm laser at 1 mW with an immersion objective for measuring in liquid (Nikon Fluor 40x 0.8 W DIC). Analysis of the recorded Raman spectra is performed using a MATLAB script, which accounts for an offset in the spectrometer by fitting the Rayleigh peak. Next Lorentzian curves are fitted to the graphene peaks to obtain their positions and intensities. The voltammetric measurement protocol was as follows. In each measurement three scans were performed in series (whereby the results of the last two scans are displayed in the graphs in this chapter). Measurements in a series were performed with a time spacing of approximately 1 minute.

Figure 4.2 Photograph of the Raman spectroelectrochemistry setup showing the dipstick device connected to the potentiostat while located in the Raman microscope. The graphene layer served as working electrode, a platinum wire as counter electrode and a silver/silver chloride electrode as reference electrode (indicated in respectively red, blue and white). The Raman spectrum (yellow) is in-situ recorded by using a 532 nm excitation laser (green).

4.4 Results and discussion

To test our hypothesis, the adsorption of the three redox active species during electrochemical experiments using in-situ Raman spectroscopy was studied by measuring on two graphene electrode devices. After measuring the baseline in background electrolyte, RuHex and FcMeOH were measured with the first graphene device. Subsequently, $\text{Fe}(\text{CN})_6$ was measured using the second graphene device. Finally, the first device was also tested with $\text{Fe}(\text{CN})_6$ to test to what extent the device history influences its behavior.

4.4.1 RuHex

To obtain an Raman spectroelectrochemistry baseline of the graphene electrode device 1 for the subsequent redox measurements, the Raman spectrum was recorded in solely the background electrolyte. Using MATLAB a smooth line* was fitted to the data points to obtain the averaged baseline curve shown in Figure 4.3. The baseline shape and position correspond well to curves obtained in similar studies reported in literature^[8,17]. Subsequent measurement results will be compared to this baseline measurement to monitor the change.

The cyclic voltammogram of RuHex at the graphene electrode is shown in Figure 4.4a. The profile is in accordance with RuHex voltammograms at graphene electrodes found in literature^[12]. In Figure 4.4b the in-situ recorded G-peak position curves are displayed, which are at about the same position as the baseline curve. Both curves are constant over several measurements, showing no change over time. This dataset indicates that RuHex adsorption to the graphene electrode was absent or below our detection limit ($\beta \approx 0$). As expected for an outer-sphere redox couple that does not need adsorption to react, a sizeable redox current was still observed.

*To all measurement points curves were fitted by the 'smooth' function with method 'rloess', which performs a local regression using linear least squares method (see also the MATLAB R2015b documentation: <http://www.mathworks.com/help/matlab/>).

Figure 4.3 The G-peak position in the Raman spectrum as a function of the applied potential measured in background electrolyte at graphene electrode device 1, serving as a baseline for the subsequent measurements.

Figure 4.4 Raman spectroelectrochemistry of RuHex at graphene electrode device 1. The voltammogram (a) shows two performed RuHex measurements and the control curve of the background electrolyte (black). The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows curves very similar to the control (black).

4.4.2 FcMeOH

The observations differ when the measurement is repeated for FcMeOH, as shown in Figure 4.5. In the G-peak position curve the charge neutrality point (the valley) has shifted from about 0.1V to about 0.0V. The peak also red-shifted (higher G-peak position). Both effects can be explained by the adsorption of FcMeOH molecules. Furthermore, the curve is wider than the baseline curve indicating a decrease in carrier mobility^[14]. Based on these observations we conclude that FcMeOH adsorbs to the graphene surface as also reported in literature^[10,21,22], with a relative large adsorption factor ($\beta \gg 0$). The G-peak curve is already displaced to its final position at the first measurement, indicating fast

Figure 4.5 Raman spectroelectrochemistry of FcMeOH at graphene electrode device 1. The voltammogram (a) shows three performed FcMeOH measurements and the control curve of the background electrolyte (black). The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows curves different from the control (black), indicating adsorption.

equilibration and a large adsorption rate constant of the FcMeOH. Furthermore, for this species we see a decreasing peak height in the voltammogram in measurement 3, which could indicate that the graphene surface becomes less reactive.

4.4.3 $\text{Fe}(\text{CN})_6$

To have a clean graphene surface (without previously adsorbed molecules), we continued the redox measurements on a fresh device (device 2). Again a baseline curve was measured, which is shown in Figure 4.6. The measured baseline curve is different from the baseline curve of the previous device (Figure 4.3). This could be caused by a difference in PMMA residues on the graphene^[14,24,25] and/or a different substrate interaction^[26]. The shape of the curve is again as expected from literature.

Subsequently, the spectroelectrochemistry of $\text{Fe}(\text{CN})_6$ was tested on this device resulting in the voltammogram shown in Figure 4.7a. During the first five scans (three from measurement one and two from measurement two) the current is increasing every scan. However, in the following two measurements the current peak height is constant, but the oxidation peak position is slightly shifting to a more positive voltage. This could be caused by the need for a higher overpotential for the reaction to take place by a (partially) changed surface. A more likely explanation is that the graphene electrode resistance is increased by the (local) doping effect of more adsorbed molecules, causing a lower graphene-solution voltage at the same applied device voltage whenever a Faradaic current is flowing. This local doping can be observed by the blue-shift (lower Raman shift) of the G-peak position at 0.6 V. The measured graphene sheet resistance multiplied by the measured current results in a voltage drop of about $1.6\text{ k}\Omega \times 28\text{ }\mu\text{A} \approx 45\text{ mV}$, which is in the range of the observed peak shift in the voltammogram. Since the graphene sheet resistance is affected quite easily by a change in charge carriers, this is a plausible explanation.

In Figure 4.7b the G-peak position curve is shown. During the first cycle a large

Figure 4.6 The G-peak position in the Raman spectrum as a function of the applied potential measured in background electrolyte at graphene electrode device 2, serving as a baseline for the subsequent measurements.

Figure 4.7 Raman spectroelectrochemistry of $\text{Fe}(\text{CN})_6$ at graphene electrode device 2 (measurement series 1). The voltammogram (a) shows the results of a sequence of five $\text{Fe}(\text{CN})_6$ measurements and the control baseline curve measured in the background electrolyte (black). The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows curves different from the control (black), indicating adsorption.

horizontal shift is observed, but unexpectedly red-shifted (higher G-peak position). The expectation is, that a shift to a more positive voltage is accompanied by a red shift, as described in the closing paragraph of Section 4.2. For the following measurements (2-5) the pattern is slightly different, the G-peak position valley is lower than in the first measurement and is slightly moving to the right with each measurement. Both observations can be explained by $\text{Fe}(\text{CN})_6$ adsorption, whereby the difference between the first and the subsequent measurements suggest two adsorption states. Also the slope becomes shallower, in accordance with the theoretical prediction in Section 4.2. The observations are as expected for the inner-sphere redox couple $\text{Fe}(\text{CN})_6$, that needs adsorption before reacting.

To test whether also evidence for desorption of $\text{Fe}(\text{CN})_6$ can be found, the reservoir was three times rinsed with background electrolyte and subsequently the measurements were performed with the results shown in Figure 4.8. The voltammogram shows a quite different behavior: the distance between the redox peaks has reduced from approximately 0.9 V to approximately 0.4 V and the current has decreased 50-fold. This could be explained if we assume two adsorption sites with different overpotentials. The voltammogram in Figure 4.8a is quite similar to the one on graphite, where reaction takes place at reactive edge sites with low overpotential. The traces in Figure 4.8a can then be explained by redox reactions at a relatively low number of electroactive sites (grain boundaries) at graphene. The currents also remain stable after an initial decrease, indicating a very low desorption rate of this fraction of $\text{Fe}(\text{CN})_6$. In the first measurement the minimum in the G-peak position curve is still quite similar to the position in Figure 4.7, indicating still extensive adsorption, presumably at the basal plane. The low current measured however then is slightly puzzling. The above indicates that the theory as developed in Section 4.2 does not apply, as it predicts a proportionality of adsorption and current, assuming just one type of reactive sites. In the subsequent measurements of the G-peak position curve, a clear recovery towards the control

Figure 4.8 Raman spectroelectrochemistry of background electrolyte at graphene electrode device 2 (measurement series 2) to test the desorption of $\text{Fe}(\text{CN})_6$. The voltammogram (a) shows three performed measurements and the control curve of the background electrolyte (black). The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows the gradual recovery to the control curve (black).

state can be seen, indicating desorption, presumably from the basal plane. The voltammogram however does not entirely recover to the situation of the control experiment. The residual current could be caused by a fraction of defect-adsorbed $\text{Fe}(\text{CN})_6$ that is hard to desorb, similar to FcMeOH .

Finally, the $\text{Fe}(\text{CN})_6$ was measured again in the $\text{Fe}(\text{CN})_6$ solution with the results as shown in Figure 4.9. The aim was to establish whether the signal shown in Figure 4.7 could be recovered. The voltammogram oxidation peak is located at a slightly higher voltage, which can be explained by the shift in the CNP of the graphene indicating the Fermi level to a higher value (0 V) than in Figure 4.7 (−0.1 V). Alternatively, it could be caused by a further decreased graphene charge

Figure 4.9 Raman spectroelectrochemistry of $\text{Fe}(\text{CN})_6$ at graphene electrode device 2 (measurement series 3). The voltammogram (a) shows three performed $\text{Fe}(\text{CN})_6$ measurements and the control curve (black) of solely the background electrolyte. The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows again a curve different from the control (black).

carrier concentration.

4.4.4 $\text{Fe}(\text{CN})_6$ after FcMeOH

In addition to the preceding experiments, $\text{Fe}(\text{CN})_6$ Raman spectroelectrochemistry was also applied to device 1 following the experiment with FcMeOH . In the resulting voltammogram shown in Figure 4.10a the redox peaks of FcMeOH appear absent and the $\text{Fe}(\text{CN})_6$ reduction peak is shifted to a more negative voltage. The G-peak position curve in Figure 4.10b is revealing more on the details of adsorbed molecules. By comparing the curve to the case of FcMeOH in Figure 4.5b, we see that during the first two measurements the FcMeOH is still adsorbed on the graphene, judging from the shift in G-peak position relative to the bare graphene. In subsequent measurements the G-peak shifts to a position similar to the one observed in Figure 4.7 and 4.9, indicated that the $\text{Fe}(\text{CN})_6$ is adsorbing to the graphene and potentially replaces a fraction of the adsorbed FcMeOH . In the final measurement 5 (green trace) a combination of both the FcMeOH and $\text{Fe}(\text{CN})_6$ curves is found, thus indicating that both species are adsorbed to the graphene surface. Also in this case we therefore observe that there is no direct relation between FcMeOH adsorption and its electroactivity. In Section 4.4.6 we revise our model using the new information acquired in the previous sections.

4.4.5 Maximum applicable graphene potential

In electrochemical experiments on graphene its potential window is of great interest^[9]. The potential window is defined as the range of potentials where neither the solvent nor the electrolyte reacts at the electrode material. The maximum applicable graphene potential was investigated by cycling between a constant negative voltage of -0.4 V and increasingly positive voltages, and monitoring the in-situ Raman spectrum. Upon application of a cyclic voltage with a maximum value of 1.2 V , the Raman spectrum was found to be changing over time as can be seen in Figure 4.11. During the scans an increasing intensity of the D-peak

Figure 4.10 Raman spectroelectrochemistry of $\text{Fe}(\text{CN})_6$ at graphene electrode device 1 (on which previously the adsorption of FcMeOH was tested as described in Section 4.4.2). The voltammogram (a) shows five performed $\text{Fe}(\text{CN})_6$ measurements and the control curve of the background electrolyte (black). The G-peak position extracted from the in-situ recorded Raman spectrum vs the applied potential (b) shows curves different from the control (black).

Figure 4.11 Raman spectroelectrochemistry of graphene indicating increasing crystal disorder introduced upon application of the extreme positive voltage observed by the increasing intensity of the D-peak ($\sim 1345\text{ cm}^{-1}$) with each cycle. The measurement is performed in background electrolyte by applying voltages from 1.2 V to -0.4 V, see also Figure 4.12.

was observed, as also evident in Figure 4.12, indicating an increasing disorder. The (local) generation of oxygen could be expected at this voltage, therefore our findings could indicate that the graphene is being oxidized causing this observed increasing disorder. The intensity decrease of the 2D-peak could also indicate an oxidation of the graphene, since this low peak intensity (compared to the D- and G-peak) is also observed in graphene oxide^[27]. The conclusion is, that the observed maximum applicable potential of our graphene extends to maximally 1.2 V vs Ag/AgCl.

4.4.6 Model revision

Based on our observations shown in the previous sections we will now propose a modified model to describe the adsorption and electron transfer mechanism. In the model, the occupation factor β as visible from the Raman spectrum, and the current density J_m were directly coupled. The data for RuHex, an outer sphere redox substance, were not in conflict with this model, as for such substances redox activity is independent of adsorption. For FcMeOH, another outer sphere redox substance, still adsorption was found. This, however, is in accordance with literature reports, whereby it could not be established whether this adsorption contributes to the redox activity. The results for $\text{Fe}(\text{CN})_6$ were also in line with expectations, as we observed both adsorption and electroactivity for this inner sphere redox couple. We however observed in the $\text{Fe}(\text{CN})_6$ desorption experiments that two type of reactions occur, with low and high overpotential. The latter one has a major contribution to the current. The former one is persistent and remains when the solution is flushed. We hypothesize that we here see reactivity at the

Figure 4.12 Raman spectroelectrochemistry of graphene indicating increasing crystal disorder by the increasing D-peak intensity with each cycle. The behavior was induced upon application of extreme positive voltage to graphene (electrode device 1) performed in the background electrolyte. The applied voltage (E vs Ag/AgCl) and current (I) over time show the triangular cyclic voltammogram signal and its measured graphene current. The peak intensities are normalized to the second order silicon peak (at 960 cm^{-1}), displaying the increase of the D-peak intensity with the high positive voltage applied each cycle. In the three lower graphs the D-, G- and 2D-peak positions can be found.

Figure 4.13 General schematic of redox active species adsorbing and optionally exchanging electrons at the graphene surface. The black line represents the graphene basal plane and the *-symbol a grain boundary, edge or other site which has a higher reactive capability. In each of the two pathways a series of steps are drawn, in the pathway on the left: (a), **adsorption of a molecule** at a reactive graphene site (b), **electron exchange and adsorption** for a certain average time τ_{ad} (c) and **desorption from the graphene surface** (d). In the pathway on the right (e), **adsorption of a molecule** to the graphene basal plane (less reactive) (f), **electron exchange** for some of the adsorption species **and adsorption** for a certain average time τ_{ad} . This electron exchange rate is much lower on this at this basal plane than the (more) reactive sites, however the vast majority of the graphene surface consists out of graphene basal (g), and **desorption from the graphene surface** (h).

basal plane (high overpotential) and local defect sites (low overpotential, almost permanent bonding). The redox reaction kinetics for graphene thus are more complex, since the ability for electron exchange is *not* uniform over the surface. Also in literature we find that at defects in the graphene, such as grain boundaries, the electron exchange rate is locally orders of magnitude higher^[10,11,28]. The revised model is schematically depicted in Figure 4.13. In literature we find that the reaction rates of the outer-sphere reactions such as RuHex and FcMeOH (that not depend on adsorption) mainly depend on the availability of these more reactive sites^[12]. In the in-situ Raman spectroscopy experiments the adsorption (and possibly the approach) of redox species thus can be probed independently of the remainder of the electrochemical behavior. To better explain the electrochemical voltammogram data, we will thus distinguish adsorption and electron exchange at reactive sites (Figure 4.13a-d) from adsorption and electron exchange (with a different overpotential) at the basal plane (Figure 4.13e-h).

A further complication in the analysis of the cyclic voltammograms is that the

graphene conductivity is influenced by adsorbed species in two ways. Firstly, the adsorbed molecules on the basal plane (the smooth homogeneous graphene crystals) influence the conduction by changing the carrier concentration. For FcMeOH (uncharged) the charge neutrality point V_{CNP} shifted to a more negative voltage and for $\text{Fe}(\text{CN})_6$ (-3 and -4 charge) to a more positive voltage, suggesting that the charge of the molecule determines whether n- or p-doping is induced. Secondly, graphene electron mobility is reduced by grain boundaries (which can be visualized by mapping the intensity of the D-peak in the Raman spectrum) [29,30]. Species adsorbed on these grain boundaries could increase the conductivity [31,32]. For larger currents ($I > \sim 1 \mu\text{A}$) a lower conductivity affects the voltammogram by increasing the required overpotential (shifting the peaks to more extreme voltages) and lowering the current peak heights.

4.5 Conclusion

Evidence for the adsorption state during redox reactions at graphene in the Raman spectrum was found. The adsorption state was probed by analyzing the G-peak position in the measured in-situ Raman spectrum during electrochemical experiments. Prior to every experiment a G-peak position curve was recorded for the bare graphene, serving as a baseline for subsequent measurements. For RuHex no change in the G-peak position curve was found during the electrochemical experiment compared to the baseline in solely background electrolyte, which was as expected. In case of FcMeOH a clear stable negative shift in the G-peak position curve was observed, indicating a strong adsorption state to the graphene, potentially caused by π -interactions or electrostatic interactions. For $\text{Fe}(\text{CN})_6$ a clear positive shift in the G-peak position curve could be seen, however for this species the measurement required some time to settle towards a constant voltammogram and G-peak position curve. This is suggesting that FcMeOH and $\text{Fe}(\text{CN})_6$ interact differently with the graphene. Furthermore, when measuring $\text{Fe}(\text{CN})_6$ on the graphene electrode after FcMeOH we found no clear difference in the voltammogram compared to $\text{Fe}(\text{CN})_6$, while the G-peak position curve indicated that both species were adsorbed.

Based on these findings we conclude that Raman spectroelectrochemistry on graphene is a tool to obtain in-situ information on adsorbed species on graphene, isolated from the rest of the electrochemical behavior, making graphene an even more interesting electrode material. We found indications that the adsorption of species for the larger part takes place on the less reactive basal plane, while local reactive sites determine the electrochemical behavior. We also observed additional effects of the adsorbed species to the graphene surface, where a slight change in the electrochemical behavior most probably caused by changes in graphene charge carrier density and passivation of the surface.

4.6 References

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5

Ionic transport characteristics of suspended graphene membranes*

This chapter presents the results of ionic transmembrane transport through chemical vapor deposited (CVD) graphene membranes suspended over silicon nitride supports. We study the conductance through nanoscale intrinsic defects in the CVD graphene that serve as solid state nanopores. The current-voltage characteristics of such nanoporous suspended graphene devices is investigated in a case by case analysis, enabling us to distinguish the unique characteristics of each device. Clear indications of a pH-dependent behavior were found, supporting the hypothesis that protonatable groups are involved. At higher applied voltages we find a progressively larger conductance, which we attribute to a progressive detachment of the graphene from the substrate driven by electrowetting, overcoming adhesion forces. Since graphene nanopore devices generally involve suspension over silicon nitride pores and reliance on adhesion forces for sealing, the results of this research can have profound consequences for the study and use of graphene nanopores.

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5.1 Introduction

Solid state nanopores have attracted growing interest since new fields of application, notably in DNA sequencing and desalination, have recently opened up^[1,2]. Because of their size nanopores are useful for processes involving individual molecules, e.g. DNA sensing and potentially sequencing with subnanometer resolution^[3,4]. In this context graphene in particular is being researched for fabrication of novel ultra-thin nanopore devices because of its atomic thickness and mechanical strength^[5], theoretically enabling highly optimized sensing and filtration processes^[6–9].

Graphene nanopores have been intentionally generated in pristine (not chemically modified) graphene by ion and electron bombardment^[10,11], by chemical methods^[12] or by using pulsed electrical potentials^[13]. Intrinsic nanopores also exist in CVD graphene. Recent studies on the ionic transport through nanopores in CVD graphene, formed as intrinsic defects of sub-2 nm diameter^[14,15], show unique transport behavior fundamentally different from larger pores^[15,16]. The chemical properties of these intrinsic graphene defects are known to be different from pores generated by bombardment, since only the latter ones are attacked upon exposure to an oxidant (KMnO_4 in H_2SO_4) which etches unsaturated carbon bonds^[11]. This different behavior towards oxidants is an indication for a different state of the edge carbons near an intrinsic pore compared to a pore generated by bombardment. Furthermore, it was found in the recent study by Jain et al. of the electrical conductance through intrinsic graphene pores, that even though a wide variety of current-voltage measurements exists, the pores can be categorized into three distinct behaviors: linear, rectified and activated^[15]. This variation in ionic transmembrane transport is also predicted by simulations that show a wide range of selectivity depending on the exact pore edge termination configuration such as single/double oxygen groups^[17,18]. Effects such as ion dehydration and electrostatic interactions are thought to play a role in ionic transport. These effects are expected to vary from pore to pore as they are influenced by the pore size and the existence of a charged group on the graphene in the vicinity of the nanopore. In addition, some of the intrinsic graphene nanopores show occasionally rapid switching behavior, in which the (de)protonation of charged groups in the vicinity of the pore may be involved^[15]. In Figure 5.1 simple examples of defective graphene are shown that have one or more vacancy sites that could potentially be terminated by oxygen and/or hydrogen atoms creating deprotonatable groups (OH or COOH)^[17–19]. A better understanding of these pores and their ionic transport could be utilized to fabricate future solid state nanopore devices that might improve existing applications such as desalination or enable novel nanopore functionality.

For transmembrane experiments, such as DNA translocation through nanopores, commonly devices are fabricated in graphene is transferred to a silicon nitride membrane^[9,15,16,21–24]. In some studies limits in the applied voltage were reported, described as “Applying bias voltages in excess of $\approx 250\text{mV}$ gradually degraded the insulating properties of the membranes”^[16] and as “Higher voltages applied across atomically thin graphene membranes often resulted in a peculiar behavior”^[23]. This depicts that in these type of systems forces are in play which are not yet recognized^[15,16,23].

Figure 5.1 Schematics of the graphene structures of depicting 1 to 4 carbon vacancy sites (unterminated) including the carbon-carbon distances of the open nanopore areas. The graphene carbon-carbon lattice distance is 142 pm^[20].

In this chapter the ionic transmembrane transport characteristics of suspended graphene membranes are studied in detail, for which the paper of Jain et al.^[15] serves as a basis. In our devices we transfer CVD graphene to a silicon nitride membrane with a single nanopore of ~ 52 nm which defines the probed area. Intrinsic pores in CVD graphene have an estimated spacing between 70 and 100 nm^[15,25] and a pore size in the range of 0 to 2 nm^[15]. This makes it likely to isolate a single graphene nanopore in the suspended graphene. We study the current-voltage characteristics of suspended graphene in a case by case analysis of these nanopore devices, enabling us to distinguish the unique characteristics of each device. Our focus of interest is thereby to find indications for the number of pores in the probed graphene area. In addition, we are interested in the presence and nature of the charged groups present in the vicinity of the intrinsic graphene nanopore(s) which, together with the subnanometer pore size, facilitate the (non-linear) ionic transport. This rectification has been taken to be the result of the charge being localized at some distance (e.g. 0.172 nm)^[15]. The effects of protonatable groups

in the vicinity of the intrinsic graphene nanopores are investigated by performing current-voltage measurements at a wide range of pH values. The expectation is that the pH will influence the (de)protonation of the charged groups in the vicinity of the nanopore, causing rectifying behavior when localized at some distance. The linear and activated behavior can still also be expected, since these are solely the result of the pore diameter. In addition to this existing explanation, we hypothesize that a rectification could also be caused by a mechanical asymmetry, since defects induce (local) graphene buckling^[26].

Part of our investigations furthermore aim at a better understanding of the behavior at larger applied graphene transmembrane voltages, which as yet have not been understood. As we will show, we find support for the hypothesis that at high applied transmembrane voltages the graphene (partially) detaches^[27,28], which dramatically increases the probed graphene area.

5.2 Theory

The transmembrane ionic conductance of a nanopore G for high salt concentrations has two contributions and can be calculated from the pore geometry as follows^[6]:

$$G_{\text{pore}} = (R_{\text{ch}} + 2R_{\text{ac}})^{-1} = \sigma \left(\frac{4w}{\pi d^2} + \frac{1}{d} \right)^{-1} \quad (5.1)$$

in which the first part is the resistance of the channel R_{ch} and the second twice the access resistance R_{ac} . In the Equation, σ is the bulk ionic conductivity, w is the membrane thickness and d the pore diameter. To neglect the entrance resistance R_{ac} , the pore diameter needs to satisfy the following condition: $d < \frac{4w}{\pi}$. In Figure 5.2 the nanopore conductance as function of pore diameter is plotted using the parameters of our experiment. With conductance measurements and

Figure 5.2 Transmembrane ionic conductance G of a nanopore with pore diameter d for membranes for a membrane thickness w of 41 nm and 1 M KCl as electrolyte solution, see also Equation 5.1.

this equation, the diameter of the nanopore in the silicon nitride membrane is estimated prior to the graphene transfer. The bulk conductivity σ for 1 M KCl is $11\,\Omega^{-1}\text{m}^{-1}$, while for the KCl solution at pH 1 the added HCl increases σ to $15\,\Omega^{-1}\text{m}^{-1}$ [29,30]. Thus the electrolyte conductivity at pH 1 is increased with a factor 1.36 compared to the other pH values (pH = 3, 5 and 9). For pore radii above $\sim 9\text{nm}$ this continuum model agrees reasonably, however for smaller radii the model starts to deviate and semicontinuum modeling is required; the subcontinuum approach proved to be necessary when the pores radius is smaller than $\sim 0.9\text{nm}$, where in practice this results in a relatively constant conductance curve for a wide range of pore radii [15,31].

In addition to transport through intrinsic pores in the graphene, small ions are capable of diffusing through non-defective graphene. According to simulation transmembrane transport is possible for small ions: the energy barrier for a proton to diffuse through the graphene basal plane is 1.4eV [32] and for a lithium ion 10.2eV [33]. Experimental limitations prevent us to overcome these barriers in our experiments (see Section 5.3.3). However, graphene defects will drastically lower the energy barrier locally, making transmembrane transport possible [34]. Thus at the applied voltages in our experiment, we do only expect to see ionic transport through defects. Assuming a single graphene nanopore, an upper limit for the nanopore diameter can be calculated from the measured transmembrane conductance using the theory in Jain et al. [15]. In our analysis, we will make use of this calculation to estimate the maximum nanopore size in our graphene.

5.3 Experimental

Firstly, the cleanroom fabrication of the silicon nitride membrane and the extensive membrane cleaning prior to graphene transfer is described. Subsequently, measurement setup details are provided such as the chip holder and the used electrodes. Finally, the upper and lower bounds for applied voltage and electrolyte pH are determined.

5.3.1 Chip fabrication

The fabrication process for the graphene membrane devices is schematically shown in Figure 5.3. On the silicon wafer stoichiometric silicon nitride was deposited, since the internal tensile stress prevents the final membrane from buckling [35,36]. To decrease the transport of silicon nitride caused by heating during the nanopore fabrication with the Focused Ion Beam (Fei, Nova600 Dualbeam FIB/SEM), a layer of chromium was applied to the silicon nitride and a pulsed FIB program was tuned for this specific membrane (4000 cycles of $0.1\,\mu\text{s}$ with beam on:off ratio of 1:10, with a total duration of 0.44s per nanopore). This process enabled us to fabricate nanopores reproducibly as shown in Figure 5.4, having an apparent diameter of $52\text{nm} \pm 7\text{nm}$ ($N=8$). To reduce the chip leakage current, 100nm of thermal oxide was grown. A layer of photoresist was applied on the wafer by spinning (Olin OiR 908-35 at 1000rpm for 30sec to protect the membranes during dicing. Subsequently, the wafer was diced in chips of $16 \times 16\text{mm}$. The silicon nitride thickness of the final device was 41nm (measured using Woolam M-2000UI ellipsometer).

Prior to the graphene transfer, an extensive cleaning protocol was applied to the nanopore chip. In conductance measurements of solely the silicon nitride

Figure 5.3 Schematic overview of the fabrication process of the suspended graphene device. On a silicon wafer (a) 50 nm of stoichiometric silicon nitride is deposited (b). Using a conventional lithography process and dry etching (CHF_3 and O_2) a window in back side silicon nitride was patterned (c) for defining the silicon volume which is removed by KOH wet etching (25%_w at 75 °C for ~ 9 hours, etching the silicon nitride with ~ 1 nm/hour) (d). 50 nm of chromium was deposited by e-beam evaporation (e). Subsequently, the nanopore is fabricated using a Focused Ion Beam (FIB) (f). The chromium was stripped by wet etching (Merck 111547, ceric(IV) ammonium nitride) (g). To reduce the chip leakage current, wet oxidation (45 min at 900 °C) was performed (h). After an extensive cleaning protocol, the graphene is transferred to the membrane (i).

nanopore, the extensive cleaning protocol proved to be necessary for a clean surface and proper wetting of the silicon nitride nanopore. The chips were cleaned in nitric acid (HNO_3), RCA2 ($\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} \ 1 : 1 : 5(\text{vol})$), piranha ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 \ 3 : 1(\text{vol})$) all at 80 °C for at least 15 min and was submerged 4 times in fresh DI water after each step. Subsequently, the chips were exposed to air plasma generated by a Plasma Cleaner (PDC-002, air plasma at 500 mTorr and ~ 25 W for at least 15 min) and immediately submerged in DI water. Finally, graphene was transferred to the cleaned chips by the protocol explained in Section 2.3.

In addition to the fabrication process described above, graphene transfer to a silicon nitride membrane coated by a hydrophobic coating was performed. After the extensive cleaning protocol a FOTS-coating (trichloro(1H,1H,2H,2H-perfluorooctyl)silane) was applied to the silicon nitride surface. The coating pro-

Figure 5.4 Scanning Electron Microscopy (SEM) image of a fabricated nanopore in the Cr/Si₃N₄-membrane at an angle, showing the nanopore sidewall (angle of incident 30°, a) and schematic view with the nanopore sidewall in green (inset, a). Perpendicular SEM image showing the nanopore shape and allowing to measure its diameter as 53 nm (angle of incidence 0°, b).

protocol consists of 2 h FOTS vapor phase deposition and 2 h annealing at 120 °C. After coating the membrane chips, the scooping step in the graphene transfer process proved to be more difficult, because of the large contact angle. Furthermore, the transferred graphene layer showed tears and micropores, which could be caused by water patches bursting during subsequent steps in the protocol^[37]. Moreover, the hydrophobic coating prevented the back side access hole from filling with water. For these reasons, ionic transmembrane conduction measurements were not performed on these FOTS-coated devices.

5.3.2 Measurement setup

The fabricated chip was clamped in between two o-rings ($\varnothing_{ID} = 12.42\text{mm}$, $\varnothing_{CS} = 1.78\text{mm}$ Viton) using a holder shown in Figure 5.5 and the reservoirs were filled with electrolyte for performing the transmembrane measurements. As an electrolyte 1 M KCl was used, set to a pH series of 1,3, 5 and 9 by adding either HCl or KOH. Reference electrodes (XR110, calomel) served as interface to the

Figure 5.5 The chip holder consists of two Teflon (PTFE) parts with on each side an o-ring (a), clamping the membrane chip by thread bars, washers and wing nuts (b).

Figure 5.6 Schematic cross-section of the chip clamped in o-rings. The working electrode is always connected to the electrode positioned on the top side to which the graphene has been transferred. The reference and counter electrode are both connected to the electrode positioned on the bottom side of the chip.

solution. Electrical potentials and currents were applied and measured using a Biologic SP300 potentiostat as shown in Figure 5.6. The cyclic voltammograms were always at a scan rate of 10 mV/s unless noted otherwise, saving one averaged measurement point every 62 ms. For the small voltage scans 4 cycles and for the wide voltage scans 6 cycles were always recorded in the cyclic voltammograms (CVs). Prior to every series of transmembrane experiments, the maximum voltage drop over the electrodes was checked by performing a chronopotentiometric experiment, monitoring the voltage upon application of a series of currents (0.1, 1 and 10 nA). This revealed a voltage drop consistently lower than 1 mV. It is essential that the graphene device is not dried after performing measurements, since the surface tension of the receding front of aqueous liquid can cause graphene delamination from the silicon nitride. Step detection is performed on the current voltage measurements in MATLAB. First, a moving average is applied (window size of 4 samples, representing 248 ms), then this averaged current signal is differentiated by calculating the difference between the successive elements. Spikes in the resulting signal represent step events and are detected using a threshold of 85 pA s and 0.9 nA s for the small voltage scans and to the wide voltage scans respectively.

5.3.3 Voltage and pH limitations

Discussion exists in literature about the maximum allowed transmembrane voltage over suspended graphene. In study of Garaj et al. it is claimed that voltages in excess of 0.25 V degrade the insulating properties of the graphene^[16]. However, Kaun et al. show that at a pulsed voltage of 7 V pores are generated and 5 V pulses are enlarging existing pores^[13]. Jain et al. show transmembrane measurements with a voltage of 0.8 V^[15]. We have shown (see Section 4.4.5) that a voltage of 2.0 V between the graphene and the solution will generate defects in the graphene, suggesting a maximum allowable transmembrane voltage of 2.4 V. Considering all of this, we will apply a maximum transmembrane voltage of 1 V over the graphene to avoid any damage in the graphene.

For investigation of the dependence of transport on pH we tested electrolytes with a wide range of pH values. The applicable pH range is limited by the possible etching of the silicon nitride chip by very basic solutions^[38], for which reason we

chose a pH of 9 as a maximum. As a lower pH bound we used a pH of 1, since we expect that a lower pH will not provide more information while making the analysis more complex.

5.4 Results and discussion

To understand the transmembrane transport behavior, we here analyze the current voltage measurements. First the cyclic voltammograms (CVs) as recorded for silicon nitride membranes without graphene are discussed, both for a closed membrane and a membrane with a nanopore, which will be serving as a baseline for subsequent graphene measurements. Next the CVs of graphene suspended over a silicon nitride membrane with a single nanopore ($\sim 52\text{nm}$) are analyzed in a case by case discussion, first with a small voltage window (-200mV to 200mV) and then with a large potential window (-1V to 1V). On the basis of all of these measurements we will attempt to build a more extensive understanding of CVD graphene ionic transmembrane transport.

5.4.1 Baseline characterization

The CV currents in this study are dominated by two components: resistive and capacitive. The resistive component is caused by an ohmic current showing the conductance G as $I_R = G \times V$. The capacitive component is caused by the charging current at the set scan rate, calculated as $I_C = C \times \text{scan rate}$, resulting in a rectangle CV. At the interface of the electrolyte to the silicon nitride membrane, both silanol groups ($\text{p}K_b = -2$ and $\text{p}K_a = 6$) and amino groups ($\text{p}K_b = 4.75$) are present that are susceptible to (de)protonation upon a change of pH or application of an electrical voltage^[39,40]. The chemical proton buffer capacitance of the surface is a function of the applied potential and contributes to the total interfacial capacitance^[40,41]. Two baseline CVs of closed silicon nitride

Figure 5.7 Typical voltammograms of closed silicon nitride membranes (without nanopore and graphene), measured in 1 M KCl. To the forward and reverse scan of the first voltammogram (a, 10mV/s) two linear lines are fitted, resulting in a capacitance of 142 nF and conductance of $\sim 0.6\text{ nS}$. The non-linear deviation is further investigated by a wider scan window (b, 20mV/s), showing a CV that we found to be characteristic for silicon nitride membranes on a silicon substrate. The arrows indicate the forward and reverse scan. The dashed lines show the linear fits to the forward and reverse scans, used to calculate the nanopore conductance.

membranes without graphene are shown in Figure 5.7. The non-linear current is explained by the changing buffer capacitance of the complete chip surface as a function of applied voltage.

The conductance of an open single nanopore in the silicon nitride membrane was measured to obtain the maximum possible current for subsequent graphene transmembrane measurements. In Figure 5.8 this CV shows a clear ohmic characteristic with a capacitive current equal to the closed silicon nitride membrane. The value obtained for the nanopore diameter by ionic conductance (57 nm) is in good agreement with the one obtained by the SEM method (53 nm). The deviation between the methods can be explained by a slightly tapered nanopore causing an increase in average diameter not observable by SEM.

5.4.2 Small voltage scans

The series of CV measurements performed on device 1 is shown in Figure 5.9. When scanning forward (from negative to positive voltages), a step change to a higher conductance is observed at approximately 50 mV. In the reverse scan (from positive to negative voltages), the higher conductance did not decrease to its initial value until approximately 0 mV was reached. This pattern is observed for the pH values of 1, 3 and 5. At pH 9 the pattern is different, as no conductance step is seen and the conductance equals the higher conductance seen for the other pH's. The conductivities for the low case (7.9 nS at pH 3 and 5) and the high case (11.6 nS at pH 9) would correspond to uncharged nanopores with upper diameters of approximately 1.8 nm and 3.3 nm, respectively^[15].

We attribute the step change in conductivity to be the result of the pore having two states with two distinct conductivities, changing from low to high conductivity is a stepwise process while the reverse process happens smoothly. A first explanation for this difference in conductance between the two states of the graphene

Figure 5.8 Voltammogram of a silicon nitride membrane with a single nanopore (with SEM determined to be ≈ 53 nm), measured in 1 M KCl. The CV revealed a conductance of 329 nS, corresponding of a nanopore diameter of 57 nm. The arrows indicate the forward and reverse scan. The dashed lines show the linear fits to the forward and reverse scans, used to calculate the nanopore conductance.

Figure 5.9 Voltammograms of graphene membrane device 1 (silicon nitride nanopore diameter of 54 nm), showing the transmembrane current for a series of pH values: 1, 3, 5 and 9. The experiments were run in order of descending pH (from pH 9 to pH 1). The arrows indicate the forward and reverse scan. As a guide to the eye straight dashed lines (red) are added for observing the current steps.

nanopores is a change in the value of a charge at the nanopore entrance. Adding a charge to a graphene nanopore ($< 2\text{ nm}$) would lead to a similar conductance difference^[15]. Since this event was found to be dependent on the pH, this suggests that a protonatable charge (OH or COOH group) is the cause. If a deprotonation mechanism is responsible, the associated pK_a should be in the range of 5 to 9, which is in accordance with theory^[42]. However, a contradicting argument for this mechanism is the absence of a linear relation between the pH and the step event voltage. An alternative explanation for the difference in conductance between the two states is the opening of additional nanopores above the silicon nitride substrate by partial detachment of the graphene around the pore. This explanation will be further explored in a following section of this chapter.

The results of the conductance measurements of device 2 are shown in Figure 5.10. Throughout this measurement series the conductance around 0 mV is lower than for device 1 and comparable to the closed silicon nitride membrane, suggesting that less intrinsic pores are present in the probed graphene area. The CVs reveals only small step events, and the corresponding step histograms reveal that the steps are mainly occurring at the end of the forward scan and at the very beginning of the reverse scan. These steps lead to an increase in the conduc-

tance, and occur at voltages higher than the steps down when the conductance decreases. Furthermore, the decrease in conductance in the reverse scan occurs again more smoothly, as also observed for device 1. Lastly, the conductance at pH 9 is higher than the conductance observed at the other pH values, possibly pointing at a role for a protonatable group. The non-linearity in the conductance curves could indicate that an activation energy (ion dehydration) is involved.

The conductance measurements of our next case, device 3, can be found in Figure 5.11. This series shows quite similar behavior to the previous case, however some differences can be observed. The behavior of the CV series can be split up into two categories: pH 1 and 3 show a lower conductance than pH 5 and 9. Furthermore, the step events are only observed at positive voltages for pH 1 and 3, whereas they are present for both positive and negative voltages for pH 5 and 9. Again we observe in all measurements that step events lead to an increase in conductance in the forward scan and also that the conductance smoothly decreases in the reverse scan when the voltage approaches 0 V.

In addition to the pH dependence, the ionic transport behavior was also found to be influenced by the order in which the experiments are performed. In Figure 5.12 the CV series of device 4 is shown which shows measurements performed with the electrolyte pH sequence of 1, 3, 5, 9, 1 and 9. In this device, a clear increase in conductance is observed for each successive experiment. In the first three measurements a conductance is seen that is comparable to the closed silicon nitride membrane. Surprisingly, the fourth measurement (d) at pH 9 shows an increased conductance (13.5 nS at 0 V corresponding to a graphene nanopore with an upper single diameter of 5.2 nm). An increase in conductance caused by etching of the membrane in our slightly basic solution is not expected, since hot highly concentrated KOH is etching silicon nitride with 1 nm/hour (see also Section 5.3.1). When the measurement for pH 1 is then repeated (e), the conductance is observed to be increased (5.9 nS at 0 V corresponding to an upper single nanopore diameter of 1.6 nm) compared to the first measurement at pH 1 (a). Finally, when the measurement at pH 9 is repeated, the conductance is again slightly increased (19.6 nS at 0 V corresponding to an upper single nanopore diameter of 10.1 nm)^[15] with respect to the first measurement at pH 9.

The conductance at pH 9 was found to be higher than at pH 1 in both cases, which is in line with the previous experiments. Striking is the increase in conductance for successive experiments, starting from a closed membrane situation to a highly conductive graphene membrane. The shape of the last three CV curves is comparable to current rectification induced by a nanopore under 1 nm where an off-center charge causes the curve to be more non-linear^[15]. Given this information, the non-linear current curves found have too large an amplitude to be caused by a single nanopore, since in this conductance regime (> 12 nS) the nanopore access resistance starts to dominate^[15]. Based on this, the number of probed nanopores must have increased in order to explain the measured current curves using existing theory. In the following sections we will discuss experiments at higher applied voltages that will lead to a possible explanation of these observations.

Figure 5.10 Voltammograms of graphene membrane device 2 (silicon nitride nanopore diameter of 55 nm), showing the transmembrane current for a series of pH values: 1, 3, 5 and 9 (a, c, e and g, respectively). The arrows indicate the forward and reverse scan. The order of experiments was from pH 9 descending to pH 1. The histograms of the step analysis (b, d, f and h) show the detected steps up (blue) and down (red) during the forward and reverse scans.

Figure 5.11 Voltammograms of graphene membrane device 3 (silicon nitride nanopore diameter of 52 nm), showing the transmembrane current for a series of pH values: 1, 3, 5 and 9 (a, c, e and g, respectively). The arrows indicate the forward and reverse scan. The order of experiments was pH 9, pH 1, pH 3 and pH 5. The histograms of the step analysis (b, d, f and h) show the detected steps up (blue) and down (red) during the forward and reverse scans.

Figure 5.12 Voltammograms of graphene membrane device 4 (silicon nitride nanopore diameter of 55 nm), showing subsequent transmembrane current measurements for a series of pH: pH 1 (a), pH 3 (b), pH 5 (c), pH 9 (d), pH 1 (e) and pH 9 (f). The arrows indicate the forward and reverse scan.

5.4.3 Wide voltage scans

To further investigate the ionic graphene transmembrane conductance, a CV series of device 3 are recorded with a wider voltage window as shown in Figure 5.13. In all measurements a higher current is observed for a positive applied voltage than for a negative. Furthermore, the current amplitude is found to be larger for pH 5 and 9 than for pH 1 and 3. When having a closer look at the currents for negative applied voltages in the CVs recorded at pH 5 and pH 9, it can be seen that only few current steps are detected in the forward scans. This enables us to study this single current step event, which as we find gives rise to an increased linear conductance, indicating uncharged graphene nanopores with a diameter of $> 1\text{ nm}$ ^[15]. In the forward scans at the positive potentials on the other hand, the current steps generate an exponential current-voltage response. Furthermore a potential window of about 200 mV can be observed where no or only rarely a current step is found. If the step count plot of pH 1 (b) is compared with pH 9 (h), this potential window is shifting from $[-600\text{ mV} - 400\text{ mV}]$ to $[-850\text{ mV} - 150\text{ mV}]$. This means that for 8 pH-units difference the potential window is shifted by -250 mV, corresponding to approximately -31 mV/pH . Apart from the larger current amplitude at pH 5 and 9, this pH dependence of the location of the step-free window is another indication that protons are involved in the current step process. We will identify a possible cause for this window in the discussion below.

5.4.4 Model evaluation

We will consider two models to explain the observed step behavior with its pH dependence. The first model assumes a protonatable group in the vicinity of the graphene nanopore with a protonation state that is stabilized during a scan by local ionic accumulation. The second model assumes that the graphene can reversibly ad- and desorb from the silicon nitride substrate in the close vicinity of the silicon nitride nanopore, thereby changing the probed graphene area and the number of pores observed. Both models are capable of explaining most of the found transport characteristics. Another less likely candidate for explaining the increased conductance in the CV measurements is the occurrence of redox reactions taking place at the graphene surface (e.g. oxygen reduction). We will not consider this model, since it does not provide an explanation for the observed current step events. In addition, in the silicon nitride nanopore the required graphene current density would need to be unfeasible high in order to provide this redox current (see also the graphene baseline CVs in Chapter 4).

Before proceeding with further in depth modeling, we first summarize the found transport characteristics in the CV currents. The most prominent result found is that the increase in conductance occurs preferentially for positive applied voltages. Often also a conductance increase is found for negative voltages, however the current amplitude here is always (much) lower. Furthermore, during the forward scan the current increases with a step event and then remains increased (distinct states) while in the backward scan the current decreases often smoothly (slow recovery when returning to 0 mV). Distinct conductance states are separated by step changes in the measured current traces. These step events preferentially take place when applying high voltages ($|V_{\text{ap}}| > 400\text{ mV}$). In some devices step events are also found at lower voltages ($|V_{\text{ap}}| > 100\text{ mV}$) which can involve a single step

Figure 5.13 Voltammograms of graphene membrane device 3 (silicon nitride nanopore diameter of 52 nm), showing the transmembrane current for a series of pH values: 1, 3, 5 and 9 (a, c, e and g, respectively). The order of experiments was pH 3, pH 9, pH 1 and pH 5. The arrows indicate the forward and reverse scan. The histograms of the step analysis (b, d, f and h) show the detected steps up (blue) and down (red) during the forward and reverse scans.

event or a slight increase in conductance. The event frequency increases with the applied voltage and whenever scanning backwards towards more neutral voltages, the current smoothly decreases until the current is equal to the one of the forward scan at ≈ 0 mV.

When comparing the observed current profiles within the measured pH range of 1 to 9, the pore conductance seems to be consistently pH dependent (increased conductance for higher pH). From further analysis on the shape of the CV profile together with the calculated graphene nanopore diameters, we conclude that multiple small graphene nanopores (< 2 nm) must be involved and capable of generating non-linear current traces.

Deprotonation

As a first working model we postulated the deprotonation of chemical groups in the vicinity of the intrinsic graphene defects. In the vicinity of graphene nanopores chemical groups can be present that can be deprotonated upon application of a certain pH, transmembrane voltage or a combination of both^[17–19]. We expect that charged groups in vicinity of the intrinsic graphene nanopores are comparable to the side groups in (reduced) graphene oxide, which have pK_a 's ranging from 4.3 to 9.8^[42]. When such groups deprotonate, the pore becomes ion permselective and the nanopore conductance is increased. If a transmembrane voltage is then applied, the resulting transmembrane ion flux generates accumulation and depletion zones at the entrances of the nanopore, giving rise to sustained local pH gradients. The generated pH gradient could assist in retaining the deprotonation state of the reactive group whereby the effect continues as long as the transmembrane voltage is maintained. Furthermore each deprotonation and protonation event would generate a step event in the current trace. When the voltage is removed, the generated ionic concentration gradients will disappear, the chemical groups will revert to its original protonation state and thus the conductance will smoothly recover to the lowest conductance state (depending on the bulk pH).

This model is supported by the increased current observed at pH 9 when compared to pH 1, which is taken to be non-trivial since the pH 1 bulk electrolyte is more conductive. Thus the explanation that the nanopores become more conductive by the deprotonation of pore edge groups seems to suitably fit our observations. The step events are then explained by deprotonation and protonation, leading to the distinct conductance levels as seen in the current profiles. In the measurements step events consistently occurred more frequently at positive applied voltages. This asymmetry in transport could be explained by an asymmetric location of the deprotonatable groups (e.g. on the side of the substrate). Such an asymmetry is not unlikely as the history of the two graphene sides in the graphene synthesis and transfer process is different (see also Figure 2.1). The observed current profile of pH 9 is of a distinctly different shape than other pH's, suggesting that another mechanism is (also) involved in the deprotonation.

Detachment due to graphene electrowetting

Our second working model is that the graphene can reversibly ad- and desorb from the substrate near the nanopore, changing the probed graphene area and thus increasing the measured conductance. Graphene adhesion is provided by van der Waals' interaction forces, where the dominating interaction forces are caused

by the surface polar modes of the substrate and the water layers on the interface between the graphene and the substrate^[37,43–45].

The detaching mechanism that we postulate is based on the capacitive attraction of charges to the graphene surface, and thereby also to the layer of water between graphene and nitride. These charges cause a phenomenon similar to electrowetting, as schematically shown in Figure 5.14. Charging of the extra graphene capacitor above the silicon nitride substrate lowers the energy of the system to an extent that can overcome the adhesion energy between the graphene and the nitride and thus can lead to detachment of the graphene from the substrate. The supply of ions for charging this graphene capacitor is possible assisted by current-induced convection^[46]. Stepwise detachment of the graphene at higher applied potentials will one by one expose more intrinsic nanopores to the electrolyte, leading to stepwise conductance increases. The voltage dependence of the conductance events and the observed step-free potential window is also captured by this model because for the detachment to occur, a minimum threshold voltage is required to overcome the interfacial graphene substrate adhesion force (assuming a silicon dioxide surface). The reversibility of the process is also captured as when the membrane voltage is removed the ions flow back to bulk, the graphene adheres again to the substrate and the conductance decreases to its original value.

Traditionally, two contributions dominate the free energy of two interacting surfaces as in our case the graphene and the silicon nitride surface, namely van der Waals and diffuse layer interactions. For a separation distance z the attractive van der Waals force decays with $E_{vdw}(z) \propto -z^{-2}$ and $\sim -z^{-3}$ ^[43] and the repulsive electrical double layer force with $E_{cdl} \propto \lambda_D e^{-z/\lambda_D}$ in case of two plates in close proximity, generating an osmotic pressure (the disjoining pressure) caused by the increased number of ions in the gap^[47–50]. The characteristic length for the diffuse layer, Debye length λ_D is for the electrolyte in our experiment 1 M KCl $\lambda_D \approx 0.3 \text{ nm}$ ^[51,52].

Assuming an electrowetting mechanism, the voltage at which graphene detachment occurs can be calculated by equating the capacitive energy and the net

Figure 5.14 Schematic depicting the graphene (black) detaching from the silicon nitride membrane (green) for an electrolyte pH equal to the pH at point of zero charge pH_{pzc} (a) and for an electrolyte pH much higher. The plus and minus signs show the ionic surface charge distribution on the graphene (capacitive, red) and silicon nitride substrate (counterions, blue).

interfacial energy^[53]:

$$\frac{1}{2}C_{\text{gr}}V_{\text{ew}}^2 > \Delta\gamma \quad (5.2)$$

where the interfacial capacitance of graphene $C_{\text{gr}} \approx 0.08 \text{ F/m}^2$ ^[54,55] and V_{ew} the applied voltage over the graphene. Instead of silicon nitride (Si_3N_4) we will now calculate the energies on the basis of the better known silicon dioxide (SiO_2)/graphene system. Since the silicon nitride surface is strongly oxidized, we expect it to be not much different from the silicon dioxide surface. The net interfacial energy $\Delta\gamma$ is calculated by subtracting the silicon dioxide to water $\gamma_{\text{SiO}_2\text{-H}_2\text{O}}$ and the graphene to water $\gamma_{\text{Gr-H}_2\text{O}}$ interfacial energies from the interfacial energy $\gamma_{\text{Gr-SiO}_2}$:

$$\Delta\gamma = \gamma_{\text{Gr-SiO}_2} - \gamma_{\text{SiO}_2\text{-H}_2\text{O}} - \gamma_{\text{Gr-H}_2\text{O}} \quad (5.3)$$

The graphene to substrate interfacial energy $\gamma_{\text{Gr-SiO}_2}$ is dependent on the exact state of the substrate and the amount of water layers between the graphene and substrate. The upper limit for this interfacial graphene force is estimated as 0.45 J/m^2 for single layer (0.31 J/m^2 for multilayer graphene), and decreases with the amount of water layers and increased hydroxylation of the silicon dioxide surface^[45,56]. The values for the latter two parameters are $\gamma_{\text{SiO}_2\text{-H}_2\text{O}} \approx 0.26 \text{ J/m}^2$ ^[57,58] and $\gamma_{\text{Gr-H}_2\text{O}} = 0.029 \text{ J/m}^2$ ^[59]. Together, these values result in an upper limit for the net interfacial energy $\Delta\gamma_{\text{max}} \approx 0.06 \text{ J/m}^2$. In turn, this results in an upper limit for the applied threshold voltage $V_{\text{ew,max}}$ of 2.0 V , which value rapidly becomes lower when the graphene substrate interfacial energy $\gamma_{\text{Gr-SiO}_2}$ would be lower. Since all the interfacial energy values listed here have a significant uncertainty, the value found for the threshold voltage is in reasonable agreement with the value found (0.2 V) giving additional confidence in the approach. Also, the interfacial energy will decrease with increasing substrate roughness, and might be lower for our substrate. When the applied voltage is higher than this threshold voltage V_{ew} , the graphene will detach from the silicon nitride surface. Based the decay of the repulsive force E_{cdl} , we conclude that height of detached graphene layer to the substrate is in the order of a couple of λ_{D} .

If we add this effect to the theory above, this leads to an extra repulsive contribution in the electrical double layer force, since more ions are being attracted to the graphene surface upon application of the transmembrane voltage. Suppose a graphene transmembrane voltage of 1 V , the surface charge at the graphene is $\sigma = C \times V = 0.08 \text{ F/m}^2 \times \pm 0.5 \text{ V} = \pm 40 \text{ mC/m}^2$, where the sign depends on the polarity of the applied voltage. We can now also explain the pH dependence of the observed currents by a pH dependence of the graphene detachment. This pH dependence can then be explained by the (de)protonation of silicon nitride surface (for silicon dioxide surface $\text{pH}_{\text{pzc}} \approx 2$ ^[60] and for silicon nitride surfaces $\text{pH}_{\text{pzc}} \approx 5$ ^[61]). If the silicon nitride surface charge is large ($\text{pH} \gg \text{pH}_{\text{pzc}}$), more ions are present between the graphene and the silicon nitride, generating a larger disjoining pressure. Therefore more defects are opened and a high transmembrane conductivity is measured.

With increasing voltage the detachment of the graphene will continue until the total conductance of the summated graphene nanopores is approximately equal to

the bare silicon nitride nanopore. The voltage drop in that case not only occurs over the graphene but also over the nanopore (as described in Section 5.2, thereby limiting the applied graphene voltage V_{ew} and hence the voltage driving the electrowetting. When we divide the average conductance of a graphene membrane device which is not detached (here assumed to be $\sim 8\text{ nS}$, see Figure 5.9) by the conductance of a bare silicon nitride nanopore (329 nS , see Figure 5.8, a factor of 165 is obtained. This factor then indicates the number of expected number of pores. Multiplying the area of the bare silicon nitride pore by this factor, an area of $0.094\text{ }\mu\text{m}^2$ is obtained which we will assume is the area of the detached graphene. The stepwise detachment of the graphene is comparable to the observed behavior in systems that are dominated by stick-slip friction. Similar phenomena are also seen in force-distance curves of Atomic Force Microscopy tips for the characterization of adhesion forces^[62].

In this proposed mechanism, the graphene adhesion will also be influenced by the substrate roughness. When we analyzed the silicon nitride roughness by AFM measurements, locally a wavelength over height factor $\lambda/h_0 = 7$ was found. This value is on the threshold of the critical roughness below which graphene will completely conform to the surface (amplitude corrugation factor of 0.96, where 1 is full conformation)^[63]. This slight lack of conformation in our system could facilitate the proposed detachment process.

If the mechanism proposed above indeed is at work, we can ask the question what the ‘safe’ potential window is for operation of graphene/SiN membrane systems. As described it will depend on the interfacial energies involved (especially the graphene/SiN interfacial energy) and the graphene capacitance, as well as the roughness of the silicon nitride. A potential window of 2.4 V was calculated, while a window of about 0.5 V was found. The best approach to maximize the window size is by using SiN of minimal roughness and monolayer graphene to maximize the graphene/SiN interfacial energy.

5.5 Conclusion

We characterized the suspended graphene on silicon nitride system by conductance measurements. A profound voltage and pH dependence was found. At low applied voltages the observations can be explained by single nanopores with or without charged protonatable groups. At higher applied voltages we find a progressively larger conductance, which we attribute to a progressive detachment of the graphene from the substrate driven by electrowetting, overcoming adhesion forces. Since graphene nanopore devices generally involve suspension over silicon nitride pores and reliance on adhesion forces for sealing, this research has profound consequences for the study and use of graphene nanopores.

5.6 References

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6

Microfluidic pumping using rotating microspheres around disks*

We demonstrate a novel, flexible and programmable method to pump liquid through microchannels in lab-on-a-chip systems without the use of an external pump. The pumping principle is based on the rotation of ferromagnetic Janus microspheres around permalloy disks, driven by an external rotating magnetic field. By placing the disks close to the edge of the microchannel, a pumping rate of at least 0.3 nL/min was measured using tracking microspheres. Geometric programming of the pumping direction is possible by positioning the magnetic disk close to the side wall. A second degree of freedom in pumping direction is offered by the rotation direction of the external magnetic field. The method is especially suited for flow-controlled recirculation of chemical and biological species in microchannel applications – for example medium recirculation in culture chambers – opening the way towards novel, portable, on-chip applications without the need for external fluidic or electrical connections. Additional material on this chapter is available in Appendix B.

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6.1 Introduction

Lab-on-a-chip technology involves the development of miniaturized biomedical and environmental on chip systems. It creates new opportunities for life-science applications: faster and compacter analysis while using less sample. Active transportation of sample liquid through microchannels is generally essential in such devices. Often, flows are externally generated for example by a syringe pump to introduce a sample volume into the chip. These setups are often large and inflexible, consuming much space. Alternatively, electroosmotic flow (EOF) can be used for liquid displacement. However, EOF needs external connections too, and also high voltages are required to generate flow in microchannels. Such high voltages and the accompanying heating are often incompatible with the application.

In closed systems, pumping using external pressure or EOF is not possible, since these techniques are actuated from the outside world. To make pumping in closed microfluidic systems possible, a wide range of methods have been explored that make use of on-chip moving features. On-chip fluid flow is obtained by controlling the on-chip features with externally applied fields for which the chip material is transparent (*e.g.* optical, electrical, magnetic). Using optical traps, microspheres can be spun around their axis, generating a flow of 12 pL/min when located close a channel wall^[1]. For optical actuation a large setup is required and only few particles can be actuated at once. An electrostatic system with artificial cilia can be used for the generation for flow in microfluidic systems, but with this system only pumping in one direction is possible^[2].

A wide range of on-chip pumping methods is available that make use of magnetic actuation. Ferrofluids have been used to fabricate an on-chip pump, using moving plugs in a circular channel^[3]. Alternatively, fast moving magnetic features can generate pumping by the creation of vortices at high Reynolds number^[4]. At low Reynolds number, slower moving features have been used as well, generating a net flow due to their asymmetric movement^[5,6]. One can obtain locally different flow directions on-chip with a single externally applied field by using a freely moving object trapped in a microchannel sidepocket^[7], reaching pumping rates up to 60 nL/min^[8]. This method has the drawback that objects in the small size cavities have to be rather large (0.4 to 1 mm). Additionally, pumping can also be achieved by using freely, vertically rotating chains of superparamagnetic microspheres^[9].

In this paper we present a magnetically actuated pump that allows for highly localized flow control in a closed microfluidic channel. The motion of magnetic microspheres can be controlled by soft magnetic elements located at the bottom of the channel^[10,11]. The pumping action is caused by the movement of magnetic microspheres around magnetic disks in an external rotating magnetic field. Since the disks are positioned close to the channel wall, the microspheres experience a difference in drag when they are facing the wall or the channel, resulting in a net flow along the channel axis. Therefore the flow direction can be programmed locally by positioning the microspheres on either side of the channel and actuated with use of only one actuating external magnetic field. The pumping action is multiplied by the array of disks along the channel wall. The advantage of this microfluidic system compared to other microfluidic pumping systems is the controllable transport locally on-chip in combination with mixing.

The pump is realized by conventional microfabrication of the microchannel

and magnetic disks, in combination with directed assembly of the magnetic microspheres on the disks by magnetic attraction upon application of the external field. Initial experiments showed that superparamagnetic microspheres, containing magnetite, did not possess a sufficient magnetic moment for generating a measurable net flow rate. We therefore investigated ferromagnetic Janus microspheres, exploiting the effect that one half of the microsphere will experience a strong force towards the disk. This guided motion did result in more efficient pumping compared to the use of uniform superparamagnetic microspheres with the same magnetic moment.

6.2 Theory

6.2.1 Magnetic force

The magnetic microspheres are attracted to the magnetic disks by the interaction of their magnetic moments. To estimate the force, we assume the external field saturates the magnetisation in both the magnetic disk and the microspheres, and that the magnetisation is aligned with the field. In the disk, magnetic charges will be located at the edges^[12], hence the magnetic microspheres are located at the edge of the disks^[10,11].

The stray field of a uniformly magnetised disk can be rather well approximated by a dipolar field in the plane of the disk, for distances larger than about three times the radius of the disk (see Appendix B.4). The shape of the magnetic film on the microsphere is a semi-dome with the film thickness decreasing towards the edges. We approximate this magnetic microsphere by a dipole as well.

As a first order approximation, the permalloy microsphere and disk are assumed to be two magnetic dipoles ($\mathbf{m}_1$ and $\mathbf{m}_2$) aligned with the external field, see Figure 6.1. The magnetic field $\mathbf{B}_1$ [T] of a dipole $\mathbf{m}_1$ [Am²] at position $\mathbf{r}$ [m] from the centre of the dipole can be expressed in SI units as

$$\mathbf{B}_1(\mathbf{r}) = \frac{\mu_0}{4\pi} \left(\frac{3\mathbf{r}(\mathbf{m}_1 \cdot \mathbf{r})}{r^5} - \frac{\mathbf{m}_1}{r^3} \right) \quad (6.1)$$

From the derivatives of the energy of dipole $\mathbf{m}_2$ in the field of dipole $\mathbf{m}_1$

$$U = -\mathbf{m}_2 \cdot \mathbf{B}_1 \quad (6.2)$$

Figure 6.1 The forces on the magnetic microsphere can be estimated by assuming that both the magnetic disk and the microsphere are point dipoles with moment m , separated by a distance r that is approximately equal to the radius of the disk r_d .

we obtain the force along the line of the dipoles

$$F_r = -\frac{\partial U}{\partial r} = \frac{-\mu_0 m_1 m_2}{4\pi} \frac{3(3\cos^2\theta - 1)}{r^4} \quad (6.3)$$

which has a maximum for $\theta=0$. The force along the circumference of the disk is

$$F_\theta = -\frac{1}{r} \frac{\partial U}{\partial \theta} = \frac{-\mu_0 m_1 m_2}{4\pi} \frac{6\cos\theta\sin\theta}{r^4} \quad (6.4)$$

which has a maximum at $\theta=45^\circ$. For $\theta > 54.7^\circ$ the force reverses sign and the magnetic microsphere detaches from the disk.

The magnetic moment is the total volume of the magnetic material of the disk or microsphere, multiplied with the magnetisation of the permalloy at the applied field strength ($M \approx 600$ kA/m, see Appendix B.3). When the microspheres touch the disk, r is approximately the radius of the disk r_d and the maximum transverse force becomes

$$F_{\theta,\max} = \frac{3\mu_0}{4} \frac{M^2}{r_d^2} V_{ps} t_d \quad (6.5)$$

Here V_{ps} is the volume of magnetic material on the microsphere (m^3), and t_d the thickness of the magnetic disk (m). For the drag force on a moving microsphere with radius r_b moving in a liquid with viscosity η_{vis} holds

$$F_d = 6 \pi r_b v_b \eta_{vis} \lambda \quad (6.6)$$

Here v_b is the velocity of the microsphere, which can be expressed as the rotation frequency of the magnetic field f_m multiplied by the circumference of the magnetic disk $2 \pi r_d$. A correction factor λ is included for the increased drag of the translating sphere at close distance to the planar wall. An analytical approximation is given by^[13]

$$\lambda = \frac{8}{15} \ln\left(\frac{\delta}{r_b}\right) - 0.9588 \quad (6.7)$$

where δ is the gap between the surface and the sphere, which is assumed to be a couple of nanometers ($\lambda \approx 5$). Equating the drag force to the maximum transverse force Eq. 6.5, an expression for the maximum actuation frequency $f_{m,\max}$ could be derived

$$f_{m,\max} = \frac{\mu_0 M^2 V_{ps} t_d}{16 \pi^2 \eta_{vis} \lambda r_b r_d^3} \quad (6.8)$$

Using the parameters of our experiment, a maximum actuation frequency of in the order of 300 Hz is obtained. This serves as absolute maximum for the pumping.

The dipole approximation predicts that the attractive force between microsphere and disk scales with the volume of the ferromagnetic material on the microsphere and of the disk itself. The magnitude of the force will therefore be determined by the thickness of the magnetic material. There is an advantage in reducing the size of the disk, since it will increase field gradients. This increased

gradient will lead to an increased maximum actuation frequency. Other possibilities to increase the maximum actuation frequency are to increase the magnetisation and the amount of magnetic material, since this leads to a higher magnetic moment.

The dipole approximation becomes very inaccurate when the disk and sphere touch, and a more detailed analysis would be required to estimate the magnitude of this effect. Such an analysis (*e.g.* numerical) should take into account the height of the magnetic disk, the complex shape of the magnetic film on the microsphere and their non-symmetric orientation with respect to each other. However, this would not lead to an analytical solution and therefore not lead to more insight into the system. Despite ignoring these effects in our dipole approximation, we found an upper limit for the system actuation.

When the microspheres detach from the disks, they will spin around their axis. This torque is generated by remanent magnetisation because of their shape and the amount of magnetic material.

6.2.2 Pumping effect

The rotation of the external in-plane magnetic field causes the magnetic microspheres to rotate along the edge of the disks. The drag of the moving microspheres on the surrounding liquid then causes it to move. This displacement of the liquid averaged over the channel can be estimated by combining a Stokes drag model for a sphere with a pressure-driven flow approximation for flat microchannels. The derivation can be found in Appendix B.1. For the geometries used in our experiment, this results in a ratio of the average microchannel liquid linear flow velocity to the microsphere velocity, $\eta_{m \rightarrow c}$, of 6%. This number is based on one pumping unit cell (as shown in Figure 6.2) with a length of 95 μm . To maximize the pumping effect, the magnetic microspheres should be as large as possible, on the condition that they still fit in the channel. Larger microspheres displace more liquid per cycle (larger efficiency $\eta_{m \rightarrow c}$) and also experience a higher force towards the disks, leading to an increased upper limit for the rotation frequency.

The magnetic disks are located off-centre in the microchannel, as shown in Figure 6.2. Because of the asymmetry in the liquid displacement during the forward

Figure 6.2 When a magnetic microsphere (black) rotates around a disk (yellow) which is located close to the wall in a microfluidic channel, the asymmetry in liquid displacement of the forward and backward movement results in net pumping.

and backward movement of the magnetic microspheres, a net fluidic pumping is obtained. We define the pumping efficiency η_p as

$$\eta_p = \frac{u_f - u_b}{u_f} \quad (6.9)$$

where u_f and u_b are the fluid pumping velocity during the forward and backward movement respectively. Assuming Stokes flow of a moving sphere and neglecting channel wall conditions, this pumping efficiency can be estimated by numerically integrating the 3D velocity profile over the channel boundaries. This first order calculation shows that the pumping efficiency is strongly dependent on the gap between the rotating microsphere and the wall, with the highest efficiency being achieved by minimizing this gap. Applied to the geometry in our experiment, a theoretical net pumping effect η_p of 18% is obtained: the difference between the average flow rate caused by a microsphere moving in the center of the channel and close to the wall. More precise simulations of the system in COMSOL Multiphysics showed a net pumping effect of 33%, see Appendix B.2 for more detailed information. The rotational frequency of the external magnetic field determines the movement of the magnetic microspheres and therefore the generated net liquid flow. All together, the average pumping velocity $\bar{u}_c$ (m/s) estimated for our experiment is

$$\bar{u}_c = 2\pi r_d f_m \eta_p \eta_{m \rightarrow c} \quad (6.10)$$

where r_d is the radius of the disks in the array (12.5 μm) and f_m is the rotation frequency of the magnetic field (5 – 20 Hz).

Applied to our geometry, we obtain a pumping velocity of 4 $\mu\text{m/s}$ for the analytical net pumping effect and 8 $\mu\text{m/s}$ for the simulated net pumping effect. The pumping force is multiplied through the microchannel by using an array of magnetic disks as shown in Figure 6.3.

Figure 6.3 The two tested designs incorporating a closed pumping channel with permalloy disks (yellow) on either the inside curve (a) or the outside curve (b). Scale bar is 100 μm .

6.2.3 Flow direction

Two degrees of freedom are present for determining the flow direction. The first one is geometrical, determined by the positioning of the magnetic disks at the inner or outer curve of the circular microchannel. The second independent degree of freedom is the rotational direction of the actuating magnetic field, which can be clockwise or anticlockwise. Four combinations are thus possible, as shown in Figure 6.4.

6.3 Experimental

6.3.1 Fabrication of microfluidic chips

To fabricate the fixed magnetic disks, a 480 nm thick permalloy film (nickel 81 wt%, iron 19 wt% composition with a purity of 99.95%) was sputtered on a silicon wafer and patterned using conventional lithography and etching, yielding an array of disks each with a diameter of 25 μm . Two designs were fabricated, with disks on the inside and outside curve of circular channels, as shown in Figure 6.3. To improve the adhesion of the permalloy to the silicon a chromium adhesion

Figure 6.4 Two degrees of freedom: the magnetic field rotation direction and the location of the disks, create four possible combinations.

Figure 6.5 Microscope images of the fabricated microchannel, in gray the fixed magnetic disks and in black the rotating magnetic microspheres. The tracking microspheres are the smaller black microspheres. On the left, the disks are located on the inside of the curved channel, on the right they are on the outside. Scale bar is 100 μm .

Figure 6.6 Fabrication process flow for the microfluidic chip containing permalloy (NiFe) disks.

layer of 30 nm was applied. The permalloy disks were coated with 425 nm of silicon dioxide, capping the permalloy to protect it from oxidation. The 23 μm high fluidic microchannels were defined by a SU-8 lithography process. Lastly the channels were sealed by bonding the silicon wafer to a Borofloat wafer at 150 $^{\circ}\text{C}$. The advantage of this low temperature bonding method is that the oxidation of the permalloy by heating is minimal, hence not deteriorating the magnetic properties. The permalloy could almost be saturated using a permanent magnet above the microfluidic chip (see Appendix B.3 for the magnetization curve of the permalloy on top of the chromium adhesion layer). Microscope images of the resulting channel during actuation are shown in Figure 6.5.

6.3.2 Fabrication of magnetic microspheres

To obtain magnetic Janus particles, polystyrene microspheres of 17 μm (Thermo Scientific, catalogue number: 7516A) were first dissolved in ethanol. Next silicon substrates were submerged into the solution and dried at a vertical position. The resulting monolayer was covered with 100 nm of permalloy by means of sputtering, as shown in Figure 6.7. Permalloy is a soft magnetic alloy with a strong magnetic response combined with a low coercivity. By using permalloy, the microspheres fall back to a low remanance state upon removal of the field. This helps avoid undesired clustering before the directed assembly process takes place. The coated microspheres are released from the support wafer by means of sonification, and subsequently centrifuged. Filtering of the magnetic microspheres was performed by stirring the sample with a permanent magnet and removing the part which was not attracted to the magnet.

Figure 6.7 Microscope image of a monolayer of polystyrene microsphere before sputtering on the left and after sputtering with permalloy on the right. Scale bar is 25 μm .

6.3.3 Experimental procedure

To perform the pumping experiment, the previously fabricated magnetic Janus microspheres were loaded into the microchannel. No permanent magnetic clustering of the magnetic microspheres as a result of mutual magnetic attraction was observed, indicating that the remanent magnetization is sufficiently low. The occupancy of the magnetic disks by one or two magnetic microspheres is governed by the Poisson distribution. To obtain the maximum amount of microspheres per disk, the concentration of magnetic microspheres was optimized. A low concentration is causing a low occupancy of the disks by microspheres and therefore a low flow rate. A higher concentration of microspheres is expected to lead to a higher flow rate, however when the concentration becomes too high a part of the microspheres will not be attached to disks. These unattached microspheres will lower the flow rate, because of their random distribution through the microchannel. When the magnetic microspheres were loaded into the chip, the pump (consisting of disks and magnetic microspheres) assembled on application of the external magnetic field.

Polystyrene tracking microspheres of 3 μm diameter (Polysciences #17137 polystyrene red dyed microspheres 3.0 μm , Thermo Scientific) were added to visualize the flow. For the flow measurements, the chips were filled with the magnetic microspheres and tracking microspheres, and placed on top of an inverted microscope stage. Their movement was recorded and post-processed with a MATLAB script. The external magnetic field was generated using a permanent rare-earth magnet at a distance of 1.5 cm (Q-51-51-25-N Block magnet from www.supermagnete.nl), creating an in-plane magnetic field. The actuating magnet was placed as close as possible to the chip, resulting in field strength of about 24 mT at the position of the channel. The magnet could be rotated in a large range of frequencies using an electric motor. The exact actuation frequency was measured by a nearby Hall sensor connected to an oscilloscope.

6.4 Results and Discussion

6.4.1 Magnetic microsphere rotation

The rotating microspheres are generating the highest pumping rate when all disks are occupied by magnetic microspheres and rotate at the maximal rotation

Figure 6.8 The disk occupancy as a function of rotating frequency. The occupancy is decreasing rapidly for higher actuation frequencies.

frequency. At a rotation frequency of 5 Hz the starting occupancy was approximately 60%, for higher actuation frequencies this occupancy decreases, as can be seen in Figure 6.8. The microspheres no longer perform an exclusively circular motion. A transition is observed from microspheres moving around the magnetic disks to detachment of microspheres from the disks after which they perform a spinning motion around their axes. A possible cause for this detachment is that the drag force for the rotating microsphere increases as function of actuation frequency. For low actuation frequencies the microsphere is attracted to the disk, since their magnetic moments are aligned. However for higher actuation frequencies the magnetic moments get parallel and therefore they repel each other, as is illustrated in Figure 6.9.

Figure 6.9 The microdisk (in yellow) possesses the magnetic moment m_1 and the microsphere (in black with a yellow gradient for the permalloy coating) possesses a magnetic moment m_2 . For slow actuation the magnetic moment of the disk and the microsphere are aligned, therefore the microsphere performs a circular motion around the disk (t_{1a-3a}). However, for fast actuation the magnetic moment of the disk and the microsphere get parallel, resulting in a repelling force (t_{3b}).

6.4.2 Liquid flow velocity

The flow in the microchannel was measured by analysing the trajectories of the non-magnetic tracking microspheres. The frequency dependent flow velocity is shown in Figure 6.10. Upon increasing the frequency, the flow velocity slightly decreases. This is caused by a lower disk occupancy by magnetic microspheres, which counteracts the increased magnetic microsphere velocity. Above 12 Hz an unexpected increase in flow velocity is observed. Observed is that at these higher actuation frequencies most of the magnetic microspheres are detached from the disk and are spinning around their axis. They however still experience a very weak interaction force towards the disk, keeping them located close to the channel walls. However, this resulting pumping action is rather uncontrolled, since the exact microsphere position is not determined by the disks.

Using a tracking algorithm, the pumping motion over the entire circular microchannel could be visualized. Figure 6.11 shows the four different control combinations. A rather uniform and consistent pumping motion was found. At an actuation frequency of 5 Hz, the tracking microspheres moved with 3.0 $\mu\text{m/s}$, which is in agreement with theory. This velocity was determined for tracking microspheres at some distance of the magnetic microspheres to get a proper estimation of the net flow in the microchannel. We can obtain an estimate for the minimum average pumping velocity of 2.0 $\mu\text{m/s}$, if we assume that the tracking microspheres move close to the maximum velocity in the channel. Multiplying this lowest estimate of the average flow velocity by the area of the microchannel, gives a pumping rate of 0.3 nL/min. A slight difference in density between the liquid and the tracking microspheres could cause a non-uniform distribution of tracking microsphere position in the parabolic flow profile. This makes it difficult to exactly relate the tracking microsphere velocity to the pumping rate.

Apart from the observed pumping motion, mixing occurs by the stirring action of microspheres, which is inherent to the pumping principle. This mixing could be helpful in *e.g.* microreactors. Furthermore, the pumping method can also be useful for biological applications needing slow and constant pumping in complex channel systems.

Figure 6.10 The velocity of the tracking microspheres as a function of actuation frequency.

Figure 6.11 Clockwise flow velocity of the tracking microspheres for an actuation of 5 Hz, showing the quadrant of pumping control. The magnetic field rotation direction can be either clockwise (a and c), or counterclockwise (b and d). Additionally, the disks can be located on the inside curve (a and b), or on the outside curve (c and d).

6.5 Conclusion and Outlook

We have demonstrated a pumping method suitable for pumping in entirely closed channel systems based on magnetic microsphere rotation around magnetic microdisks. The system offers two degrees of freedom, the rotational direction of the externally applied magnetic field and the location of the disks in the microchannel. This actuation method combined with the geometrical programmability results in four possible configurations. High versatility is obtained since geometric programming can be applied at any position in the chip.

After loading, approximately 60% of the permalloy disk were occupied with one or two magnetic microspheres. They remain on the disks at a rotation frequency of 5 Hz. The occupancy reduces down to 20% at 20 Hz. At 5 Hz rotation frequency the magnetic microspheres move at $390 \mu\text{m/s}$. Their movement results in a tracking microsphere velocity of $3 \mu\text{m/s}$. From this we conclude an average pumping velocity of at least $2 \mu\text{m/s}$. This is slightly lower than the theoretical pumping speed of 4 to $8 \mu\text{m/s}$. The tracking microsphere velocity is relatively independent of rotation frequency, varying between 1.5 and $3.5 \mu\text{m/s}$. From this tracking microsphere velocity we estimate a pumping rate of at least 0.3 nL/min . It should be noted that this is a lower estimate for the pumping rate. By geometry optimisation of the system and increasing the amount of magnetic materials, this flow rate could be increased. In addition to this, the flow rate would be increased by obtaining a better inter-microsphere distance during loading the chip. This could be achieved by changing the loading method by for instance making use of Dean forces to space the microspheres equally^[14]. Above 12 Hz, the velocity

increases due to spheres rotating around their axis, rather than around the disk. However, this is a less controlled way of actuating, since the exact microsphere motion is not determined by the disks.

Despite a low flow rate compared to other pumping methods, the system offers several advantages over existing systems. The method is capable of pumping of aqueous solutions in complex branched channel networks by applying only a single rotating external field. Additionally, the fabrication of the moving parts is simply achieved by directed assembly when the magnetic field is applied. An advantage of the use of small magnetic microspheres is that the amount of dead volume is minimized. Furthermore, the fabricated magnetic Janus microspheres have a large magnetic moment and are giving freedom to tune their properties.

At present the system is only partially biocompatible, since only the microdisks are covered by a silicon dioxide layer. In a later stage, a capping layer, of *e.g.* silicon dioxide, could be sputtered on the magnetic microspheres making them biocompatible too, thus making the complete system suited for biological experiments. In such experiments the pump could provide the supply of nutrients in *e.g.* long-term cell culture^[15], embryo development^[16] and organ on chip systems^[17,18]. Further optimisation would lead to an increase in the flow rate, enabling on chip recirculation of liquids for a broader spectrum of applications.

6.6 References

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7

Summary and Outlook

This work reported in this thesis was aimed at developing novel technologies for functional micro- and nanofluidic devices, as well as exploring the functionality of first examples of such devices. The technologies explored centered around graphene (Chapters 2 - 5), and additionally the use of magnetic materials was explored (Chapter 6). In all cases the use of cleanroom technology was indispensable for the developments.

Considering graphene synthesis, in the research reported in this thesis two methods for graphene synthesis have been used: one by chemical vapor deposition on a copper foil and one by chemical vapor deposition on a thin copper film silicon dioxide accompanied by dewetting of the copper. In Chapter 2 synthesis by the first method is reported, which encompasses graphene synthesis on copper foil and subsequent transfer to the desired insulator substrate. The graphene sensing and membrane devices reported in Chapters 4 and 5 were fabricated with graphene obtained using this method.

Chapter 2 reports on the details of the graphene synthesis method on copper foil as well as the protocol that was developed to transfer the graphene to a silicon dioxide surface. Finally it provides details on the quality of the graphene by using Raman spectroscopy. Since the method presented in Chapter 2 includes several manual steps such as cutting of the foil and scooping of a floating sample, which makes it labor-intensive and cumbersome, a method was developed for direct synthesis of graphene on silicon dioxide, without intervening manual steps. This method is presented in Chapter 3. Our aim was to spatially control the dewetting of the copper and hence the locations of graphene deposition on the insulator sub-

strate. We found that the dewetting process could be controlled by a combination of a grooved substrate separated by mesa lines and deposition of a thin copper layer at an angle. The substrate was then treated by a typical graphene chemical vapor deposition synthesis process at elevated temperature. Directional dewetting of the copper into the grooves was observed while graphene was deposited on the mesas in between the grooves. In Chapter 3 both the dewetting process and the synthesized graphene layer are characterized by AFM, Raman spectroscopy and electrochemical measurements of the graphene properties. The method is a non-manual, controllable and wafer scale process, and therefore opens new possibilities for the construction of functional graphene devices such as transistors.

In Chapter 4 the electrochemistry at graphene is investigated using spectroelectrochemistry. The electrochemistry on graphene is of particular interest because of graphene's high surface area, high electrical conductivity and low interfacial capacitance. The mechanism behind many of its specific properties however are still not fully understood. To understand and improve the performance of graphene for electrochemical applications and energy storage, we undertook an investigation to obtain a better understanding of molecular adsorption during electrochemical reactions at graphene surfaces. The technique of electrochemical Raman spectroscopy is very useful to obtain information about analyte adsorption during Faradaic reactions on the surface of graphene. Because the graphene Fermi level can be probed by its strong Raman signal, information on the graphene doping can be obtained that is potentially caused by adsorbed atoms or molecules. The graphene we used was chemical vapor deposited (CVD) graphene on copper foil, obtained via the transfer protocol described in Chapter 2. The analysis was successfully performed using three different electroactive substances. We found indications that the adsorption of species for the larger part takes place on the less reactive basal plane (changing the doping but not necessarily leading to electrochemical reaction), while local reactive sites for a large part determine the redox behavior. We also observed additional effects of the adsorbed species to the graphene surface, where a slight change in the electrochemical behavior most probably caused by changes in graphene charge carrier density and passivation of the surface. The conclusion of this chapter was, that electrochemical Raman spectroscopy on graphene is a valuable tool to obtain in-situ information on adsorbed species on graphene, isolated from the rest of the electrochemical behavior. The outlook of Chapter 4 is, that the monitoring of molecular adsorption on graphene by the Raman signal offers a potential sensing method. If the graphene would e.g. be spotted with a range of different single stranded DNA chains, hybridization could give a change of Raman signal, providing a DNA microarray.

In Chapter 5 we investigated transport through nanoporous graphene suspended over (larger) silicon nitride nanopores. Solid state nanopores have generated a growing interest and have a large field of potential applications such as desalination (pore arrays) and molecular sensing (single pores). Because of the small size of the graphene nanopores (around 1 nm) and the thinness of the graphene membrane, such graphene nanopores might be useful for single molecule DNA sequencing. The recent study of the Karnik group on the ionic transport behavior through CVD graphene nanopores of nm-range diameter suspended over a larger pore in a silicon nitride membrane showed unique transport behavior fun-

damentally different from larger pores. In Chapter 5 the pore conductance characteristics of suspended nanoporous graphene membranes were further studied to test the hypotheses formulated by the Karnik group. Especially the influence of pH was studied, to investigate the hypothesis that charged protonatable groups at the pore edge are an important cause of the observed current-voltage behavior. In accordance with Karnik's results it was observed that every pore possessed a unique character. Clear indications of a pH-dependent behavior was also found, supporting the hypothesis that protonatable groups are involved. Importantly, a hypothesis was formulated on the basis of the measurements, that an electrowetting process leads to progressive delamination of the graphene from the silicon nitride at higher applied electrical fields, leading to a progressive recruitment of additional nanopores and an increasing conductance. The chapter adds to the existing knowledge of silicon nitride-graphene pore devices, and underlines the need for proper applied voltage limitations if single pore behavior needs to be studied.

In Chapter 6 we reported work on a novel, flexible and programmable method to pump liquid through microchannels in lab-on-a-chip systems without the use of an external pump. The pumping principle we developed is based on the rotation of ferromagnetic Janus microspheres around permalloy disks, when driven by an external rotating magnetic field. By placing the disks close to the edge of the microchannel, a pumping rate of at least 0.3 nL/min (3 μ m/s) was measured using tracking microspheres. Geometric programming of the pumping direction is obtained by the side wall which is nearest to the magnetic disks. A second degree of freedom to control pumping direction is offered by the rotation direction of the external magnetic field. The method is especially suited for flow-controlled recirculation of chemical and biological species in microchannel applications - for example medium recirculation in culture chambers - opening the way towards novel, portable, on-chip applications without the need for external fluidic or electrical connections. Since the permalloy will be incompatible with biological specimens, an additional silicon oxide layer needs to be deposited for such applications.

What are the most promising applications of graphene in lab-on-a-chip systems? The research reported in this thesis makes clear that much work has still to be done before graphene can be used in a reliable manner as a barrier material for lab on a chip applications. We showed that the stable adhesion of graphene to silicon nitride, which is generally relied upon, has clear limits when electrical fields are applied across the graphene, since electrowetting energy can overcome the adhesion energy. Furthermore we found that every graphene membrane device we studied has a different current-voltage characteristic, indicating a different graphene pore with possibly different charged edge groups. A reliable pore formation protocol is thus essential when graphene membranes with reliable transport properties are to be obtained. Nevertheless, the extreme thinness of graphene and the opportunity to selectively functionalize the pore edges to tune the transport properties on the molecular level still offer an alluring prospect.

The second area of application of graphene in lab-on-a-chip systems can clearly be sensing. Our spectroelectrochemical measurements showed the possibility of sensing adsorption to the graphene by monitoring the position of the G-peak as a function of applied voltage to the graphene. This procedure could very well form the foundation of a sensor application, e.g. by monitoring the G-peak position of a

7. SUMMARY AND OUTLOOK

spot of ss-DNA after exposure to a solution with complementary strands. Multiple spots could be measured with such a system in an array-type measurement. From a fundamental point of view, the ability to independently from their electrochemical activity assess the adsorption of compounds is a valuable addition.

Our method of selective dewetting has promise as a direct wafer-scale technique to deposit graphene selectively on predetermined areas, and represents an clear advance in this area. Here an important future aim will be to further improve the quality of the deposited graphene.

The magnetic pumping method presented in Chapter 6 has clear advantages over many existing methods, as the actuation is non-contact and the pumping direction can be chosen at will as well as pre-programmed in the chip. Technological advances were booked in the deposition of the permalloy patches as well as the manufacturing of magnetic Janus beads. In this area further work needs to be done to increase the pumping speed as well as to cover the beads with a thin layer of ceramic to prevent metal leaching in biotechnological applications.

Additional material on: Graphene
synthesis by directional copper dewetting

A.1 Optical microscopy data

Table A.1 A selection of the optical data which is processed by a MATLAB script to analyze the relative dewetting width as a function mesa width. Three dewetting regimes for three deposition copper angles α_{Cu} are displayed. The silicon dioxide dewetted mesas (blue), with copper (light orange) separated by the grooves (out of focus) as schematically shown in the bottom row. Scale bar is 20 μm .

A.2 Raman spectroscopy fitting results

Figure A.1 Graphene quality results as function of the hydrogen and methane gas flow settings, aiming for defect free, single layer graphene. 2D-to-G peak intensity ratio I_{2D}/I_G (a); this ratio gives a rough indication for the number of graphene layers. D-to-G peak intensity ratio I_D/I_G (b); the lower this ratio, the less defects present in the graphene. Full width half maximum (FWHM) of the 2D peak (c); single layer graphene possesses a sharp 2D peak. G peak position (d); a higher G peak position is related to fewer graphene layers. Green indicates better quality graphene and red lesser quality graphene.

A.3 Atomic force microscopy data

Figure A.2 AFM recording of the mesa area directly after the CVD process. The ridges are caused by the dewetting of the copper.

Figure A.3 AFM recording of the mesa area after 13 min of 500 W O₂-plasma to strip the deposited graphene. The ridges are still present and the amplitude did not change significantly, thus the silicon dioxide surface has been ridged.

Figure A.4 AFM recording of the mesa area after 120 sec of etching in 1% HF solution, which etches silicon dioxide for ~ 10 nm. The amplitude did not change significantly, thus the graphene layer is continuous.

A.4 Energy selective backscatter data

Figure A.5 Energy selective backscattered (EsB) detector (left), High efficiency secondary electron (HE-SE2) detector (right). On the right image some copper particles are clearly visible next to the mesa. In right image this gives a clear contrast, since this detector is sensitive for difference in elements.

Figure A.6 Energy selective backscattered (EsB) detector (left), High efficiency secondary electron (HE-SE2) detector (right). When zooming in to the mesa area, the grooves are visible with some white particles in the right image. The particles give strong signal in the left image, thus they must also be copper. EDX analysis conforms that silicon, oxide, copper and carbon are the only elements present on the sample.

A.5 CVD log data

Figure A.7 The log data of a typical CVD treatment showing the temperature profile, hydrogen, methane and argon gas flows and the pressure over time.

B

Additional material on: Microfluidic
pumping using rotating microspheres
around disks

B.1 Pumping effect of moving microsphere

Microspheres are moving through an aqueous solution in the Stokes flow regime. For a moving microsphere the drag force is known as:

$$F_d = 6 \pi \eta_w r_d u_m \quad (\text{B.1})$$

where η_w is the viscosity of the liquid, r_d the radius of the microsphere and u_m the velocity of the microsphere.

Figure B.1 a series of microspheres moving with a separation distance Δx

This drag force of a series of moving microspheres is exerted on the fluid as shown in Figure B.1 and Equation B.1, generating a pressure difference Δp in the channel:

$$\Delta p = \frac{F_d}{h w} \quad (\text{B.2})$$

Where h is the height and w the width of the microchannel. This pressure difference is generated in every unit cell having a length of Δx . In flat microchannels the average fluid flow (u_c) can be written as^[1]

$$\overline{u_c} = \frac{h^2}{12 \eta_w} \frac{\Delta p}{\Delta x} \quad (\text{B.3})$$

with Equations B.1, B.2 and B.3, the ratio between the average channel fluid velocity $\overline{u_c}$ and the microsphere velocity u_m can be calculated

$$\eta_{m \rightarrow c} = \frac{\overline{u_c}}{u_m} = \frac{\pi h r_d}{2 w \Delta x} \quad (\text{B.4})$$

This approximation gives insight in the magnitude and scaling of the generated pumping motion. The ratio of velocities does not depend on the viscosity. A wider channel will decrease the flow rate, since there is more volume to displace. A higher channel will increase the flow rate (less hydrodynamic resistance), the model, however, is only valid under the flat channel approximation. Larger microspheres will displace more fluid, especially when they are placed close to each other (small Δx). A minimum height and width of the channel is determined by the size of the microspheres.

The geometries in our experiment are: channel height $h = 23 \mu m$, channel width $w = 105 \mu m$, microsphere radius of $r_d = 17 \mu m$ and a separation distance $\Delta x = 95 \mu m$. This results in a velocity ratio $\eta_{m \rightarrow c}$ of 6%.

B.2 Simulation results of flow rate

Using COMSOL Multiphysics 4.2a the flow was simulated using a 2D model. The Fluid-Structure Interaction physics module and incompressible flow neglecting the inertial terms were used.

Figure B.2 2D simulation of the Stokes flow around a circle making a circular motion in the microchannel. The color indicates the magnitude of the flow in horizontal direction, the arrows indicate the direction of the flow.

Figure B.3 The output flow rate at the end of the simulated cell. This flow rate was calculated by integrating the velocity over the right boundary and dividing by the boundary length ($1/w \int_{width} u_x dy$). It can be seen that there is a clear asymmetry in the flow rate. This simulation model results in a pumping efficiency $\eta_{m \rightarrow c}$ of 33%.

B.3 Magnetic properties of the permalloy

Figure B.4 shows the magnetic hysteresis loop of the 480 nm continuous permalloy ($\text{Ni}_{80}\text{Fe}_{20}$ film), similar to the one used to fabricate the disks. The peculiar shape of the loop is due to stripe domains, which is typical for permalloy film of this thickness. These stripe domains are caused by an out-of-plane component in the anisotropy^[2], most likely caused by crystalline growth with a preferred orientation. Even though the susceptibility is far from optimal, these films reach a magnetisation of about 75% of their saturation value of 790(50) kA/m at the field of 24 mT applied in the experiments.

Figure B.4 The magnetization curve of the permalloy disks, showing saturation at about 800 kA/m for fields above 50 mT.

B.4 Dipole field approximation

The stray field of magnetic disc of radius r_d and thickness t_d , saturated to its saturation magnetisation M_s , can be approximated by a magnetic line charge with charge density

$$\lambda = M_s t \cos \theta \quad [\text{A}], \quad (\text{B.5})$$

where θ is as defined in Figure B.5. This approximation is correct for points that lie much further from the edge of the disc than its thickness ($r - r_d \gg t_d$). Integration over infinitesimal charge packages $\lambda r_d d\theta$ yields for the magnitude of the magnetic field $\mathbf{B}$ at location $\mathbf{r}$ in Figure B.5

$$B = \frac{\mu_0 M_s t}{2\pi r_d} \int_0^\pi \frac{(x - \cos \theta) \cos \theta}{(x^2 - 2x \cos \theta + 1)^{(3/2)}} d\theta \quad [\text{T}] \quad (\text{B.6})$$

with $x = r/r_d$. The integral was solved numerically, and compared to the field of a point dipole with a moment equal to the volume of the disk times the saturation magnetisation

$$B_{\text{dip}} = \frac{\mu_0 M_s t}{2r_d} \frac{1}{x^3}. \quad (\text{B.7})$$

The ratio between the line charge approximation and the dipole field is shown in Figure B.5. For $r > 3r_d$ the error made by using a dipole approximation is less than 10%.

Figure B.5 The magnetic field of a saturated disc can be approximated by a line charge, with a charge density proportional to $\cos \theta$.

Figure B.6 The error made by assuming the disc to be a dipole as a function of the distance from the center of the disc.

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Publications

Journal papers

van den Beld, W.T.E., Loessberg-Zahl, J.T., Vervuurt, R.H.J., Weber, J.W., Bol, A.A., van den Berg, A. and Eijkel, J.C.T. (2016). Ionic transport characteristics of suspended graphene membranes, in preparation.

van den Beld, W.T.E., Odijk, M., Vervuurt, R.H.J., Weber, J.W., Bol, A.A., van den Berg, A. and Eijkel, J.C.T. (2016). Raman spectroelectrochemistry on graphene, in preparation.

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Conference contributions

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Contributions

Here collaborations within the group but also with external people are described to acknowledge the contributions that made this research possible. Throughout the whole project Jan Eijkel en Albert van den Berg contributed by having many fruitful discussions, from which original ideas arose that finally resulted in this thesis.

Chapter 2

The chemical vapor deposition graphene experiments discussed in this chapter were performed in the lab of the Plasma & Materials Processing department of the Eindhoven University of Technology, headed by Ageeth Bol. The graphene synthesis experiments were carried out by Jan-Willem Weber en René Vervuurt from this department.

Chapter 3

The scanning electron microscopy images displayed in this chapter are recorded by Hai Le The and Johnny Sanderink.

Chapter 4

For the larger part of the spectroelectrochemistry experiments, shown in this chapter, the electrochemistry part was performed together with Mathieu Odijk.

Chapter 5

The nanopore fabrication process in the silicon nitride membranes, described in this chapter, was developed in collaboration with Henk van Wolferen. Furthermore, Josh Loessberg-Zahl contributed greatly to the transmembrane conductivity experiments.

Chapter 6

Leon Abelmann and Eddy de Weerd contributed to the discussions on the magnetic modeling of the system and on magnetic materials described in this chapter. Together with Johan Bomer and Bjorn de Wagenaar the process for fabricating the microfluidic permalloy devices were developed. Natalia Cadena (visiting PhD-student from Tecnológico de Monterrey, Mexico) contributed to the pumping experiments using magnetic Janus microspheres.

Nederlandse samenvatting

Grafeen is een veelbelovend koolstofmateriaal dat veel belangstelling heeft gekregen de afgelopen tien jaar vanwege zijn unieke eigenschappen zoals zijn mechanische sterkte en ondoorlaatbaarheid voor gassen. De kern van een potlood bestaat uit verschillende materialen waarvan het grootste gedeelte grafiet. Dit grafiet bestaat uit opgestapelde koolstoflaagjes en recent is ontdekt dat een enkele laag geïsoleerd stabiel is. Een monolaag van dit materiaal heet grafeen en bestaat uit een honingraat of kippengaas van koolstofatomen. De eerste methode waarmee het lukte om een enkele atoomlaag grafeen te isoleren was met de zogeheten plakbandmethode. Hierin worden met plakband grafeenlagen verwijderd tot op de laatste laag die beter vast zit aan het substraat (meestal een ondergrond van siliciumoxide, een soort glas). Dit nieuwe koolstofmateriaal bleek interessant te zijn voor een breed scala aan toepassingen. Grafeen kan worden gebruikt als ultradun membraan met nanoporiën dankzij zijn atomaire dikte van slechts ~ 0.37 nm samen met zijn mechanische sterkte, dat in theorie sensor- en filtratieprocessen sterk kan verbeteren. Daarnaast is grafeen interessant voor elektrochemische toepassingen en voor energieopslag door zijn grote oppervlak en hoge geleidbaarheid. Informatie over de hoeveelheid ladingsdragers in het grafeen (dotering of doping) kan eenvoudig worden bemeaten door zijn sterke Raman-sigitaal (optische karakterisatiemethode).

Het werk in dit proefschrift was gericht op de ontwikkeling van nieuwe technologieën voor functionele micro- en nanofluidische chips en daarnaast ook de werking van een aantal van deze chips te onderzoeken. De verkende technologieën waren gericht op grafeen (Hoofdstuk 2 tot en met 5) evenals het gebruik van magnetische materialen (Hoofdstuk 6). In beide gevallen is het gebruik van cleanroomtechnologie onmisbaar voor de ontwikkelingen.

In het onderzoek beschreven in dit proefschrift zijn twee grafeensynthesemethoden gebruikt. De eerste methode maakt gebruik van een chemisch opdampproces op koperfolie. In de tweede methode vindt het chemisch opdampproces plaats op een dunne koperlaag op een siliciumoxide substraat, waarbij een grafeenlaag wordt gedeponeerd tijdens het opballen van het koper op hoge temperatuur (ook wel dewetting). In Hoofdstuk 2 zijn de details van de grafeensynthesemethode op koperfolie en het protocol om dit grafeen over te brengen naar een isolerend substraat te vinden. Tenslotte is ook de kwaliteit van het grafeen onderzocht. Het overbrengingsprotocol omvat een aantal handmatige stappen zoals het snijden van

de folie en het opscheppen van een drijvend folietje, wat het nogal omslachtig maakt. Om deze reden werd een nieuw syntheseprotocol ontwikkelend dat deze handmatige stappen overbodig maakte, die wordt beschreven in Hoofdstuk 3. Het doel was om de dewettingrichting van het koper vast te leggen en dus de locatie van grafeendepositie op een isolerend substraat. We vonden dat het dewettingproces kan worden bepaald door een combinatie van een substraat met groeven gescheiden door vlakke gedeeltes (mesa's) en de depositie van het koper hierop onder een hoek. Hierna wordt een chemisch opdampproces uitgevoerd op hoge temperatuur (1000 °C). Na het uitvoeren van dit proces heeft het koper zich teruggetrokken in de groeven terwijl grafeen gedeponereerd is op de mesa's tussen de groeven. In Hoofdstuk 3 worden de eigenschappen van de gedeponeerde grafeenlagen onderzocht met een aantal technieken zoals atomic force microscopy (AFM, vrij vertaald als aftastmicroscopie), Raman spectroscopie en elektrochemische transistormetingen. Met deze methode zorgt voor grafeensynthese zonder handmatige stappen, op een gecontroleerde manier en is geschikt voor gebruik op grote schaal, en maakt de fabricage van nieuwe grafeenchips mogelijk zoals transistoren.

In Hoofdstuk 4 wordt de elektrochemie op grafeen onderzocht met behulp van Raman spectro-elektrochemie. De elektrochemie op grafeen is interessant vanwege zijn grote oppervlak, hoge geleidbaarheid en lage capaciteit. Het precieze werkingsmechanisme van veel van zijn eigenschappen wordt nog niet volledig begrepen. Om hiervan meer begrip te verkrijgen en de prestaties van grafeen voor elektrochemische toepassingen te verbeteren, hebben we de adsorptie van moleculen op grafeen onderzocht tijdens electrochemische experimenten. Raman spectro-elektrochemie is bruikbaar om informatie te verkrijgen over de adsorptie van analyten tijdens Faradische reacties op grafeen. Omdat het Fermi-niveau kan worden bemeaten via het sterke Ramansignaal van grafeen, kan informatie worden verkregen over de grafeendotering dat mogelijk veroorzaakt wordt door geadsorbeerde atomen of moleculen. Het grafeen dat we hiervoor gebruikt hebben is gemaakt met het chemisch opdampproces op koperfolie, overgebracht met het handmatige overbrengingsprotocol beschreven in Hoofdstuk 2. De adsorptiemeting werd uitgevoerd met drie verschillende analyten die elektrochemisch actief zijn. In deze metingen vonden we indicaties dat de analyt-adsorptie voornamelijk plaatsvindt op het minder reactieve basisvlak (dat de dotering verandert maar niet per se leidt tot een elektrochemische reactie), terwijl lokalere reactieve gedeeltes grotendeels het elektrochemische gedrag bepalen. Daarnaast hebben we ook een aanvullend effect waargenomen van de analyt-adsorptie op grafeen, waar kleine veranderingen in het elektrochemisch gedrag hoogstwaarschijnlijk veroorzaakt worden door veranderingen in de hoeveelheid ladingsdragers in het grafeen en door passivatie. De conclusie was dat Raman spectroelectrochemistry op grafeen een waardevolle methode is om in-situ informatie te verkrijgen over geadsorbeerde analyten, waarbij de adsorptie een losgekoppelde stap is binnen het elektrochemische gedrag. In de toekomst kan deze methode mogelijk gebruikt worden als sensorsysteem waarbij moleculaire adsorptie op grafeen gemonitord kan worden. Een voorbeeld is als op het grafeenoppervlak lokaal enkelstrengs DNA met verschillende sequenties wordt geadsorbeerd en dat vervolgens hybridisatie met een complementaire DNA-streng een verandering het in het Ramansignaal teweegbrengt. Voor een snelle analyse zouden meerdere DNA hybridisaties parallel uitgevoerd kunnen worden.

In Hoofdstuk 5 wordt het transport door nanoporiën in grafeen onderzocht op een siliciumnitride substraat met een grotere nanoporie. Voor nanoporiën is er steeds meer interesse en ze hebben een breed scala aan mogelijke toepassingen zoals het ontzouten van water (met vele poriën) en moleculaire detectie (enkele porie). Vanwege de uiterst kleine diameter van de nanoporiën (ongeveer 1 nm) en zijn atomaire membraandikte kunnen dergelijke grafeennanoporiën geschikt zijn voor de sequentiebepaling van een enkele DNA-streng. Een recente studie van de groep van Karnik aan het MIT (Boston, VS) heeft het transportgedrag van ionen door grafeen geanalyseerd, dat gemaakt was met een chemisch opdampproces. De nanoporiën in het grafeenmembraan, opgehangen boven een grotere siliciumnitride nanoporie, vertoonde uniek transportgedrag dat fundamenteel anders is dan dat van grotere poriën. In Hoofdstuk 5 werd de geleiding van de grafeenporiën verder in kaart gebracht om de hypothesen, geformuleerd door de Karnik-groep, te verder testen. Op de invloed van pH werd gefocust om de hypothese over geladen protoneerbare groepen aan de rand van de porie te toetsen. In overeenstemming met de resultaten van Karniks groep werd waargenomen dat elke porie een uniek karakter bezat. Indicaties voor een pH-afhankelijk gedrag waren gevonden, wat de hypothese voor de aanwezigheid van protoneerbare groepen aan de rand van de porie ondersteunt. Belangrijker nog, op basis van de experimenten was een hypothese geformuleerd dat het grafeen loslaat van het siliciumnitride substraat door een electrowettingproces bij het aanleggen van hogere voltages. Dit proces heeft tot gevolg dat er meer nanoporiën worden geopend, waardoor de totale geleiding toeneemt. Dit hoofdstuk is een toevoeging aan de bestaande kennis van siliciumnitride-grafeenporie-systemen en benadrukt de noodzaak tot het limiteren van de aangelegde voltages als het gedrag van één enkele porie bestudeerd moet worden.

In Hoofdstuk 6 is het werk beschreven aan een nieuwe, flexibele en programmeerbare methode om vloeistof te pompen door microkanalen in lab-on-a-chip systemen zonder gebruik te maken van een externe pomp. Het pompprincipe dat wij ontwikkeld hebben is gebaseerd op de rotatie van ferromagnetische Janus microbolletjes rond schijfjes van permalloy (legering van ijzer en nikkel), gedreven door een roterend extern magnetisch veld. Door de schijfjes dicht bij de rand van het microkanaal te plaatsen werd een pompsnelheid van ten minste 0.3 nL/min (3 μ m/s) gemeten met behulp van kleinere bolletjes die meebewegen met de bewegende vloeistof. Geometrische programmering van de pomprichting is mogelijk door de positionering van de magnetische schijfjes bij een van de twee zijwanden. Een tweede vrijheidsgraad om de pomprichting in te stellen is de rotatierichting van het externe magneetveld. Deze pompmethode is geschikt voor toepassingen waarin recirculatie van chemische of biologische stoffen in microkanaaltjes nodig is, bijvoorbeeld de recirculatie van kweekmedium in microkweekkamers. Dit maakt nieuwe draagbare op-chip toepassingen mogelijk zonder dat vloeistofverbindingen of elektrische verbindingen naar de buitenwereld nodig zijn. Aangezien het permalloy schadelijk is voor biologische systemen, is een extra bescherm laag nodig van bijvoorbeeld siliciumoxide (een soort glas) voordat de methode gebruikt kan worden voor deze toepassingen.

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