Fabrication and Applications of a Focused Ion Beam Based Nanocontact Platform for Electrical Characterization of Molecules and Particles

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Abstract

The development of new materials with novel properties plays an important role in improving our lives and welfare. Research in Nanotechnology can provide e.g. cheaper and smarter materials in applications such as energy storage and sensors. In order for this development to proceed, we need to be able to characterize the material properties at the nano-, and even the atomic scale. The ultimate goal is to be able to tailor them according to our needs.

One of the great challenges concerning the characterization of nano-sized objects is how to achieve the physical contact to them. This thesis is focused on the contacting of nanoobjects with the aim of electrically characterizing them and subsequently understanding their electrical properties. The analyzed nanoobjects are carbon nanosheets, nanotetrapods, nanoparticles and molecular systems.

Two contacting strategies were employed in this thesis. The first strategy involved the development of a focused ion beam (FIB) based nanocontact platform. The platform consists of gold nanoelectrodes, having nanogaps of 10-30 nm, on top of an insulating substrate. Gold nanoparticles, double-stranded DNA and cadmium telluride nanotetrapods have been trapped in the gaps by using dielectrophoresis. In certain studies, the gold electrodes have also been coated with conducting or non-conducting molecules, prior to the trapping of gold nanoparticles, in order to form molecular junctions. These junctions were subsequently electrically characterized to evaluate the conduction properties of these molecular systems. For the purpose of better controlling the attachment of molecules to the nanoelectrodes, a novel route to synthesize alkanedithiol coated gold nanoparticles was developed. The second contacting strategy was based on the versatility of the FIB instrument as a platform for in-situ manipulation and electrical characterization of non-functionalized and functionalized carbon nanosheets, where it was found that the functionalized samples had an increased conductivity by more than one order of magnitude.

Both contacting strategies proved to be valuable for building knowledge around contacting and electrical characterization of nanoobjects

Keywords: Focused Ion Beam, FIB, Scanning Electron Microscopy, SEM, Nanogap electrodes, Nanostructuring, Nanofabrication, Electron Beam Lithography, Electrical characterization, Dielectrophoresis

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Till min familj
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. Reprints were made with permission from the respective publishers.

I Fabrication and characterization of highly reproducible, high resistance nanogaps made by focused ion beam milling
Blom T., Welch K., Strømme M., Coronel E. and Leifer K.
*Nanotechnology*, v.18, 285301 (2007)

II Assessment of a nanoparticle bridge platform for molecular electronics measurements
*In manuscript*

III Measurements of low-conductance single molecules using gold nanoelectrodes: limitations and considerations
Welch K., Blom T., Leifer K. and Strømme M.
*In manuscript*

IV Low-temperature synthesis of photoconducting CdTe nanotetrapods
Sugunan A., Jafri S. H. M., Qin J., Blom T., Toprak M.S., Leifer K. and Muhammed M.

V Conductivity engineering of graphene by defect formation

VI An in-situ prepared nano-manipulator for electrical characterization of graphene like carbon nanosheets inside a FIB-SEM
Blom T., Jafri S. H. M. and Leifer K.
*In manuscript*
Comments on my contribution to the papers

I  I designed and fabricated the structures and contributed to the measurements and the analysis of the results. I wrote the major part of the manuscript.

II  I fabricated the structures, prepared some of the samples, contributed to the experiments and the analysis of the results. The first and second author contributed equally in writing the manuscript.

III  I designed and fabricated the structures used in this study. I contributed to the discussions of the results.

IV  I fabricated the structures used for the trapping and the electrical measurements and took part in the discussions of the results.

V  I performed the in-situ manipulation experiments and the contacting of the sample. I performed parts of the electrical measurements and the analysis of the results. I wrote parts of the experimental section of the manuscript.

VI  I developed the protocol for sharpening the probe needle, performed the contacting of the sample and I wrote the manuscript.

VII I fabricated the nanogaps, performed most of the SEM analysis, participated in the discussions of the results and wrote parts of the experimental section of the manuscript.
Also published

Biomimetic calcium-phosphate coatings on recombinant spider silk fibres
Yang L., Hedhammar M., Blom T., Leifer K., Johansson J., Habibovic P. and van Blitterswijk C. A.
Submitted to Biomedical Materials

Using a molten organic conducting material to infiltrate a nanoporous semiconductor film and its use in solid-state dye-sensitized solar cells
Fredin K., Johansson E. M. J., Blom T., Hedlund M., Plogmaker S., Siegbahn H., Leifer K. and Rensmo H.
Synthetic Metals, v.159, 166 (2009)

Antireflection treatment of Thickness Sensitive Spectrally Selective (TSSS) paints for thermal solar absorbers
Lundh M., Blom T. and Wäckelgård E.

Multilayer piezoelectric copolymer transducers
Lilliehorn T., Blom T., Simu U., Johansson S., Nilsson M. and Almqvist M.

Dielectrophoretic trapping of gold nanoparticles on SAM-prepared nanogaps: A comparative study of different molecular systems
Blom T., Jafri H., Welch K., Strømme M. and Leifer K.
Oral presentation at the International Conference on Molecular Electronics, Emmetten, Switzerland (2010).

Molecular electronics on non-perfect electrode surfaces
Leifer K., Blom T., Jafri H., Welch K., Strømme M., Coronel E. and Grigoriev A.
Poster presentation at the International Conference on Molecular Electronics, Emmetten, Switzerland (2010).

In-situ contacting of nanosheets and remote EMCD
Hjörvarsson B., Liebig A., Schattschneider P., Stöger-Pollach M., Hurm C., Zweck J. and Leifer K.
Oral presentation at the 2nd International Workshop on Remote Electron Microscopy and In-situ studies, Gothenburg, Sweden (2009).

Fabrication and use of high resistance nanogaps for application in molecular electronics
Poster presentation at the Micro and Nano Engineering conference (MNE2009), Ghent, Belgium (2009).

Electrical Characterization of Defect induced Graphene Nano-sheets
Oral presentation at Nanotech Europe 2009, Berlin, Germany (2009)

Using a nano-contact platform for evaluating molecular electronics response
Jafri S. H. M., Blom T., Welch K., Strømme M. and Leifer K.
Poster presentation at Nanotech Europe 2009, Berlin, Germany (2009)

Dielectrophoretic trapping of gold nanoparticles on SAM-prepared nanogaps: A comparative study of different molecular systems
Poster presentation at the European Conference on Molecular Electronics (ECME2009), Copenhagen, Denmark (2009).

Fabrication and characterization high resistance nanogaps used for studies of different molecular electronics systems
Blom T., Jafri H., Welch K., Strømme M. and Leifer, K.
Poster presentation at Scandem, Reykjavik, Iceland (2009).

Assessment of electrical properties of graphene nanosheets containing defects
Oral presentation at the *1st Nordic Workshop on Graphene*, Uppsala, Sweden (2009).

**In-situ nanomanipulation setup for electrical characterization of graphene nanosheets inside a FIB-SEM**
Poster presentation at the *1st Nordic Workshop on Graphene*, Uppsala, Sweden (2009).

**Do-It-Yourself graphene production, transfer and characterization**
Calvaca F., Jafri S. H. M., Blom T., Akhtar S., Rubino S. and Leifer K.
Poster presentation at the *1st Nordic Workshop on Graphene*, Uppsala, Sweden (2009).

**Fabrication and characterization of highly reproducible, high resistance nanogaps made by focused ion beam milling**
Blom T., Welch K., Strømme M., Coronel E. and Leifer K.
Oral presentation at the *European Microscopy Congress 2008* (EMC2008), Aachen, Germany (2008).

**Fabrication and characterization of nanogaps made by Focused Ion Beam milling**
Blom T., Welch K., Strømme M., Coronel E. and Leifer K.
Poster presentation at the *International Conference on Nano Science and Technology* (ICN+T), Stockholm, Sweden (2007).

**Fabrication and characterization of highly reproducible, high resistance nanogaps made by focused ion beam milling**
Blom T., Welch K., Strømme M., Coronel E. and Leifer K.
Poster presentation at the *3rd European FIB & DualBeam UserClub Meeting*, Eindhoven, Netherlands (2007).

**Nano-contact fabrication by using Electron Beam Lithography and a Focused Ion Beam**
Blom T., Welch K., Strømme M., Coronel E. and Leifer K.

**Anti-reflection treatment of TSSS paints for thermal solar absorbers**
Lundh M., Blom T. and Wäckelgård E.
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<th>Abbreviation</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
</tr>
<tr>
<td>EBID</td>
<td>Electron Beam Induced Deposition</td>
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<tr>
<td>IBID</td>
<td>Ion Beam Induced Deposition</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental SEM</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>HSQ</td>
<td>Hydrogen Silsesquioxane</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol or Isopropanol</td>
</tr>
<tr>
<td>LOM</td>
<td>Light Optical Microscopy</td>
</tr>
<tr>
<td>MCBJ</td>
<td>Mechanically Controllable Break-Junction</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl Isobutyl Ketone</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl Methacrylate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>I-V</td>
<td>Current-Voltage</td>
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1. Introduction

Nanoscience and nanotechnology have become very hot topics over the last decade. The definition of nanotechnology is not very strict but one short definition is the manipulation of atoms, molecules, and materials to form structures on the scale of nanometers (from Britannica Concise Encyclopedia). Another definition concerns structures and materials with physical dimensions smaller than 100 nanometers (nm). It is very hard for most people to imagine something with the size of 100 nm or smaller. 100 nm does not mean very much if it is not put into perspective or is compared to something else.

Comparisons can be helpful in understanding the scale of the dimensions involved. The proportion of a nanometer to a football is the about the same as that of a football to the earth. Here is another one. If a drop of water would be spread out over an area of 1 m² it would be 1 nm thick (Leydecker, 2008). Nanotechnology can be seen as the study and manipulation of individual atoms and molecules to make novel materials, devices and systems. By allowing scientists to essentially construct matter from its basic building blocks, nanotechnology facilitates the enhancement of material properties as well as the creation of entirely new materials, properties and systems (Arabe, 2004).

Nanotechnology has its general focus on developing applications which can contribute to our welfare. More specifically we would like nanotechnology to give us e.g. more reliable and sensitive medical diagnostic tools for finding illnesses and intelligent medicine to cure them. We would like cheaper and faster computers with low power consumption and we would very much like to be able to drive our car and produce electrical power without polluting the environment. Nanotechnology has already contributed to some extent in many of these areas. There is a constant development in e.g. the production of high-density batteries for storage of electrical power, the production of nano-composite materials with increased strength and decreased weight suitable for space- and aircrafts and in the production of cheaper and more efficient solar cells.

In order for nanotechnology to do all of this, we need to know how to control the properties of different materials sometimes down to the atomic scale. When novel nanomaterials are synthesized there is an increased need for advanced tools to accurately characterize them down to this scale. Many nano-sized objects like e.g. nanoparticles and molecules can be characterized
in liquid form or on large surface areas by different techniques such as e.g. NMR, FTIR and UV-Vis spectroscopy (Shankar, 2004; Zamborini, 2001) providing average results over many nanoobjects. But when it comes to the investigation of the electrical properties of individual nanoobjects, the critical parts which have to be well controlled are the interfaces between them and the nano-electrodes building up a contact or device to which electrical measurement equipment can be connected. The nano-electrodes and their spacing must be in the size range comparable to the nanoobjects. One of the key challenges is therefore how to achieve a well-defined physical connection between the measurement setup and the nanoobject in order to obtain reproducible characterization of their electrical properties. The procedure to achieve the physical contact to nanoobjects can be summarized as nanocontacting.

1.1 Nanocontacting

Nanocontacting is the general word for connecting nanoscopic objects to our macroscopic world consisting of e.g. measurement instrumentation such as microscopes and source-meters. It can be enough to disperse the nanoobjects on a substrate for e.g. size measurements by using a microscope but sometimes they might be accurately contacted to metallic wires or leads to investigate their individual properties without the influence of another object. The creation of electrical contacts to small objects like nanowires, molecules and nanoparticles has always been challenging. The great challenge lies within the extremely small interfaces which have to be controlled in order to obtain reliable and reproducible measurements. Nanocontacting also implies that there is a requirement on the use of advanced structuring techniques in order to facilitate the junctions and interfaces between the nanoobjects and the metallic leads. The essential parts of the fabricated structures closest to the contacted nanoobjects are electrodes spaced by a distance comparable to the size of the object. There are different approaches on how to connect a single object to an experimental measurement setup.

A Mechanically Controllable Break Junction (MCBJ) is an experimental setup where the separation between two electrodes can be monitored by observing the conductance between them. The setup is very useful for investigating the electron transport through single molecules in a solvent (Huber, 2008; Martin, 2008). A similar approach is to use an Atomic Force Microscope (AFM) (Cui, 2001) or a Scanning Tunneling Microscope (STM) (Xu, 2003) for making and breaking the contact between the conducting tip and the substrate in the presence of molecules. Another way is to ‘simply’ place the tip on top of molecules sticking out from a substrate and perform electrical measurements of the static setup. The molecules in the solutions can be anchored to the metal electrodes (typically made of gold) with thiol (Sulphur-
Hydrogen) or amine (Nitrogen-Hydrogen) groups located at each end of the molecule. The groups will form covalent bonds to the electrodes and thus provide pathways for the electron transport through the molecule which is bridging the gap. The MCBJ, AFM and STM are suitable techniques for obtaining fundamental knowledge of the electron transport properties (e.g. conductance) at a molecular scale with good statistics.

In order to take advantage of the properties of molecules and nanoparticles, they should be incorporated in a more applied setting as in a circuit or device. One way is to utilize nanogap electrodes (Li, 2010) to form metal/nanoobject/metal junctions. The substrate, on which the nanogaps are fabricated, typically consist of an insulating material (e.g. silicon dioxide) grown on top of highly doped silicon. The silicon substrate can be contacted and work as a backgate in order to enable the investigation of transistor properties of the nanogap devices. The nanogaps are suitable building blocks for integrating molecular and nanoparticle systems in applications like e.g. switches (Collier, 1999), memory devices and transistors (Kubatkin, 2003; Park, 2000). Nanogaps can be fabricated by using different techniques such as; electron beam lithography (Fischbein, 2006), photolithography (Niatoh, 2006), electromigration (Park, 1999), electrochemical deposition (Morpurgo, 1999), focused ion beam milling (FIB) (Nagase, 2006; Gazzadi, 2006) and nanoimprint lithography (Austin, 2004).

Some limitations and considerations of the above techniques concerning the fabrication of nanogaps are described in the following paragraph.

The electron beam lithography process (described in Chapter 3) must be optimized (e.g. electron resist properties, electron exposure dose and development procedure) in order to give reproducible nanogaps with sizes of a few nanometers. Instead of electron beam lithography, photolithography can be used in a two-step process with shadow evaporation, oxygen plasma ashing and electromigration but this will yield in laterally large electrodes without well-defined shapes (Naitoh, 2005). Electromigration is a technique where a current is forced through a metallic nanowire until it breaks. The electrode spacing can be precisely monitored but the technique is typically quite time consuming and without control of the shape of the electrodes. Depending on the choice of materials, the electrodes can be very pointy and closely spaced but end up in more rounded shapes after some period of time due to the relaxation of the electrode material. The electrodeposition technique requires predefined micro- or nanofabricated electrodes as a starting point. In an electrochemical process, material can be deposited onto the electrodes, resulting in more rough electrodes but with smaller gap spacing as compared to the predefined structures. The size and the shape of the final electrodes are difficult to control. Nanoimprint lithography can be used to produce a large number of nanogaps but has the disadvantage that it requires a master fabricated by other means (e.g. by using electron beam lithography or FIB). The pattern of the master is transferred to a substrate coated with a polymer film.
by pressing them together. The shape and resolution of the master determines the size of the finest details of the fabricated structures. The quality of the master might degrade upon extensive usage.

The techniques utilized in this thesis are electron beam lithography for fabrication of nano-sized wires in combination with fast, parallel patterning of micron-sized contact pads by the use of photolithography. Thin film deposition by evaporation is used for the metallization of the structures. The final step, which is the nanogap fabrication process, is done by using the FIB for precise milling of the nano-sized wires. The result of the fabrication of each gap is seen directly, by using the scanning electron beam in the dualbeam focused ion beam / scanning electron microscope (FIB/SEM). The great advantage with using the electron beam is that the size of the fabricated nanogap can be measured directly after creation and the fabrication parameters can be adjusted prior to the milling of the next gap. Most other nanogap fabrication techniques are performed without direct observation of the result. The versatility of the FIB microscope is also shown in this thesis due the usage of it as a tool for manipulation, contacting and electrical characterization of nanoobjects. In this thesis, a commercially available Omniprobe™ manipulator, installed in the FIB/SEM, has been used but other products are also available on the market (Peng, 2008).

1.2 Molecular electronics

Molecular electronics is the interdisciplinary branch of nanotechnology which is meant for integrating molecules in nanostructures in order to form molecular electronics devices. Nanogaps are the fundamental building block in molecular electronics. This field of research is not mature enough today to take over where the silicon based semiconductor process technology ends. Today, molecular electronics is more focused on the fundamental research involving electron transport through molecules as well as electron transfer within or between them. The functional devices based on molecules published today are mostly considered as “prototypes” for demonstration of proof-of-concepts. In general, molecular structures have some major advantages (Heath, 2003):

- **Size.** The size scale of molecules is typically between 1 and 100 nm. This permits functional nanostructures with accompanying advantages in cost and power dissipation.
- **Assembly and recognition.** Specific intermolecular interactions can facilitate nanoscale self-assembly. Molecular recognition can be used to modify electronic behavior, providing switching and sensing capabilities on the single-molecule scale.
- **Synthetic tailorability.** By choice of composition and geometry, one can extensively vary a molecule’s transport, binding, optical, and
The properties of the molecules can be evaluated by different means. The most common characterization technique of a molecule in a nanogap is a current-voltage (I-V) measurement. From such measurement it is seen whether it has an ohmic, non-linear, a diode or switching behavior. Current fluctuations in the I-V curve can e.g. be caused by the mobility of the anchoring groups to the electrodes or by conformational changes inside the molecule. The I-V data can be plotted in different ways in order to obtain different information. If the data is plotted in a Fowler-Nordheim plot (\(\ln(I/V^2)\) vs. 1/V), the shape of it can reveal the transition between direct tunneling and Fowler-Nordheim tunneling (i.e. field emission) (Beebe, 2008). Inelastic Electron Tunneling Spectroscopy (IETS) is an important tool for identification of molecular species in molecular junctions. The IETS spectra can be recorded by applying a small (~mV) AC voltage, added to a DC bias, across the junction. The acquired spectra carry information about specific molecular vibrations and by comparing to other measurement techniques (e.g. Infra-red and Raman spectroscopy) as well as to theoretical calculations, each peak in the IETS spectra can be attributed to vibrational modes associated with molecules (Galperin, 2008; Song, 2009). There are many other measureable properties and phenomena of molecular junctions and several are mentioned in a recently published review article about charge transport through molecular switches (Molen, 2010). Most of the molecular signatures are seen in the I-V curves at low temperatures and preferably under vacuum conditions. However, in order to take the next step into the development towards a possible device application based on molecules, the molecular response should be investigated under ambient conditions. For this purpose, the electrical characterization of the molecular systems, presented in this thesis, was done under ambient conditions.

Most devices coming from the field of molecular electronics today have not reached the commercial stage yet, but there is a huge potential in e.g. memory storage capacity in molecular electronics devices. One recent work shows the fabrication of a molecular electronic memory circuit patterned at a density of \(10^{11}\) bits/cm\(^2\) which is expected to be the standard for memory devices in 2020 (Green, 2007).

1.3 Mind the gap

This brings me to the words stated on the cover page of this thesis: *Mind the gap!* It is not meant that we should only mind or consider the ‘macroworld’ that we live in or the ‘nano-world’ which we are trying to reach and benefit from. We should ALSO mind the intermediate gap between these dimen-
sions and hopefully control the many interfaces that are created on the way of joining them together.

The thesis is organized in the following way. Chapter 2 presents the motivations and aims of the thesis. Chapter 3 presents the different micro- and nanostructuring techniques as well as the nanomanipulation technique that has been utilized throughout this work. The structuring techniques have been used to fabricate a nanocontact platform suitable for electrical characterization of nanoobjects and molecular systems. The fabrication process of a platform is described in Chapter 4 with a detailed process scheme presented in Appendix I. In Chapter 5, the results from electrical characterization of nanoparticles, carbon nanosheets, nanotetrapods and molecular systems including nanoparticles are presented. A novel synthetic route to protect and deprotect molecules upon request is also presented in the chapter. Important limitations and considerations of low current measurements using a nanocontact platform are presented and discussed. Chapter 6 concludes the main results of the thesis and gives an outlook.

In Paper I, the development and the fabrication process of the nanocontact platform is presented. A proof-of-concept is also shown by doing trapping and electrical characterization of gold nanoparticles. Paper II involves the systematic assessment of the nanocontact platform as an applied tool to measure different molecular systems and to investigate their response in this platform. In Paper III, important limitations and considerations about surface cleaning and low current measurements are shown and discussed. In Paper IV the nanocontact platform is used to investigate the photoconduction properties of CdTe nanotetrapods. The electrical characteristics were compared under both white light illumination as well as under no illumination. In Paper V, manipulation, contacting and electrical characterization of functionalized and non-functionalized carbon nanosheets, inside the FIB/SEM, is shown. Paper VI describes the technical aspects of the FIB/SEM as a manipulation and contacting tool for performing reproducible electrical measurements in situ. Paper VII shows the development of a novel synthetic route to produce alkanedithiol coated gold nanoparticles protected by triphenylmethyl groups. These groups can be split off by acid treatment providing a controlled way of achieving chemical linkage between the trapped nanoparticles and the nanoelectrodes. This provides major improvements in the stability and reproducibility of the electrical characterization of molecular gold nanoparticle systems.
2. Motivations and aims of the thesis

The general aim with this thesis is to manipulate, electrically contact and characterize micro- and nanoscopic objects. The motivation for this study is to increase the knowledge about the electrical properties of nanoobjects and molecular systems and to understand their conduction properties.

The entities which have been investigated are nanoparticles, carbon nanosheets, nanotetrapods and molecular systems. In order to fulfill this aim, two strategies have been used. The first strategy was to combine different cleanroom based techniques and instruments to develop and apply a nanocontact platform for trapping and electrical characterization of nanoparticles, nanotetrapods and molecular systems. The second strategy was to develop an in situ manipulation and electrical characterization setup for functionalized and non-functionalized carbon nanosheets.

More specifically, the nanocontact platform was developed by using different micro- and nanostructuring techniques. Their advantages and disadvantages were considered so that optimum yield and high quality (small enough electrode spacings) was obtained of the fabricated structures. The platform proved to work as a tool for trapping of down to single nanoparticles and for forming molecular systems with nanoparticles. The charge transport properties through the junctions and the trapped entities were investigated by electrical characterization. The in situ manipulation setup inside the FIB/SEM was used to view carbon nanosheets ‘live’ during a precise contacting procedure prior to the electrical characterization of them. The setup enabled data acquisition of several samples in order to obtain good statistics.
3. Nanostructuring, manipulation and characterization techniques

This chapter summarizes the main techniques used in this thesis to fabricate and to characterize nanostructures. The main possibilities, advantages and disadvantages of the techniques are presented. The techniques are FIB microscopy, EBL and photolithography, resistive and electron beam evaporation, scanning and transmission electron microscopy (TEM) and electrical characterization. They are in most cases cleanroom based techniques and especially the electron microscopes are even placed on a concrete fundament fixed deep down into the bedrock and physically decoupled from the surrounding buildings. This provides a very stable environment for materials analysis down to the atomic scale.

3.1 The Focused Ion Beam microscope

Historically, the main applications for the FIB included quality control, wafer repair, modifications of photolithography masks and microelectronic failure analysis in the semiconductor industry (Wirth, 2009; Amano, 2009). Later on, the technique has also been used in research for prototyping and nanostructuring of all sorts of materials. The advantages of the FIB technique include high resolution of micromachined features, maskless processing, rapid prototyping and inherent flexibility to adapt to various materials and geometries (Zhang, 2009; Volkert, 2007; Wilhelmi, 2008). The main drawback of the technique is that it is relatively slow due to the single ion beam and not intended for e.g. large scale production of patterns. Another extensively used application is TEM sample preparation because of the site-specific advantage this technique provides (Giannuzzi, 1998).

The microscope used in this thesis is a FEI Strata DB235 FIB/SEM equipped with a field emission gun (FEG), see Figure 3.1. It consists of an electron beam and an ion beam. The electron beam column is vertically oriented and the electron energies can be varied between 0.2 and 30 keV. This beam can be used for acquiring high resolution scanning electron images, electron beam induced deposition (EBID) and for acquiring information about the chemical composition of the sample together with the Energy Dispersive X-ray Spectroscopy (EDS) detector. The microscope can also be
equipped with additional features like e.g. enhanced removal of carbon based materials (such as diamond and polymers), metals or silicon based materials as well as detectors for obtaining 3D images of grains and their orientations inside a material.

Figure 3.1. Photograph of the FEI Strata DB235 FIB/SEM located at the Ångström laboratory, used in this thesis.

The ion beam column is tilted to an angle of 52° with respect to the electron column as shown schematically in Figure 3.2. It consists of positively charged Gallium ions accelerated to energies between 5 and 30 keV where 30 keV ions have been used in this work. The beam can be used to generate secondary electrons and ions which can be used to form images. Due to the larger mass and size of the ions as compared to electrons, they can be used to remove material from the sample by sputtering. The geometry of the two beams allows for modifications of the sample with the ion beam while imaging with the electron beam.
Figure 3.2. Schematic image of the geometry of the electron- and ion beam columns. The sample should be placed at a working distance of 5 mm from the objective lens of the electron column.

Figure 3.3 shows a photograph taken from inside the FIB chamber where the sample should be positioned in the coincidence point of the two beams, which is placed 5 mm from the electron column and 19.5 mm from the ion column. The vacuum chamber is large as compared to typical SEMs but still the space is limited due to all the accessories (detectors, gas injection systems and a manipulator) that the instrument can hold. A 4” silicon wafer fits also inside and is allowed to be tilted to 52° with respect to the electron beam. The FIB/SEM used in this thesis is equipped with a secondary electron detector (SED), a through-the-lens detector (TLD), a continuous dynode electron multiplier (CDM) detector and an EDS detector. The SED is the most common detector used for observing the sample at low magnifications. The TLD is commonly used in ultra high resolution (UHR) mode where an immersion lens with a small working distance applies a magnetic field around the sample. Secondary electrons are trapped in this field and can only move freely in a vertical direction but not horizontally. A positive bias on the TLD will attract slow electrons inside the lens so that they can be detected.

The CDM detector can detect both secondary ions (CDM-I) and secondary electrons (CDM-E). CDM-I is especially useful for acquiring images of the different grains in a polycrystalline sample due to the fact that differently oriented grains gives rise to different contrasts in the image. If a grain is
oriented in a way that the atomic columns form long straight paths for the ions to travel, less may come out and become detected. This phenomenon is called channeling. The EDS detector will detect the x-rays produced in the sample upon electron irradiation and they have specific energies depending on which element that they were generated in.

The ions are emitted from a liquid metal ion source (LMIS), see Figure 3.4, consisting of a tungsten filament (tip radius of ~2-5 μm) with a reservoir close to it filled with Gallium. When the filament is heated, the gallium becomes liquid and wets the tungsten surface. An extractor voltage of typically 12 kV is applied in order to extract the ions from the tip. The extractor voltage is typically held at a constant value whereas a suppressor voltage (between -2150 and +2150 V) is used to generate emission current from the LMIS. The emission current is typically held constant at 2.2 μA for the Stra-ta DB235. The source is generally operated at low emission currents (~1-3 μA) to reduce the energy spread of the beam and to yield a stable beam. At low emission current, the beam may consist of singly or doubly charged monomer ions and neutral atoms. As the current increases, the probability of forming dimers, trimers, charged clusters and charged droplets increases (Giannuzzi, 2005).

By reducing the suppressor voltage, the emission current can be decreased to e.g. 1 μA resulting in a smaller ion beam spot. This is useful for making...
high resolution structuring down to about 10 nm (see Chapter 5 for more information). Though, a too low emission current (<1 μA) will yield in an unstable beam where the emission stops with irregular intervals.

Figure 3.4. Upper part: schematic image of a Liquid-Metal-Ion-Source (LMIS). Lower part: A commercial LMIS (courtesy FEI company). Adapted from (Giannuzzi, 2005).

The experimental work in this thesis is mainly focused on the use of the FIB instrument as a tool for creating nanogaps and for manipulating as well as performing electrical characterization of nanoobjects.
3.1.1 In situ manipulation in the FIB

The FIB is equipped with an Omniprobe™ manipulation setup with an exchangeable tungsten probe needle at the end. The needle can be maneuvered in x, y and z as well as rotated (manually). It is typically used for lifting out lamellae, which are cut out from a sample by using the ion beam, and transferring them to a sample holder for analysis in the TEM. However, in Paper V and VI the probe needle and the sample stage are electrically connected to a source-meter so that a voltage can be applied to the tip and the current through the sample and the stage can be measured. Figure 3.5 shows the probe needle in contact with a single carbon nanosheet, studied in Paper V and VI. The precision of the positioning of the tip is in the order of 50-100 nm. Mechanical vibrations are visible on the probe needle and are transferred to the carbon nanosheet as seen in the image.

![Figure 3.5. SEM image of the tungsten probe needle in contact with a single carbon nanosheet. Adapted from Paper VI.](image)

3.1.2 Sputtering and etching with the ion beam

The impact from a large and fast Gallium ion can cause severe damage to any material standing in its way. Ion milling is the result of physical sputtering of the sample and occurs as the result of a series of elastic collisions where momentum is transferred from the incident ions to the sample atoms. A surface atom may be ejected as a sputtered particle if it receives a compo-
component of kinetic energy that is sufficient to overcome the surface binding energy of the sample material (Giannuzzi, 2005).

A large ion beam current (20 nA) results in a beam with a diameter of hundreds of nm which makes it possible to produce high aspect ratio structures with several μm in depth during a short period of time (minutes). The drawback with using a large current is that the milling resolution is poor and that the large amount of removed material will be redeposited on the side walls of the fabricated structures. On the other hand fine polishing of the rough structures can be carried out by using a lower ion beam current. Fine polishing typically takes a long time (minutes to hours) but fine surface structures can be visualized. The smallest ion beam current (1 pA) results in a beam size of only a few nanometers in diameter and can also be used for structuring of e.g. nanopores in membranes. Figure 3.6 shows an SEM image of a 12 nm pore made in a silicon membrane by using the 1 pA ion beam current.

![Figure 3.6](image_url)

Figure 3.6. SEM image of a 12 nm (diameter) pore made in a silicon membrane by using an ion beam current of 1 pA.

Such FIB produced nanopores can be used in bio-applications for translocation of e.g. DNA molecules (Dekker, 2007).

Chemically enhanced sputtering (or etching) is a process where a gas precursor is injected into the vacuum chamber and adsorbed onto the sample surface followed by deposition of energy by the focused ion (or electron) beam. The ion beam interacts with the gas and produces radicals which will react with the sample surface and produce volatile products or products
which have higher sputtering rate than the native sample material. The removed material will be pumped away by the vacuum system.

Water vapor is typically used in combination with the ion beam to selectively etch carbon based materials such as diamond. Other gases are xenon difluoride (XeF₂) and iodine (I) for enhanced removal of silicon and metal based materials, respectively.

Redeposition is important to consider during the fabrication of high aspect ratio (i.e. tall and narrow) structures such as narrow trenches and nanogaps. The deeper the structures get, the more material will be redeposited on the side walls. The properties of the sample material and several milling parameters will affect the shape and the depth of the structures. The important milling parameters are the ion beam current, the time it spends in each point on the sample during milling (dwell time), how much (in percent) the beam is moved between each milling point. If the next point is moved one beam diameter away from the last point, the overlap is 0 %. If it is moved one beam radius away, the overlap is 50 %. Figure 3.7 shows the principle of the overlap as a function of the overlap as a function of the beam position during patterning with the ion beam or the electron beam. The circles represent the beam diameter. An overlap of e.g. -900 % means that the distance between two milled positions is nine beam diameters which is also demonstrated in Figure 3.7.

![Figure 3.7. Schematic image showing the principle of the overlap (in %) as a function of the beam separation. Adapted from (Kim, 2010).](image)

The sputtering of nanogaps or trenches is a complex process and fabrication of structures with large aspect ratios can cause difficulties. When the milling depth exceeds the trench width, the respective side walls are larger and material redeposition occurs to a greater extent. Then the bottom area decreases which will transform milled boxes into V-shaped trenches. Figure 3.8 shows
SEM images of 50 keV Ga\(^+\) FIB milled trenches of a) 50 nm and b) 300 nm nominal widths in silicon with ion doses of (starting from left) 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 nC/μm\(^2\) (Lugstein, 2003).

As seen in Figure 3.8, the trenches become narrower with increasing ion dose due to increased redeposition on the side walls. This observation together with the fact that the redeposition also causes changes in the shape of the bottom of the structures is very important to consider during the fabrication of nanostructures and devices. Simulations and theoretical modeling can help understand the different phenomena that are observed in the sputtering process and might also help solving some problems.

Concerning the fabrication of nanogaps in metal wires, the redeposition can be a positive effect if it will shrink the gap. The quality of each fabricated gap has to be evaluated by inspection with the electron beam as well as by performing electrical measurements to find out if there is residual material in the gap.
3.1.3 Deposition

The electron and the ion beam can be used in combination with precursor gases allowing for deposition of materials like e.g. platinum, tungsten and silicon dioxide (TEOS). The gases are delivered locally to the sample inside the vacuum chamber by separate gas injection systems (GIS). A GIS consists of a container, where the gas is stored outside the vacuum chamber, and a needle with an inner diameter of about 500 μm placed inside the chamber. There is one GIS for every precursor gas used in the chamber.

One of the most common gases in the FIB is a platinum containing organometallic precursor for deposition of platinum. The precursor will decompose under the beam and form a solid film on the sample surface. The metal can be deposited either by IBID or by EBID. IBID typically result in deposits with a larger content of platinum (compared to EBID) and therefore has lower resistivity. The drawback with IBID is that the ion beam can sputter the substrate if the material transport rate and the decomposition yield of the precursor is too low. The gas must also have sufficient sticking probability in order to stay on the surface in sufficient quantity. It must decompose faster than it is removed by the ion beam. The platinum deposits typically contain a lot of carbon (~70 at %), platinum (~20 at %) but also a significant amount of gallium (~10 at %) from the ion beam (Telari, 2002). Oxygen can also sometimes be found in the deposits. These relative concentrations depend on several parameters such as the ion beam current, the overlap, dwell time, precursor gas flux, substrate temperature etc. Figure 3.9 shows an SEM image of an inserted GIS needle above a truncated diamond sample tilted to 52°. The sample is a part of a diamond anvil cell and can be used for magnetoresistance, Hall resistivity and high pressure phase transition studies of different materials (Boye, 2004; Gavriliuk, 2009; Matsuoka, 2009).
Figure 3.9. An SEM image of an inserted GIS needle positioned approximately 100 μm from the diamond sample surface.

The GIS needle is placed approximately 100 μm above the sample surface. In Figure 3.10, platinum stripes have been deposited by using IBID on top of the diamond sample.

Isolating samples can cause charging problems during imaging with either electrons or ions. Charging is caused by an unbalance between the amount of incoming charges from the beam (ions or electrons) and the outgoing charges from the sample. If the sample is non-conductive, it can accumulate charges which give rise to an electric field around the sample. This will deflect the incoming (primary) electrons and is observed as if the sample would be moving on the screen. The charging problems can often be solved using different strategies. One strategy is to use a charge neutralizer. It consists of a tungsten filament which emits electrons onto the sample in order to balance the positive (Ga⁺ ions) and negative charges (electrons) and avoid charging problems. When the sample stays still on the viewing screen, the positive and the negative charges are balanced and deposition, sputtering or imaging can be performed.
Figure 3.10. SEM image of IBID of four Pt stripes on a diamond sample (tilted to 52°). The deposition is assisted by a charge neutralizer.

An example of EBID together with IBID is shown in Figure 3.11. Here, a mechanically exfoliated graphene flake is contacted by using EBID directly on the flake as seen in the inset. Graphene is strictly speaking a monolayer of carbon atoms but also a few layers can be considered as graphene. The advantage with EBID is that sputtering of the sample is avoided but on the other hand, the deposits have very low conductivity. IBID is used to extend the EBID platinum leads and to make large and more conductive leads and contact pads for contacting with e.g. probe needles in a probe station.
3.2 Electron beam lithography and photolithography

The EBL used in this thesis has been performed on an Environmental Scanning Electron Microscope (FEI ESEM xl30) together with the software Nanometer Pattern Generation System (NPGS) (Nabity, 2000). Figure 3.12 shows, schematically, the electron beam lithography starting with a) a clean substrate such as a silicon wafer, b) spin coating of an electron sensitive polymer (called resist) and baking on a hot plate in order to evaporate the solvent, c) exposure of the resist with the electron beam and d) development of the exposed area by using a chemical solution (called developer). There are two types of resists; positive and negative. The difference is that upon electron irradiation, the polymer chains will break into shorter, soluble,
chains for the positive resist whereas they will crosslink into non-soluble chains for the negative resist. The result is that an exposed positive resist will be removed by the developer whereas the exposed negative resist will remain on the substrate. The next step after the development of the EBL structures is either metallization by using e.g. evaporation (described in section 3.3) or etching.

![Figure 3.12. Schematic view of the electron beam lithography process with a) a substrate, b) spin coating of a (positive) resist, c) exposure with an electron beam (e-beam) and d) pattern development with a chemical solution.](image)

There are several different resists with a variety of molecular weights available for different purposes. Sometimes the resist should work as a mask for metallization and lift-off or as a mask during e.g. reactive ion etching of the substrate.

Poly(methyl methacrylate) (PMMA) is a common positive resist used for high resolution patterning (Ressier, 2007). At low exposure doses the polymer chains will break into shorter chains which are soluble in the commonly used developer methyl isobutyl ketone (MIBK). At higher exposure doses, the chains will cross-link and become insoluble in MIBK and results in a transformation of the resist from a positive to a negative character. PMMA has a poor resistance towards ion etching and therefore other resists are preferred in such cases. ZEP is also a high resolution positive resist, like PMMA, but with high ion etching resistance because of the low ion milling rate (0.84-0.96 Å/s) (Yi, 2007). Hydrogen silsesquioxane (HSQ) is an inorganic resist for high resolution purposes with the advantage that very thin (~10 nm) layers can be spun onto Si wafers. With thin resist layers, high resolution patterns can be obtained and one of the highest resolution structures fabricated is the patterning of 6 nm wide lines in a 20 nm layer of HSQ (Grigorescu, 2007).

Dedicated EBL systems are typically operated at electron energies of 50 or 100 keV. In general, high electron energies results in a small electron probe which can be used for high resolution imaging and patterning. Electrons with high energies are also less sensitive to lens aberrations in the elec-
tron microscope as compared to electrons with lower energies (~1-10 keV). When the electrons hit the resist on top of the sample, they will interact both elastically (producing forward scattered electrons causing beam broadening) and inelastically (producing secondary electrons). When the electrons travel through the resist and hit the substrate they will also produce backscattered electrons from a depth of several μm into the substrate. The forward and the backscattered electrons will contribute to the resist exposure outside the scanned area. This is called the proximity effect and will degrade the pattern quality.

Though, even at very low electron energies (1-5 keV), lines as narrow as 30 nm have been fabricated (Houli, 1993). Figure 3.13 shows three 70-100 nm wide lines made by using EBL after chromium and gold deposition and after stripping off the residual PMMA with acetone (called lift-off).

![Figure 3.13. 70-100 nm wide and ~100 nm thick metal (Au/Cr) stripes fabricated by using EBL, evaporation and lift-off.](image)

The EBL process used in Paper I and III involves spin coating of PMMA 495k A4. In Paper II, IV and VII the discovery of the possibility of spin coating double layer resist had been made. The double layer resist consist of a bottom layer of PMMA 495k A4 (molecular weight 495000 with 4% solid content in anisole), spun directly on a SiO₂/Si substrate, and a top layer of PMMA 950k A4 (molecular weight 950000 with 4% solid content in anisole). The resist with the larger molecular weight require higher dose in order to become fully exposed compared to the resist with lower molecular weight. The reason why this procedure is used in this thesis is that it will result in an undercut structure which facilitates the metal deposition and lift-off processes. Figure 3.14 shows a SEM image of a cross section of a sample after the EBL process where PMMA 950k A4 is used as a top layer and
PMMA 495k A4 as a bottom layer. The top layer is sticking out over the bottom layer creating the undercut structure.

Figure 3.14. SEM image of a cross sectional pattern after the EBL and development process of double layer resist. The top layer is PMMA 950k A4, the bottom layer is PMMA 495k A4 and an undercut of the PMMA 495k A4 is visible. The sample is tilted to 30.4°.

The resolution which can be achieved with electron beam lithography is dependent on several things like the size and the energy of the electron beam, the type of resist, its thickness and the type of substrate. Even the development process will influence the shape of the final pattern as well as its resolution. Structures with sizes down to sub-5 nm have been made with electron beam lithography (Arjandi, 2009).

In contrast to EBL, photolithography is a fast and parallel cleanroom based standard technique to pattern wafers down to a resolution of about 1 μm (in this case). In photolithography, a light sensitive polymer, called photo resist, is used in the same way as for EBL. Instead of electrons, photons from a UV lamp are used for the exposure of the resist. The spin coated sample is placed in a mask aligner underneath a photomask consisting of patterned chromium on a glass substrate. The open areas in the chromium will transmit the UV light coming from a lamp above the mask during the exposure. The light will be absorbed (or at least not transmitted) by the chromium on the glass, protecting the photo resist from being exposed. The pattern of the chromium mask will be transferred to the resist on the sample.
3.3 Resistive and electron beam evaporation

The metallization of the developed patterns produced by EBL or photolithography is done by using either resistive or electron beam (e-beam) evaporation. In resistive evaporation, the deposition material is put in tungsten boats which are clamped between two electrodes inside the vacuum chamber of the evaporator. During the evaporation, a large current (up to 60-70 A) is fed through the tungsten boat which will become so hot that the metal inside it will first melt and then start to evaporate.

In e-beam evaporation, a tungsten filament is heated by a current until it starts to emit electrons. These electrons are focused and the electron beam is bent by magnets down into a water-cooled crucible where the material which should be evaporated is placed. The electron beam will heat the material until it evaporates and the required current for this to happen varies with the material but is typically in the order of 100 mA. When the evaporated material hits the substrate, it condensates and forms a film. This works in the same way for both resistive and e-beam evaporation. The deposition will also occur on the chamber walls and everywhere else which is in the line-of-sight from the evaporation source. The evaporation process is conducted at room temperature but the chamber might become warm during the deposition. The substrate can also be heated by using an infrared lamp in order to obtain more smooth films.

The pressure in the chamber goes down to ~5*10^{-7} mbar after overnight pumping. The exact vacuum level depends on the cleanliness of the chamber as well as of the materials inside it. The deposition rate and total thickness of the deposition is measured by using a quartz crystal microbalance (QCM). A QCM is a very common tool to use in e.g. evaporators to monitor the deposition and it works in the following way. The quartz crystal is oscillating at a resonance frequency which decreases when the evaporated material is deposited onto it. The frequency change can be correlated with the deposited film thickness. The QCM has a measurement precision in the sub-nm range but the total film thickness control depends on the reproducibility of the physical placement of the substrate and the tungsten boat. A small geometrical change will have large influence on the deposited film thickness. In this thesis Cr is used as an adhesion layer for Au on top of substrates with SiO₂ grown on Si. The metal films are polycrystalline with grain sizes in the range of 50-100 nm. The grain size can play a role depending on the application. In this work, the grain size of the evaporated gold may have some effects on the
3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is used to obtain surface structure information with a resolution down to the nm range. Depending on the microscope and the detection parameters, the information about the sample can typically come from a depth ranging between some nm and a few μm.

The structural characterization in this thesis has mainly been done by using a LEO 1550 (Zeiss) with a FEG, specified to a resolution of 1 nm at 20 keV and with a working distance of 2 mm. The electron energies can be varied between 0.2 to 30 keV and the microscope is equipped with a secondary electron detector (SED), an in-lens detector, a quadrant backscatter detector (QBSD), an energy dispersive x-ray spectroscopy (EDS) detector and an electron backscatter diffraction (EBSD) detector. The strength with the LEO 1550 is the performance of the in-lens detector which enables a high efficiency in the collection of secondary electrons thanks to the short obtainable working distance and the properties of the beam booster™. The beam booster is a part of the electron column which provides electrons with the constant energy of 8 keV. The benefit with this constant value is that these fast electrons will not interact strongly with each other and produce aberrations as compared to slow electrons. This value of 8 keV cannot be changed by the user. Just before the exit from the electron column and into the chamber, the electrons are either accelerated or decelerated depending on which energy the user has chosen.

In this thesis, electrons with the energy of 15 keV have been used for imaging of the nanogaps fabricated in Paper I and described in Chapter 4. Large electron energies give rise to a small electron beam which enables high resolution imaging. However, this also increases the probability of decomposition of adsorbed hydrocarbons on the sample surface which will result in carbon contamination. An amorphous carbon film will be deposited under each scan with the electron beam. In Paper V and VI the electron beam of the FIB/SEM was operated at 5 keV and used for imaging carbon nanosheets. This energy provides a high enough resolution at the same time as the carbon contamination of the sample is low.

3.5 Transmission Electron Microscopy

The TEM work in this thesis (concerning Paper I) was done on a FEI Tecnai F30-ST 300 keV FEG instrument in order to evaluate the damage and the
influence of the ion beam on gold as well as on the substrate. Several nanogaps very fabricated in a Au/Cr wire. A thin (<100 nm) lamella was cut out and placed on a TEM sample holder by using the FIB and the Omniprobe™ manipulator (the function of the manipulator is described in Chapter 3). This is called in situ lift-out of the TEM sample (Langford, 2004). Another way is to prepare the thin lamella, cut it loose from the substrate and perform ex situ lift-out by using a sharp glass needle and an optical microscope with long working distance. Electrostatic forces will cause the sample to attach to the needle and then also detach from it when it is in contact with a carbon support grid for the TEM. The ex situ lift-out is described in (Langford, 2001).

Figure 3.15 shows a cross sectional bright field (BF) TEM image of several gaps cut in the Au/Cr wire. Pt has been deposited by using first EBID and then IBID in order to protect the structures from being sputtered during the ion beam thinning of the lamella. The thermally grown 1 μm SiO₂ on top of the Si substrate is also visible in the image.

![Figure 3.15. Bright field cross sectional TEM image of several cuts made in the Au/Cr wire by using the FIB.](image)

Figure 3.16 shows a BF TEM image of one of the gaps in Figure 3.15. The protective Pt, the Au, the Cr adhesion layer and the SiO₂ substrate is visible. The gap can be accurately measured and in this case it is 20 nm wide. The shape of the Au electrodes is clearly seen in this image and resembles the intensity profile of the ion beam. There are two notches (undercuts) visible at the two interfaces between the Au and the Cr in the gap (marked with arrows). These notches have most likely appeared during the sputtering with the ion beam since there is a large difference in sputtering yield between Au
and Cr (about 5-10 times larger for Au). The ion beam will start to sputter laterally in the Au/Cr interface before it sputters through the Cr.

![Figure 3.16. Bright field cross sectional TEM image of a single 20 nm gap. The different materials are marked in the image. The arrows show notches between the gold and the chromium layers. Adapted from Paper I and modified. Reproduced with permission of IOP Publishing Ltd.](image)

*Figure 3.16. Bright field cross sectional TEM image of a single 20 nm gap. The different materials are marked in the image. The arrows show notches between the gold and the chromium layers. Adapted from Paper I and modified. Reproduced with permission of IOP Publishing Ltd.*

*Figure 3.17 shows a high resolution TEM image of the interface between the left Au electrode and the protective Pt in the gap. Au lattice fringes are visible on the electrode surface (inset) proving that the ion milling has not destroyed the crystalline structure.*
3.6 Electrical characterization

The electrical characterization in Paper I-IV and VII has been performed by using a semiconductor parameter analyzer (Agilent B1500A), see Figure 3.18, in combination with a 4-point-probe station (Karl Süss) equipped with a light optical microscope, see Figure 3.20. The inset in the figure shows a close-up of the probe arms which can be manipulated in x, y and z. Tungsten probe needles are attached to the probe arms and can be placed on the sample with a precision of about 10-20 μm depending on the tip radius of the needles.

The probe station is placed inside a grounded metal (faraday) cage which is standing on top of a concrete table in order to reduce ambient noise and vibrations. The Agilent is equipped with two preamplifiers which are placed inside the metal cage in order to be as close to the sample as possible and to minimize electrical noise. The Agilent is specified to a current measurement resolution of 0.1 fA and is controlled with an EasyExpert™ software installed on the built-in computer. In Paper V-VI, a Keithley 6430 sub-femtoamp remote sourcemeter, see Figure 3.19, is used together with the FIB/SEM instrument (introduced in section 3.1). The Keithley has a speci-
fied current measurement resolution of 10 aA and was connected to the Omniprobe™ manipulator (presented in section 3.1.1) and the sample stage in the FIB/SEM. It is connected to a PC with the GPIB-USB card and used together with the free online software Labtracer™ from Keithley for data acquisition.

Figure 3.18. Photo of an Agilent B1500A semiconductor parameter analyzer.

Figure 3.19. Photograph of a Keithley 6430 sub-femtoamp remote source-meter. Adapted from www.keithley.com

Figure 3.20. Karl Süss probe station inside a metal shielding cage. The inset shows a close-up of the tungsten probe needles used to make connections to a sample.
The most common electrical measurements performed in this thesis (**Paper I-IV** and **VII**) are current-voltage (I-V) measurements. They are typically performed (with the Agilent) by starting at 0 V, ramping up the voltage to a desired value ‘+V’, ramping it down again, passing through 0 V and continuing to ‘-V’ and back to 0 V. This voltage scan procedure allows for measurements of possible hysteresis in the material system under study. The I-V measurements performed in **Paper V-VI** were made (by using the Keithley) from 0 V to ‘+V’ and from 0 to ‘-V’ due to the less possibilities of the software.
4. Fabrication of the nanocontact platform

The structuring techniques described in Chapter 3 have different advantages and disadvantages and can be combined together in an optimum way so that the quality and the yield of the structures are maximized. One of the aims of this thesis is (as stated earlier) to electrically contact and characterize nanoparticles and molecular systems. In order to achieve the physical connection between the measurement equipment and these objects or systems, contacts with electrodes in the same dimensions have to be manufactured. The nanocontact platform in this thesis consists of arrays of nanocontacts fabricated on top an insulating substrate.

In this chapter, a description of the fabrication process of a nanocontact platform is presented. Here, a nanocontact is defined as a metallic structure consisting of nanosized electrodes which are connected to micron sized pads accessible by e.g. probe needles or by wire bonding. The platform consists of several of these nanocontacts in order to provide good statistics from a large number of measurements. The main steps of the nanocontact platform fabrication processes are summarized in this chapter and a complete and detailed scheme, including risks and possible developments, is found in Appendix I.

The techniques electron beam- and photolithography combined with FIB milling are used to fabricate the nanocontacts. Electron beam lithography is a serial and slow process but can be used to fabricate structures in the nanometer range as compared to ‘normal’ photolithography. Photolithography is a fast, parallel and large scale process with resolution in the μm range. Focused ion beam milling is a serial and typically very slow process but can locally be very fast when used for making nanostructures which is demonstrated in this thesis.

The nanocontact platform fabrication process starts with thermal oxidation of a silicon wafer. Typically 1 μm of SiO₂ is grown. A double layer consisting of PMMA 495k A4 (bottom layer) and PMMA 950k A4 (top layer) is spin coated on the wafer and baked on a hot plate in order to evaporate the solvent. The wafer is then cracked by hand into smaller pieces (~20 by 20 mm²). The next step is one of the main steps and that is electron beam lithography.
4.1 Electron Beam Lithography

Gold nanoparticles are put in the corners of the sample (on top of the PMMA) in order to help focusing the electron beam. The desired patterns are drawn in a computer aided design (CAD) program, saved in a proper format and implemented in the patterning software Nanometer Pattern Generation System (NPGS) which is installed on an external computer and not on the microscope computer. Important parameters, such as the electron dose (in e.g. μC/cm² or nC/cm), the dwell time (in μs), the desired microscope magnification and the electron beam current (measured through the sample stage by an external source meter or picoammeter) are manually put in the NPGS software.

Typically 96 patterns are made over an area of 10 x 10 mm². Figure 4.1 (left part) shows a single pattern, ~130 μm long, which is 200 nm wide in the center and 5-10 μm wide otherwise. Figure 4.1 (right part) shows a schematic design of an entire sample with the 8 groups (as columns) with 12 contacts in each, resulting in a total number of 96 patterns.

The contacts are spaced by 200 μm vertically (within one group) and by ~2.5 mm horizontally (between groups). The reason for this design is that the contacts should not influence each other during the dielectrophoretic trapping of nanoparticles described in Chapter 5. Another reason is that the sample can be diced into four 5 mm by 5 mm sized pieces which will fit inside a chip holder which has 24 legs accessible with wire bonding, soldering or gluing. Figure 4.2 shows photographs of a chip holder with 24 legs.
(left part) where a 5 mm by 5 mm sample is fitted inside (right part) and accessed through e.g. wire bonding.

Figure 4.2. Photograph of a chip holder equipped with 24 legs (left part) and a square opening in the center where a sample containing 24 contacts is placed (right part). The legs are connected to the rectangles surrounding the sample and can be connected to the contacts by using e.g. wire bonding.

The reason for putting the sample in a chip holder is to obtain the possibility of doing low temperature experiments as well as in situ experiments inside e.g. the FIB/SEM. This possibility has not been explored in this thesis.

The EBL patterns are developed in 1:3 MIBK:IPA for 1 min and rinsed in pure IPA for 45 s. The developed patterns are checked in a light optical microscope (Olympus AX70) in order to get a brief look at the result. Figure 4.3 shows a light optical image of a single pattern after the development. Some test structures are also patterned in the vicinity of the main pattern which are used to monitor how small features that can be patterned and if they are reproducible over the whole sample.

Figure 4.3. Light optical microscope image of a nanocontact pattern after the EBL and development process.
SEM images can be taken of the developed patterns in order to obtain more detailed information about the pattern size and resist roughness. **Figure 4.4** shows an SEM image of the critical part of the pattern; the 100-200 nm wide, ~1 μm long, trench patterned in double layer resist (PMMA 950k A4 on top of PMMA 495k A4). There is no residual resist visible in the narrow trench demonstrating that the electron dose was sufficient and that the development process was successful.

**Figure 4.4.** SEM image of a developed nanocontact pattern after EBL (left) where the thinnest part of the pattern is magnified (right).

### 4.2 Metal deposition and lift-off

In this thesis, Au was chosen as a metal to deposit because of its excellent electrical properties as well as resistance towards oxidation. Another strong reason is that thiol terminated molecules (described in **Chapter 5**) will bind chemically to Au and provide a good (covalent) connection to it. Since gold is an inert material, it will not adhere very well to other materials such as SiO₂. In that case a thin (a few nm) adhesion layer of another metal should be used between the SiO₂ and the Au. Typical metals used as adhesion layers together with Au are Ti or Cr. Ti is well known as a strong gettering material which means that it reacts with many different materials and easily forms oxides and nitrides. These properties are good for adhesion materials but it also means that it absorbs lots of impurities which are not always desirable. Therefore Cr was used as adhesion layer in this thesis and it was deposited at a very low rate resulting in good control of the layer thickness.

2-3 nm of Cr (bottom layer) and 70-100 nm of Au (top layer) were deposited on the SiO₂ by using resistive evaporation. The base pressure in the vacuum chamber was typically in the 1-3*10⁻⁶ mbar range (or better) in order to give high quality films. After the deposition, the PMMA was dissolved causing the metal layer on top of it to peel off while the metal inside the patterns remained on the substrate. The PMMA was dissolved by soaking the sample in acetone for about 1 hour, then rinsing it in acetone, IPA...
and finally it was blow dried with nitrogen. Figure 4.4 shows a SEM image of the 100-200 nm wide Au/Cr wire in the center of the EBL pattern.

![SEM image of the center part of the EBL pattern after metal deposition and lift-off. The Au wire is ~130 nm wide.](image)

The roughness along the wire probably depends on a number of factors. The Au grains are typically 50-100 nm in size which affects the side wall roughness. The PMMA resist might form grains or clusters during the spin coating and baking step. The development of the exposed PMMA will be faster and easier in the grain boundaries resulting in some roughness. Though, this is a critical issue on patterns in the sub-10 nm size range, and therefore it is not a major issue in this case. The thickness of the deposited film might play a role on the roughness because if it is almost as thick as the resist layer, it might be partly connected to the metal on top of it. This will cause problems during the lift-off and may result in uneven edges with metal flakes sticking out from the structures.

The stability of the electron beam (and the beam blanker which switches the beam on and off) in the microscope also plays a role on the edge roughness of the pattern. There is a noticeable decrease in the quality of the SEM image when the cable to the beam blanker, coming from the external EBL software computer, is connected to the microscope. This is due to electrical noise which comes from the computer card where the beam blanker signal originates.
4.3 Fabrication of contact pads by using photolithography and evaporation

The fabricated Au/Cr structures have to be connected to large contact pads which can be contacted by either probe needles in a probe station or by wire bonding. In this case photolithography was used with an additional step of metal evaporation and lift-off in order to fabricate 200 μm by 100 μm pads with a thickness of a few hundred nanometers. The result after the photolithography step is shown in Figure 4.5. It shows a SEM image of a single nanocontact where the two large contact pads are connected by the smaller EBL structure.

*Figure 4.5. SEM image of a nanocontact after the photolithography, metal deposition and lift-off steps.*

*Figure 4.6 shows a SEM image of a 5 mm by 5 mm sample containing 24 nanocontacts which can be wire bonded, as shown in Figure 4.7, with gold wires to a chip holder shown in Figure 4.2 for in situ or low temperature experiments.*
Figure 4.6. SEM image of two groups, 24 nanocontacts, fabricated on a 5 by 5 mm chip.

Figure 4.7. SEM image of some nanocontacts wire bonded to a chip holder. The sample is tilted to 52°.

The in situ approach with wire bonded nanocontacts has not been a part of the scope of this thesis. All nanocontact experiments in Paper I-IV and VII have involved the use of probe needles in a probe station to contact the pads. Therefore, in the next processing step which is FIB milling, the starting point for this step is typically a non-wire-bonded sample as shown in Figure 4.6.
4.4 Focused Ion Beam milling

The final step in the fabrication process of the nanocontacts is the FIB milling. The lowest ion beam current of 1 pA is used to cut a gap in the EBL gold wire. With default microscope settings the ion beam emission current is 2.2 μA but by changing the suppressor voltage, an emission current of ~1.0 μA can be achieved. This results in a lower ion beam current (sub-pA), and therefore a smaller beam.

Prior to the milling of the gap, the appropriate milling time has to be found by cutting trenches, or lines, in the Au film with different milling times. A proper cut results in a gap which does not have any residual Au left in it. In order to evaluate the difference in ion beam probe size, test cuts were made by drawing a 1 μm long single line, using an overlap of 50 %, a dwell time of 1 μs and then varying the milling time between typically 1-2 s. The test lines were cut by using the two different emission current settings of 2.2 μA and 1.0 μA, respectively. Here, a milling time of 1.9 s was used and resulted in a width of the trenches of ~19 nm for the 2.2 μA emission current and ~13 nm for the 1.0 μA emission current. This is a reduction of about 30 % only due to the change in emission current. Figure 4.8 displays the result from the comparison of the different emission current settings.

Figure 4.8. SEM image of the two different sets of test lines, cut by using two different emission current ($I_e$) settings (2.2 μA and 1.0 μA, respectively). The upper lines ($I_e = 2.2 \mu A$) are ~19 nm wide and the lower lines ($I_e = 1.0 \mu A$) are ~13 nm wide.
The specified ion beam probe size at 1 pA beam current is ~7 nm with an emission current of 2.2 μA. If the 30 % reduction of the width of the trench is also valid for the beam probe size, the 1.0 μA emission current would correspond to a beam diameter of ~5 nm.

In Figure 4.9, a ~11 nm wide gap has been made by using the 1 pA ion beam current and the 1.0 μA emission current setting. The milling time was set to 1.2 s, the overlap was 50 % and the dwell time was 1 μs. Au nanoparticles are visible around the gap. Some came from the nanogap sputtering process itself and others from the metal deposition and lift-off step.

![Figure 4.9. SEM image of a ~11 nm nanogap cut by using the 1 pA ion beam current with 1.0 μA emission current. The milling time was 1.2 s. The small particles in the vicinity of the gap originated from the sputtering process. The larger particles in the lower part of the image come from the Au deposition and the lift-off step.](image)

In order to know for sure that the gaps are properly cut and that the electrodes are sufficiently isolated from each other, I-V measurements were performed by using the probe station and the Agilent source-meter presented in Chapter 3.
In Paper I, the I-V measurements of the nanogaps revealed extremely high empty-gap resistances (in the range of 100-1000 TΩ). A TEM sample was prepared of a few gaps and the TEM images revealed severe ion beam damage to the SiO₂ substrate. Despite this observed damage, the implanted Ga⁺ ions do not form conductive paths between the electrodes.

4.5 Fabrication of smaller gaps

4.5.1 Electrodeposition of gold

Electrical characterization of molecules puts challenging demands on the electrodes to which they are connected. The gap spacing must have a size corresponding to the length of the molecules in order for it to have the possibility to be bridged by them.

One way of achieving smaller gaps is presented here and involves electrochemistry. A galvanostat was used in combination with the probe station (presented in Chapter 3, Section 3.6) in order to perform electrodeposition of Au on FIB cut gaps. The reason for starting with FIB cut gaps and not with μm sized gaps defined by using e.g. photolithography is that the FIB cut gap is better defined with well-confined electrodes. Figure 4.10 shows schematically the experimental setup where two tungsten probe needles are connected to each one of the two contact pads of a nanocontact. They are connected together as the working electrode (WE) whereas two other probe needles are connected as counter electrode (CE) and reference electrode (RE), respectively, to a galvanostat Autolab/GPES instrument (ECO Chemie, The Netherlands). Au wires were wrapped around the tungsten probe needles functioning as CE and RE in order not to influence the reactions that are taking place during the electrodeposition process.
Figure 4.10. Schematic image of the electrodeposition setup.
The process starts by depositing a drop of Au tetrachloride solution on top of a nanocontact including the four electrodes. The CE and the RE were placed in the vicinity of the nanocontact but not in direct contact with it. By sourcing a negative constant current from the CE and to the WE, the gold tetrachloride ions were reduced to solid Au at the WE surface. If the current is reversed, the opposite reaction will take place which is dissolution of the Au electrode (WE), which is increasing the gap instead of decreasing it. The parameters that can be controlled during the process are the current, the size of the electrode surfaces (inside the gold tetrachloride solution), the deposition time and the concentration of the solution. All these parameters will influence the size and the shape of the final gap.

In Figure 4.11, the result of a successful deposition experiment is shown where a nanogap has been decreased from a width of ~20 nm down to ~5 nm. The applied current was 0.5 μA, the deposition time was 30 s and the concentration of the gold chloride solution was 0.2 mM. A low applied current will cause smooth deposition and will allow for the ions in the solution to diffuse but the deposition will take longer time as compared to a high current which will result in a rough surface as in the case for a short time. This gap has not been utilized in this thesis but the potential of this technique is demonstrated here.
4.5.2 Electromigration and Joule heating

Another way of producing small nanogaps is by forcing a current through a gold nanowire until it breaks (Hadeed, 2007). This can be done in a sophisticated way by e.g. using current feedback loops to stop the current through the wire due to e.g. certain changes in conduction. The main idea with such experiment is to cause electromigration and/or joule heating.

*Figure 4.12* shows an I-V curve of such experiment where a voltage was slowly ramped up (1.7 mV/s) resulting in a linear increase of the current through the gold wire. After 2 min 50 s the current reached a maximum (~6.6 mA) and rapidly dropped down to ~0.5 mA. The experiment was stopped manually about 6 s later and the gold wire was imaged in the SEM.
Figure 4.12. The graph shows an electromigration/joule heating experiment where an applied voltage is ramped up while the current through the gold nanowire is measured. After 2 min and 50 s the current drops rapidly and the experiment is manually stopped.

Figure 4.13 shows a SEM image of the broken gold wire where a 2-3 nm gap has been formed. The formation of the gap depends on a number of parameters like e.g. the wire material, the geometry of the wire and the speed of which the voltage is ramped up. All these things results in a relatively low reproducibility. Though, it is possible to use a more sophisticated experimental setup with a feedback loop so that the applied voltage can be accurately reduced when the wire shows a tendency to break. Due to the high mobility of Au, such small gaps might not be stable for very long. Nanogaps with polycrystalline gold electrodes fabricated inside a TEM have shown to increase by several nanometers during the first 30 minutes after the creation. For single crystalline Au and polycrystalline Pt, the widening was between negligible and 1 nm under similar conditions (Zandbergen, 2005).
Figure 4.13. SEM image of a 2-3 nm gap fabricated by forcing a current through the gold nanowire until it brakes.

An I-V measurement between -1 to 1 V of the created gap was made by using the Agilent (presented in Chapter 3) and showed a resistance in the order of $1000 \text{ T}\Omega$ proving that there were no residual metal bridging the gap.

Figure 4.14. I-V measurement of the 2-3 nm wide gap in Figure 4.13. The slope of the curve corresponds to a resistance in the order of $1000 \text{ T}\Omega$.

Such gaps created by either electrodeposition or electromigration/joule heating have not been utilized in this thesis but the experiments shows the possibilities and the varieties of ways to fabricate nanogaps.
5. Electrical characterization of Nanogaps, Molecules, Molecular systems, Carbon Nanosheets and Nanotetrapods

The nanogaps fabricated in Chapter 4 were electrically characterized in order to estimate their level of isolation. This is important to do prior to any characterization of nanoobjects that have unknown conduction characteristics. If the empty nanogaps are not sufficiently insulating, there will be significant leakage current influencing the measurements of the trapped entities in the gap. The I-V measurements of the empty nanogaps revealed extremely high resistances, more than 1000 TΩ, proving excellent isolation (see Paper I for more details).

5.1 Dielectrophoretic trapping

Dielectrophoresis is a term used to describe the motion induced by a non-uniform electric field on polarized, but uncharged, particles (Pohl, 1978; Pethig, 1992). The technique can be used to trap carbon nanotubes, nanowires, molecules and nanoparticles in between electrodes by applying an AC voltage for a certain time (Boote, 2005; Makaram, 2007; Zhang, 2009; Kumar, 2009). There are several parameters affecting the trapping procedure such as amplitude and frequency of the applied voltage as well as the trapping time. The objects must be dispersed in a solution and the concentration of the objects of interest in this solution also affects the trapping probability.

In this thesis, the contact pads of the nanoelectrodes are electrically connected to a function generator (Tektronix AFG 3102) by using tungsten probe needles in a probe station (presented in Chapter 3, section 3.6). A 6 μl drop of aqueous-suspended gold nanoparticles (EM.GC30, BBInternational, Cardiff, UK) were placed on the nanocontact and a voltage of 1-2 V_{peak-peak} with a frequency of 1 MHz was applied for 30-60 s. Two molecular-metal junctions were created for every trapped nanoparticle in the gap. This must be considered when the electrical response of this system is evaluated and compared to other experiments. After the trapping, the sample was rinsed with deionized water and blow dried with N₂ gas. All is performed in ambient conditions.
In **Paper I**, this technique was successfully used to trap gold nanoparticles in 25-30 nm gaps. This was done as a proof-of-concept to show that the trapping worked and that electrical characterization of such nanoobjects could be done by using this platform. The ultimate goal with dielectrophoretic trapping is to trap one single object in a gap. Finding the right parameters which yields in trapping of e.g. a single nanoparticle is very hard. But it happens from time to time, see *Figure 5.1*.

![SEM image of a single 30 nm gold nanoparticle trapped in a gap by using dielectrophoresis.](image)

**Figure 5.1.** SEM image of a single 30 nm gold nanoparticle trapped in a gap by using dielectrophoresis.

### 5.2 Characterization of molecules and molecular systems with gold nanoparticles

When it comes to introducing molecules in the nanogaps, there are a few different pathways to choose from. If the gaps are of comparable size as to the molecules, direct trapping can be performed if the molecules have linker groups such as thiols (-SH) or amines (-NH) like in the case with the thiolated DNA molecules presented in this thesis (**Paper III**). Another way is to coat the nanoelectrodes with a self-assembled-monolayer (SAM) of molecules. In this work the non-conducting molecule 1,8-octanethiol (OT) and the conducting molecule 4,4’-biphenyldithiol (BPDT) are used (**Paper II**).
5.2.1 double-stranded DNA

The nanoelectrodes were prepared for the experiments by cleaning for 10 min in a UV-ozone photoreactor (PR-100, UVP Inc.) to remove organic contaminants. Immediately after this treatment, the sample was placed in ethanol to remove gold oxide on the surface of the electrodes (Ron, 1998). 30 nm thiolated double-stranded DNA (ds-DNA) molecules were trapped in the nanogaps by using dielectrophoresis. A sinusoidal AC voltage of 1 V_{peak-peak} at 1 MHz was applied for 20 s. After the trapping, the sample was rinsed with deionized water for 30 s and blown dry with N₂. SEM was used to image the trapped DNA strands. Figure 5.2 shows an SEM image of what could be a trapped 30 nm ds-DNA with the corresponding I-V measurement before and after the trapping. The upper left inset shows the nanogap before trapping and the lower left inset shows a magnification of the trapped DNA strand. The resistance was measured to 115 TΩ before the trapping and 4 TΩ after the trapping, indicating a successful trapping event.

![SEM image of a trapped ds-DNA](image)

*Figure 5.2. SEM image of what could be a trapped ds-DNA. I-V curves before and after the trapping is shown in the right inset. The upper left inset shows the gap before the trapping and the lower left inset shows a magnification of the trapped strand. Adapted from Paper III.*

The difference in resistance of more than one order of magnitude between the empty gap and the same gap with a trapped ds-DNA shows that the nanogap platform can be used to characterize low conductive molecules. In this study it was also found that careful consideration must be given to the experimental setup and environmental conditions when making low current measurements of molecular systems.
5.2.2 1,8-Octanethiol

The nanoelectrodes were cleaned in a UV-ozone photoreactor (PR-100, UVP Inc) for 30 min and placed in ethanol as mentioned above. The OT SAM was formed by soaking the sample in 0.1 M of OT solution for about 24 h and after this functionalization it was blow dried with N₂ gas. Trapping of gold nanoparticles was done as described above and subsequent I-V measurements were performed in order to investigate the trapping success. In Figure 5.3, three subsequent I-V measurements of an OT coated nanogap are shown. The inset shows a SEM image of two trapped gold nanoparticles in the gap, acquired after the I-V measurements. The I-V response is primarily linear with a resistance of about 35 GΩ in the low bias (between -0.5 and +0.5 V) regime where the current fluctuations are small.

![I-V plot showing three consecutive measurements of the nanogap shown in the SEM inset. The scale bar is 100 nm. Adapted from Paper II.](image)

The measured current levels of OT are not expected to be high as the molecules are chemisorbed only on the electrodes and not to the trapped particles. Conduction through saturated chain molecules like OT occurs via coherent nonresonant tunneling, which has been shown by several studies that demonstrate an exponential dependence of conduction on chain length (Akkerman, 2008) and even the temperature independence of the conduction (Wang, 2003). Several trapping attempts were performed on the OT coated nanogaps and the resistances extracted from the linear region of the I-V measurements were evaluated in histograms, see Figure 5.4, in order to determine the average resistance.
In Figure 5.4, the majority of the resistance values are between 1 GΩ and 10 TΩ. The large dispersion of these values may be due to the variation in the number of trapped gold nanoparticles in the gaps, insufficient coverage of the SAM on the electrode surfaces as well as variation in the contact surface geometry between the nanoparticles and the electrodes.

5.2.3 4,4’-Biphenyldithiol

BPDT was chosen as a molecule because of its good conduction properties and for the fact that it has two thiols, one in each end of the molecule. The BPDT SAMs were prepared inside a glove-box filled with Argon in order to avoid oxidation of the thiols. The sample was placed in a 1 mM solution of BPDT (95% pure, Sigma-Aldrich) and ethanol (99.5% pure) for 48 hours.

Figure 5.5 shows an I-V measurement of the trapped gold nanoparticle, seen in the gap in the SEM inset. The voltage was scanned between -2 to 2 V and showed a linear response in the low bias region (roughly -0.5<V<0.5 V) but becomes non-linear at higher voltages. Higher conduction is expected through BPDT than OT due to the π-conjugation of the molecule which results in a degree of localization of electrons along the molecule. A small hysteresis is also observed in the measurement. At larger applied voltages, it is possible to align the Fermi level of the electrodes with an energy level of the molecule giving rise to a greatly increased conduction. This is typically only observed under low temperature and vacuum conditions.
Figure 5.5. I-V measurement of a trapped gold nanoparticle in the BPDT coated nanogap shown in the SEM inset. The scale bar is 100 nm.

Figure 5.6 shows two consecutive I-V curves of the three trapped gold nanoparticles visible in the gap in the SEM inset. The blue curve is recorded first, than the red. A current compliance (limitation) was set to 10 nA in order to prevent excessive current levels. The voltages are scanned from 0 V to 3 V, from 3 V to 0 V, then from 0 V to -3 V and back to 0. Both curves show large hysteresis and switching properties of conductance at both forward and reversed voltage bias.

Figure 5.6. Two consecutive I-V measurements of the trapped gold nanoparticles in the BPDT coated nanogap shown in the SEM inset. The scale bar is 100 nm.
The reproducibility of the electrical response from the BPDT devices was very low and this suggests that the molecules were not chemisorbed on the gold nanoparticles after trapping. A poor SAM formation on the electrodes is also likely to cause irreproducible results, experienced by others concerning BPDT and other phenylene based molecules (Lee, 2003). Although the BPDT SAMs were prepared in an Ar atmosphere, they were subsequently subjected to ambient conditions and the aqueous gold nanoparticle solution, which exposed the molecules to oxygen and thereby increased the likelihood of creating disulfide bonds.

5.2.4 Protection and deprotection chemistry of alkanedithiol coated gold nanoparticles

In molecular electronics applications, the stability of functionalized molecules is of great importance for the reproducibility of the electrical measurements. Certain anchoring groups, such as thiols, oxidize rapidly under ambient conditions and form disulfides. When this happens the likelihood of bridging a nanogap decreases and the result from any electrical characterization performed on such setup might be irreproducible. Therefore a desirable way to increase the control over the connection between the molecules and the electrodes in a nanogap is to protect the groups from binding to each other and from ambient conditions involving oxygen and moisture. When the molecule is in the vicinity of an electrode to which it should bind, the protective group is split off so that the molecule chemisorbs on the electrode.

Recently, a new route has been developed involving synthesis of 5-10 nm gold nanoparticles fully covered by alkanedithiols. The free thiol groups sticking out from the gold nanoparticles were protected by triphenylmethyl (trityl) groups which can be split off by acid treatment after the dielectrophoretic trapping. Figure 5.7 shows a schematic of a gold nanoparticle partly covered by trityl protected and deprotected alkanedithiols. Further details are found in Paper VII.
Octanethiol coated gold nanoparticles were trapped in nanogaps by using dielectrophoresis with similar parameters as described in Section 5.1. During trapping, the molecules were protected by the trityl groups. After trapping, the sample was rinsed with deionized water prior to the I-V measurement of the trapped and still protected octanethiol coated gold nanoparticles. The molecules were then deprotected by soaking the sample in trifluoroacetic acid with dichloromethane (1:1) together with 5% triethylsilane as scavenger at room temperature for 20-30 min.

In order to remove residual chemicals on the sample from the deprotection solution, the sample was rinsed with deionized water directly after the deprotection. Finally, an I-V measurement was performed in order to see if the deprotection had been successful by observing the current through the molecular gold nanoparticle system. Figure 5.8 shows I-V measurements before and after the deprotection together with a SEM inset of the trapped gold nanoparticles acquired after the I-V measurements. The current level increased from the fA range to the 400 pA range at 1 V after the deprotection suggesting that the chemistry worked.
Figure 5.8. I-V measurement before and after deprotection of the octanedithiol coated gold nanoparticles trapped in a gap (SEM inset). The current level increased from ~fA to ~400 pA after deprotection.

The experiments with the dielectrophoretic trapping of the protected gold nanoparticles showed a current increase by a factor of ~1000 between the protected and the deprotected octanedithiol coated gold nanoparticles.

This study of protection and deprotection chemistry of functionalized molecules solves many problems in the field of molecular electronics and provides stable and reproducible measurements of the charge transport properties of the molecules.

5.3 Carbon nanosheets

The omniprobe needle and the sample stage in the FIB/SEM were electrically connected to a source-meter (Keithley 6430) which in turn was connected to a PC for data acquisition. Figure 5.9 displays schematically the experimental setup, the orientation and the structure of the sample inside the FIB/SEM.

The tungsten probe needle typically had a radius of curvature of ~500 nm but this did not promote contacting of individual carbon nanosheets (CNSs).
Therefore the tip was in situ ion polished to a diameter of 20-40 nm. This improved the manipulation precision as well as removed the native tungsten oxide formed on the tip during storage at ambient conditions.

Figure 5.9. Schematic image of the experimental setup inside the FIB/SEM. Adapted from Paper VI.

Functionalization of graphene layers, which are the building blocks of the carbon nanosheets (CNSs), by means of hydrochloric (HCl) acid treatment, was shown to induce in-plane defects (Coleman, 2008). Divacancy defects were also theoretically modeled in the same work and the result predicted a metallic conductivity of states around this vacancy.

In Paper V, theoretical modeling of single and divacancies in graphene was studied and it was found that the resistivity decreases when the defect concentration increased. This theoretical observation was investigated experimentally by functionalizing CNSs with the same (3 h) HCl acid treatment as in (Coleman, 2008) and by measuring the conductivity by using the in situ electrical characterization setup with the manipulator in the FIB (presented in Chapter 3). The results obtained from the acid treated sample were compared to a reference sample which was treated in the same way (the same water rinsing and drying protocol as for the acid treated sample). Figure 5.10 shows a plot of the measured resistance (log scale) as a function of different bias voltages from about 100 I-V measurements for the acid treated and the reference sample. The resistance decreased with about 50 times upon the acid treatment. This was in agreement with the theoretical calculations.
Figure 5.10. Plot of the resistance (log scale) as a function of bias voltage for the acid treated and the reference sample. The error bar is the standard error from the log-normal distribution. Adapted from Paper V. Reproduced with permission of IOP Publishing Ltd.

In Paper VI, the investigation of the acid treated and the reference sample was extended to another batch consisting of four samples; a 3 h and a 6 h acid treated sample, a water treated sample (treated with the same procedure as the reference sample in Paper V) and an as-deposited sample (directly from the deposition chamber). Figure 5.11 shows the measured average resistance for the different samples. The untreated sample shows the highest resistance whereas the water treated sample shows a slight decrease in resistance. The reason for this is not clear but one possibility is that contaminations on the untreated sample are removed during the water treatment and the subsequent drying at 150°C. The average resistance of the two acid treated samples was again shown to be drastically decreased, by about 50 times, as compared to the untreated and the water treated samples. The reason why the average resistance of the 3 h and the 6 h acid treated samples were very similar could be related to some kind of saturation in the defect creation process. Any time dependent study on the change in average resistance has not been conducted to investigate this process.
5.4 Cadmium Telluride nanotetrapods

Cadmium telluride (CdTe) is a very promising material for converting solar energy into electricity (Loferski, 1956). It has been used in many photovoltaic applications in combination with other materials (Khrypunov, 2009; Chu, 1992; Ginley, 2008).

In Paper IV, CdTe nanotetrapods (NTPs) were trapped in nanogaps and their photoconduction properties were evaluated. I-V measurements were performed in dark conditions as well as under illumination with white light. Figure 5.12 shows I-V measurements under a) dark conditions and b) illuminated conditions. The inset in a), shows a TEM image of a single NTP. In b), the curve in a) is inserted in order to emphasize the large change in the current between the dark and the illuminated state. The measured current is in the fA range in the dark condition but goes up to about 3 pA at 3 V under illumination.
Figure 5.12. I-V measurements of the trapped NTPs in a) dark condition (triangles) and under b) illumination (circles), respectively. The TEM inset in a) shows a single NTP. The curve in a) is also present in b) to emphasize the difference in current between the two states. The inset shows schematically a possible geometry of two trapped NTPs in a gap. Adapted from Paper IV. Reproduced by permission of The Royal Society of Chemistry.

This kind of photo-conduction behavior can be helpful for understanding fundamental physics as well as for developing photovoltaic devices.
6. Concluding remarks

The two contacting strategies utilized in this thesis have proven to be successful in the manipulation, contacting and electrical characterization of nanoparticles, nanotetrapods, carbon nanosheets and molecular systems with nanoparticles.

The FIB based nanocontact platform showed extremely high resistances of the nanogaps prior to any trapping of nanoobjects. This makes them suitable for electrical characterization of e.g. high resistance molecules. The fabrication process of the nanogaps, involving the FIB, did not result in large enough ion implantation to cause short-circuiting of the nanoelectrodes. The optimization of the FIB milling parameters showed enhanced performance which made it possible to fabricate nanogaps down to the size of ~10 nm. This is close to the size range of many interesting molecules which could be of interest to characterize and use for molecular electronics applications.

The trapping and electrical characterization of what resembled high resistance ds-DNA, was only possible by establishing a tight control of the surface properties, such as hydrophobicity or hydrophilicity, under experiments in ambient conditions. The intrinsic high resistance of the empty nanogaps showed that this platform is suitable for electrical characterization of low conductance molecules.

Molecular junctions were created by covering the nanoelectrodes with OT or BPDT molecules and by trapping gold nanoparticles in these gaps. This approach led to the estimation that only a small number of molecules (in the order of 10 per junction) were electrically characterized in this setup in ambient conditions. The estimated resistance per molecule in these experiments agreed reasonably well with other measurements of single molecules from literature but the difficulties with attaching thiolated molecules to gold electrodes and gold nanoparticles have to be considered, especially under ambient conditions.

This challenge was assessed and partly solved by the development of the novel route to synthesize the octanedithiol coated gold nanoparticles. This route allowed for controlled protection and deprotection of the thiols located at the outer ends of the molecules sitting on the gold nanoparticles. The electrical characterization after the deprotection of trapped gold nanoparticles showed an increase in the current by a factor of about 1000 as compared to before deprotection. This showed that the chemistry worked and this will
contribute to more reliable and reproducible experiments in molecular electronics.

The FIB also proved to be a flexible tool concerning the in situ manipulation, contacting and electrical characterization of functionalized and non-functionalized carbon nanosheets. The ion beam was successfully used to polish the tungsten tip of the manipulator to a diameter of about 20-40 nm. This polishing removed the native oxide on the tip and greatly improved the contact resistance. The live imaging with the electron beam made it possible to precisely contact a single carbon nanosheet, perform an I-V measurement and move on to another sheet within a time scale of a minute. The repositioning from one sheet to another took only a few seconds. The measured resistance of the functionalized carbon nanosheets was about 50 times lower as compared to the non-functionalized carbon nanosheets. This showed that the experimental setup was very useful to determine the electrical properties of such nanoobjects and this approach can be extended to other objects such as particles, nanowires and individual grains or defects in thin films.

6.1 Outlook

Molecular electronics is a truly interdisciplinary field of research and the development of useful applications greatly depend on the successful collaborations between scientists in engineering, chemistry and physics. For the purpose of developing state-of-the-art applications in this field of research, the engineering side must develop advanced analysis and structuring techniques which can reproduce large numbers of nanogap structures and implement them into integrated circuits.

As for the scope of this thesis, more advanced structuring and analysis techniques (FIBs and EBL systems) could result in parallel fabrication of smaller (1-3 nm) gaps. With many such gaps a parallel trapping procedure can be obtained by monitoring the current through the gaps as they are placed inside a solution containing the molecules of interest. In the ideal case, when one molecule bridges the gap, the monitored current through it should increase drastically, indicating a successful trapping event.

The development in chemistry should continue towards the selective protection and deprotection of anchoring groups on the molecules and a possible development is also to have different anchoring groups on one molecule in order to have the directionality of the attachment to nanoelectrodes of different materials. This opens up the possibility to study certain diode behavior of molecules attached in certain fixed ways in the nanogaps. All measurements will benefit from comparisons to theoretical calculations from physicists.

For the purpose of studying single nanoobjects down to an atomic scale, in situ manipulators can be used inside TEMs for electrical characterization and manipulation.
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Det här är en dialog som utspelade sig mellan mig och min son Emil (då 3 år gammal) och visar på hans intresse för min forskning redan i tidig ålder:

Emil: Pappa, vad gör du på jobbet?
Tobias: Jag tittar på pyttypyttesmå saker i mikroskop.
Emil: Jaha, myror?!?
Tobias: Nja, ungefär som myror, fast ännu mindre!
Emil funderar en liten stund och säger sedan: Myrbebisar?!?
Svensk sammanfattning

Utveckling och tillämpning av en nanokontaktplattform för elektrisk karakterisering av molekyler och nanopartiklar.

Utvecklingen av nya material med unika egenskaper spelar en stor och viktig roll i förbättringen av våra liv och för vår välfärd. Forskning inom nanoteknologi kan ge oss billigare, lättnare och smartare material i tillämpningar inom exempelvis energiförvaring, sensorer och elektronikkomponenter.

För att den här utvecklingen ska kunna fortsätta krävs analyser och förståelse för de nya materialegenskaperna på nano- och ibland till och med på atomär nivå. Materialutvecklingen går mot att funktionalisera nanostrukturen, d.v.s. att blanda olika material i syfte att skapa aktiva material med specifika egenskaper, och studera deras nya fysiska och kemiska egenskaper med det slutgiltiga målet att kunna skräddarsy dem efter våra behov. Forskningen inom nanoteknologi riktar sig mot att kunna tillverka, analysera och förstå små enskilda enheter såsom nanopartiklar, molekyler och molekylära system. En av de stora utmaningarna angående karakteriseringen av enskilda nanometerstora objekt är hur de kan kopplas fysiskt till ett mätinstrument för analys av deras egenskaper.

Målet med forskningen som presenteras här är fokuserat på hur nanometerstora objekt fysiskt kan kopplas till ett mätinstrument för elektrisk karakterisering. Syftet med detta är i slutändan att kunna förstå objektens elektriska egenskaper. Nanoobjekten som har analyserats är kolnanoskikt, nanotrapoder, guldnanopartiklar samt ledande och oledande molekyler.

Två strategier har använts för att kontaktera dessa nanoobjekt. **Den första** strategin handlade om att kombinera olika tillverkningstekniker, liknande de som industrin använder för att tillverka integrerade kretsar och datorkomponenter, för att utveckla en nanokontaktplattform. Plattformen består av nanoelektroder av guld och är tillverkade så att de formar gap i storleksordningen 10-30 nm. Ett sådant gap är den centrala delen i en nanokontakt där även stora kontaktpaddar av guld ingår och som sitter ihop med nanoelektroderna för att möjliggöra den elektriska kontaktningen av gapet. Figuren nedan visar en svepelektronmikroskopbild (SEM-bild) på en nanokontakt bestående av kontaktpaddar (indikerade med ”Guld”) som separeras av nanogapet vilket syns i den infällda bilden. Kontakten är tillverkad ovanpå ett kiseldioxidsubstrat i syfte att elektriskt isolera elektroderna och kontaktpaddarna från varandra.
SEM-bild av en nanokontakt bestående av en kontaktpad av guld på vardera sidan av ett ~10 nm brett nanogap (infällda bilden).


Nanopartiklar eller andra objekt som finns lösta i ett lösningsmedel har droppas på nanokontakterna och fångats in i gapen med hjälp av dielektrofores. Det är en teknik som innebär att en växelspänning läggs över ett nanogap och gör så att nanoobjekten polariseras och dras mot det ökande fältet. Det högsta fältet finns i gapet vilket innebär att nanoobjekten kommer att samlas där. Beroende på koncentrationen av nanoobjekten i løsningen, fältstyrkan i gapet samt tiden som fältet appliceras under så kan olika antal nanoobjekt fångas in i gapet.

Genom användning av dielektrofores samt av elektrisk mätutrustning har guldnanopartiklar, nanotetrapoder och DNA-molekyler fångats in och karakteriserats med hjälp av den här nanokontaktplattformen. De infångade guldnanopartiklarna hade ett motstånd på 13 MΩ vilket visade att plattformen fungerade för infångning och karakterisering av nanoobjekt. De infångade nanotetrapoderna avslöjade intressanta fotoelektriska egenskaper under belystning med ljus.

I en annan studie har guldelektroderna även täckts med elektriskt ledande (bifenylditiol) respektive oledande (oktantiol) molekyler innan infångningen.
av guldnanopartiklar i gapen. Genom detta tillvägagångssätt är det möjligt att skapa molekylära gränssskikt mellan nanopartiklarna och elektroderna. Den elektriska karakteriseringen av dessa system visar hur bra dessa molekyler leder ström och om de har några speciella egenskaper som gör att de lämpar sig för användning inom molekylärelektroniska tillämpningar. De ledande molekylerna uppvisade främst höga ohmiska motstånd medan de ledande molekylerna uppvisade främst icke-linjärt beteende och hysteres. En möjlig tillämpning av dessa ledande molekyler kan vara i elektriska brytare eller i logiska kretsar.

Svårigheten med att på ett pålitligt sätt koppla molekylerna till nanoelektroderna har till viss del lösts i en studie där nanopartiklar täckta med molekyler har tillverkats. Ändarna på molekylerna som sticker ut från nanopartiklarna har skyddats av kemiska (trifenylmetyl-) skyddsgrupper under infångningen av partiklarna i nanogapen. Efter infångningen har dessa skyddsgrupper tagits bort med hjälp av syrabehandling vilket innebar att molekylerna då kunde binda kemiskt till guldnanoelektroderna. Elektrisk karakterisering av dessa molekylära guldnanopartikelsystem visade på en ökning av ledningsförmågan med en faktor 1000. Detta tillvägagångssätt med att selektivt skydda och avskydda molekyler öppnar upp stora möjligheter att reproducerbart utföra elektriska mätningar inom molekylärelektroniken.

Arbetet med att karakterisera molekyler och molekylära system med höga elektriska motstånd har resulterat i viktig kännedom om yteffekter på substratet och hur exempelvis plasma- samt UV-ozonrengöring kan påverka mätningar av låga strömmar i den här nanokontaktplattformen.

**Den andra strategin innebar att använda FIB/SEM:et genom att utnyttja en manipulator bestående av en mycket spetsig volframnål vilken kan manövreras i x-, y-, och z-led inuti FIB/SEM:et under direkt avbildning med hjälp av elektron- och/jonstrålen. Nålen vässades ytterligare med hjälp av jonstrålen för direkt kontaktning av enskilda funktionaliserade och ofunktionaliserade kolnanoskikten inuti FIB/SEM:et. Den här mät uppställningen tillåt elektrisk karakterisering och manipulation av nanoobjekt med hög noggrannhet och med god statistik. Förflyttning av volframnålen mellan två närliggande kolnanoskikten tar endast några sekunder vilket möjliggör snabb elektrisk karakterisering. Resultatet från karakteriseringen av kolnanoskikten visade att de funktionaliserade kolnanoskikten hade ungefär 50 gånger högre konduktivitet än de ofunktionaliserade kolnanoskikten.**

**Båda strategierna visade sig vara värdefulla för att bygga upp kunskapen och erfarenheter kring kontaktning och elektrisk karakterisering av nanoobjekt. FIB/SEM:et visade sig också vara ett mångsidigt instrument väl lämpat för tillverkning och karakterisering av nanostrukturer.**
This is a detailed flow chart of the different steps in the nanocontact fabrication process (described in Chapter 4). Risks, problems and possible developments are mentioned for each step.

1. Wafer oxidation
   - Wet oxidation of a 4'' Si(100) wafer
   - 1 µm SiO₂ is grown

2. PMMA spin coating
   - Wafer cleaning in Piranha solution: 2:1 H₂SO₄:H₂O₂ for 5-7 min
   - 1 ml of PMMA 495k A4 (~ 4% solid content in Anisole) is deposited on the wafer by using a syringe
   - Spin coating 5 s at 500 rpm increasing to 4000 rpm for 55 s
   - Baking on hot plate, 170 °C for 1 min. In the case a double layer resist, 1 ml of PMMA 950k A4 is deposited on top and spun for 5 s at 500 rpm increasing to 3500 rpm for 55 s. Baking: 170°C for 1 min
   - The single layer resist thickness is measured to ~150 nm in the atomic force microscope (AFM)

3. Dicing
   - Dicing/cleaving of the Si wafer into ~20 by 20 mm pieces

Possible Improvements?
A thinner SiO₂ layer would provide a better coupling to the Si substrate, acting as a back-gate contact.

Important parameters?
Cleanliness, oxidation time and temperature in the oven.

Possible Improvements?
Thinner resist layers improve the patterning resolution (due to less beam broadening) but result in constraints on the thickness of the deposited metal layers.

Important parameters?
Rotation speed, baking time and temperature and type of resist (and its molecular weight) affect the resulting thickness.

Possible Improvements?
Dicing of the wafer with a Bi saw results in more reproducible sample sizes. Though, the dicing involves water cooling of the saw blade. This might damage the resist.

Important parameters?
-
4. Electron Beam Lithography (EBL)

- Staining the sample in each corner with gold nanoparticles. This provides good contrast during the electron beam alignment.

- The program NPGS (Nanometer Pattern Generation System) is installed on an external computer connected to the microscope. The coordinates x, y, and z (focus) are read from the microscope in order to make a virtual tilt-map of the sample so that an accurate focus can be set in each point of the sample. The computer also controls an electrostatic beam blanker of the microscope in order to switch the beam on or off according to the designed pattern (drawn in a CAD file).

- The electron beam current passing through the sample is measured and manually inserted in the NPGS software. With the current and the set electron dose (in μC/cm²), the dwell time (in μs) of the electron beam is calculated. The dose is typically ~270 μC/cm² for PMMA on SiO₂. The maximum magnification which can be used when writing a pattern is determined from the size of the CAD pattern. The microscope magnification is set manually by the user and should not be higher than this maximum magnification.

- 96 nanocontacts are patterned over a 10 by 10 mm² area in 8 groups with 12 contacts in each group (see chapter 4 for schematic figure). The stage is moved automatically into position for the exposure of each pattern. The movements introduce stitching errors of up to 20-40 μm in x and y direction between pattern number 1 and 96. The patterning time for one single nanocontact is about 30 s which means ~48 min in total for the 96 patterns (100 pA beam current, dose ~270 μC/cm²)

- The exposed PMMA is developed in 1:3 MIBK:IPA for 1 min and is then rinsed in pure IPA for 45 s. The resulting patterns are checked in a light optical microscope and occasionally in the SEM if the result is uncertain or if some parameters were changed.

Risks/Problems?
The electron beam should be stable during the whole patterning procedure. This is not always the case. There may be degradation of the pattern quality between pattern 1 and 96. This is most likely due to the change in astigmatism, which is only adjusted once, manually, during the initial alignment of the electron beam. There is no built-in routine for automatically adjusting the astigmatism in the NPGS software.

The development procedure plays an important role for the final pattern quality.

Possible Improvements?
Increasing the microscope magnification will increase the patterning precision because of the decreasing field-of-view. This means that the maximum pattern size will also decrease and therefore mechanical stitching with the stage might be needed. In the end, this will introduce stitching errors between patterns.

Decreasing the spot size from 3 (standard) to 1 gives a reduction of the beam current (at 30 kV) from ~100 pA to ~10 pA. This results in a smaller electron beam which results in a much more noisy-SEM image but results in more high resolution patterns. The drawback is that the patterning time will increase with the same factor (10 in this case).

In literature, it has been reported that ultrasonic agitation (Chen, 1963) during development can help removing the exposed resist. Using the developer at low temperatures (5-10°C) can also help decreasing the sensitivity of the PMMA to the developer, making the process slower (Hu, 2004).

Important parameters?
A high acceleration voltage (e.g. 30 kV) gives the smallest electron spot with the largest beam current but might cause electrical charging of the sample. High energy beams are not as sensitive to lens aberrations as compared to low energy electron beams. Low energies (e.g. 1-5 kV) results in a larger electron spot but less backscattered electrons. In this work, typically 30 kV, spot 3 and an objective lens aperture of 30 μm in diameter was used.
5. Metallization by resistive evaporation

- Cleaning in oxygen plasma (descore) prior to the metallization.
- Typically overnight pumping in the evaporator. A good pressure is in the low 10⁻⁵ or 10⁻⁷ mbar range.
- Cr deposition (adhesion layer) of 2-3 nm and Au deposition of 10-100 nm from tungsten boats. The sample is rotated during deposition to get a homogenous annealing.

Possible Improvements?
- A Quartz Crystal Microbalance (QCM) is used to measure the deposition rate and resulting film thickness. It is not always very accurately calibrated. The thickness control can be improved by always evaporating the same amount of material each time. The resulting film thickness should be measured in e.g. an AFM. Some materials, like e.g. Cr, do not melt. Instead, they might sublimate from the solid phase to the gas phase. In this case, a controlled deposition of Cr can be performed by always using the same piece of material and by keeping the current through the W boat as well as the deposition time constant.

Important parameters?
- Base pressure, rotation, substrate temperature, current and deposition time.

Risks/Problems?
- If the metal layers are deposited during a long time, the resist might get too warm that it starts to degrade.

6. Lift-off

- Soaking the sample in acetone for about 1 hour.
- When the metal on top of the PMMA starts to peel off, the sample is rinsed with more acetone, IPA and finally blow dried with nitrogen gas.
- The patterns are checked in a light microscope in order to see if the lift-off is complete. Any residual resist can be removed by oxygen plasma treatment.

Possible Improvements?
- The properties of the double layer resist can be improved with different combinations of resists. A larger undercut can enhance the lift-off even more.

Important parameters?
- The soaking time in acetone.

Risks/Problems?
- If the deposited metal is too thick and covers the sample too well, it might be difficult to remove it during the lift-off process. Ultrasonication can help the lift-off but it can also damage the patterns in worst cases.

7. Fabrication of contact pads by using photo lithography

- Spin coating with (positive) photo resist (AZ 4562) for 3 s at 1000 rpm and for 45 s at 4000 rpm. Drying on a hot plate at 95°C for 2 min. The thickness of the resist is estimated to 5-6 μm.
- Sample alignment under the photo lithography mask containing the (100×100 or 100×200 μm²) contact pads.
- Exposure with UV light for 16 s.
- Pattern development in a mixture with the ratio 1:4 AZ400k:H2O for about 5 min.
- The pattern quality is evaluated in a light microscope. If no residual resist is remaining in the exposed areas the sample is taken to the evaporator.
- Residual resist can be removed by oxygen plasma treatment.

Possible Improvements?
- A perfect dose will give just enough exposure of the resist but also more straight side walls. This will improve the later lift-off.

Important parameters?
- Exposure time and development time. The cleaning time in the oxygen plasma is critical prior to the next step which is metallization.

Risks/Problems?
- If the photo resist is too thick, there will be a lot of stress in it and it might crack.
8. Metallization of the contact pads by evaporation

- 10-20 nm of either Cr or Ti (as adhesion layer) is deposited by using resistive or electron beam evaporation
- 300-400 nm of Au is deposited by using electron beam evaporation. More material can be deposited faster with this technique, avoiding excessive heating of the sample.
- The contact pads should be thick enough to sustain scratching by probe needles as well as wire bonding
- Lift-off is done as described previously

Possible improvements?
- Thicker contact pads and adhesion layers will promote the wire bonding step. But thicker pads might result in a more problematic lift-off
- Important parameters?
  - Base pressure and deposition time.

9. FIB milling

- The ion beam (1 pA current) is aligned in the vicinity (~50 μm) of the gold wire
- Test cutting of trenches in the gold film are made with different milling times. The time giving the cleanest and sufficiently small structure will be used for cutting the nanopit in the gold wire
- A quick (1.5 s scan) ion beam image is acquired of the gold wire at a low magnification (35 kHz, 0.65 μm wide field-of-view) in order to locate it without damaging it
- A 'single line' pattern is drawn and the parameters are set to 50% overlap, 1 μs dwell time and typically 1-2 s milling time
- The magnification is significantly increased (150 kHz) corresponding to a horizontal field-of-view of 2.03 μm prior to the milling
- After the milling, the created gap is evaluated by using the electron beam and the milling parameters are adjusted if needed
- The sample stage is moved to the next nanopit and the milling is repeated

Possible improvements?
- Decreasing the ion emission current from 2.2 μA to ~1 μA results in a lower ion beam current which gives a smaller beam spot. A small beam enables the possibility to fabricate smaller structures.
- Important parameters?
  - Beam current, overlap, dwell time, milling time and emission current.
References


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