In-situ TEM Probing of Nanomaterials

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- ii -
This is he of whom I said, After me cometh a man who is become before me: for he was before me.

John 1:30
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Abstract

Nanomaterials because of their small size, may have special properties unlikely to be seen in ordinary types of materials. Nanomaterials like nanotubes, nanowires and nanoparticles are best studied at the nanoscale, vital but also problematic. In this thesis we use a transmission electron microscope (TEM) combined with a scanning tunneling microscope probe. This system allows TEM images to be captured and recorded into a movie together with recorded electrical data for real time analysis.

Using this method we found that the electrical conductivity of molybdenum based nanowires \( Mo_xS_y \) can be improved by current induced transformation. This might be a general method of improving nanowires which is of high value if the wires are to be used in electrical circuits or field emission devices. The bending modulus for these nanowires were also determined, by an electromechanical resonance method, to 4.9 GPa.

The sintering phase of silver nanoparticles, used in electrical conductive ink for printing electrical circuits, were studied by the in-situ TEM probing method. We observed that percolation pathways are formed and that the dispersive agent of the particles can be pyrolysed into a net of carbon with characteristics similar to graphite.

We also developed a method for decorating nanowires and nanotubes with gold nanoparticles. Nanowire particle composites are often used in assembling more complex devices (electronic circuits) or for linking to organic molecules (biosensor applications) and existing particle decoration methods are either difficult or with low yield. By in situ TEM probing we found that carbon nanocages can be grown onto these gold nanoparticles. The size of the gold nanoparticles is controllable an thus the size of the nanocages. These nanocages may be used in medicine- or hydrogen storage-applications.

Keywords: nanotechnology, in situ, TEM, probing, nanowires, nanoparticles, ink
Sammanfattning


Acknowledgment

Very first I would like to thank my supervisor Håkan Olin. I remember that in the beginning Håkan said that as a PhD student your are not a student anymore but more of an apprentice and so being an apprentice you are supposed to learn the craftsmanship of Science. Now I personally like to look back at my PhD study in this way as being an apprentice.

There is one saying that goes something like this:

“To think freely, is good. But to think right, is even better.”

Håkan is one of the persons that really can think freely at least when it comes to the subjects of science or entrepreneurship and that is the reason why we had lots of time left over in making this thinking to be right as well.

For collaboration and useful discussions I also wish to thank the nano research group Christine Malmgren, Martin Olsen, Renyung Zhang, and Joakim Bäckström, I think we work well together. A special thank goes to my assistant supervisor Peter Glans, especially for reading the manuscript. An special thank to Göran Andersson for being supportive in all teaching and engineering related tasks. Thanks to Allan Stenberg and Nils Olander for being inspiring. I would also express my gratitude to the student classmates known from my undergraduate studies and all the people of the round coffee table with the endless mathematician vs physicist debate that is always of great satisfaction. I would also like to acknowledge the support from EU and the Desygn-IT project and for the collaboration with Justin Holmes, Cork and Dragan Mihailovic, Ljubljana. Finally, I would like to thank my family and related.

Magnus Hummelgård
Sundsvall
May, 2009
List of Included Papers

This thesis is mainly based on the following six papers, herein referred to by their Roman numerals:

Paper I

*Nanowire Transformation and Annealing by Joule Heating*
M. Hummelgård, R. Zhang, H. Olin, D. Vengust, D. Dvořek, and D. Mihailovic
Manuscript submitted

Paper II

*Bending Modulus of Mo₆S₃I₆ Nanowires Studied by Electromechanical Resonances*
M. Hummelgård, P. Isaksson, H. Olin, and D. Mihailovic
Manuscript submitted

Paper III

*Electrical sintering of nanoparticles studied by in-situ TEM probing*
M. Hummelgård, R. Zhang, H. E. Nilsson, and H. Olin
Manuscript submitted

Paper IV

*Simple and efficient gold nanoparticles deposition on carbon nanotubes with controllable particle size*
R. Zhang, M. Hummelgård, and H. Olin

Paper V

*Carbon nanocages grown by gold templating*
R. Zhang, M. Hummelgård, and H. Olin
Manuscript submitted

Paper VI

*Mo₆S₃I₆-Au composites: Synthesis, Conductance, and Applications*
R. Zhang, M. Hummelgård, H. Olin, D. Dvořek, and D. Mihailovic
Manuscript submitted
My Contributions

In the appended papers my contributions was according to follow:

Paper I to III
I did all the experimental work, equipment developing and in situ probing. I also did the major part of the writing and modeling.

Paper IV
I did the major part of the microscopy and the in situ probing experiments and contributed to the writing. I did not contributed to the wet chemistry.

Paper V
I helped out with the TEM sessions and did the modeling. I did not contributed to the wet chemistry.

Paper VI
I helped out with the TEM sessions, developed and programmed the hardware that were used for the electrical measurements. I did not contributed to the wet chemistry.
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Part I

Comprehensive Summary
INTRODUCTION

This thesis consists of two parts. Part I is a comprehensive summary of the papers that are attached in Part II. Part I consists of an introduction, with a brief description of in situ TEM probing and the results together with a background on the materials that have been studied. The introduction is followed by a method section with description of the TEM and in situ probing. The last section in the introduction is a summary of the papers together with conclusion and an outlook. There is also an appendix with some technical details.

Nanomaterials have, due to the small scale, special properties unlikely to be seen in ordinary types of materials. For example carbon nanotubes (CNT),\textsuperscript{[1]} have remarkable high critical current density\textsuperscript{[2]}, up to $\sim 10^6$ Acm$^{-2}$, and a Young’s modulus\textsuperscript{[3]} of about 1 TPa.

It is due to special properties like these that nanomaterials have been gaining so much interest and therefore characterization of these new nanomaterials is vital but also problematic due their small size. Besides standard techniques that mostly are used to characterize small batches of a sample, one also have to measure the individual properties of one single item. For example, measurements of the electrical conductivity in a pellet made out of carbon nanotubes give the mean value of several interconnecting tubes in a network. If the same kind of measurement is performed, but on a single tube, you would get a different value.

To conduct probing and characterization at the nanoscale, first an imaging system to visualize the sample is required and second a tool that makes it possible to pick out and select one piece. For imaging at the nanoscale several systems exist; (STM) scanning tunneling-, (AFM) atomic force-, (SEM) scanning electron-, and (TEM) transmission electron-microscopy. The last one allows real time high resolution
imaging combined with electron diffraction and it can also be combined with a manipulation probe, basically a scanning tunneling microscope that allows selection and individual probing of, for example, a single carbon nanotube i.e. in situ probing.

In the STM, a probe is scanned close to the surface to be imagined but can also be used to push things around and Eigler and Schweizer managed in 1990 to position single atoms, demonstrating the possibilities of manipulation at the nanoscale.[4] Later C. M. Lieber et. al. used AFM for imaging in combination with lithographic technique in which they spread out carbon nanotubes randomly on a predefined microchip and by chance some of the tubes crossed conducting sites allowing electrical measurements of single tubes.[3] This illustrates the problems in positioning and testing of individual nanomaterial items. The SEM, that usually do not operate at the same small nanoscale as the other instruments, also has advanced manipulation systems using piezo motors that allows three dimensional positioning.[5] P. Poncharal et al. used the TEM combined with a piezo and microscrew driven in-situ probe and they determined electrical and mechanical properties of carbon nanotubes.[6,7]

In this thesis I describe the experiments were we use a JEOL-2000FX transmission electron microscope combined with a scanning tunneling microscope probe.[8,9] This set-up combined with redesigned software and electronic, is a highly flexibly system, easily configurable to different types of tasks. The system also allows the TEM image to be captured and recorded into a movie together with electrical data, making real time studies possible.

In paper I we describe a study of rope bundles of MoS2J6 nanowires by in situ probing, showing that the electrical conductivity of these nanowires can be improved by current induced transformation. The process was studied in real time, showing that the resulting transformation into molybdenum nanowires leads to an increase in electrical conductivity to almost bulk value. In paper II we determined, by resonance method, the bending modulus for these MoS2J6 rope bundles, to be 4.9 GPa, a value that agrees with sound velocity measurements done by others.[10]

In Paper III a study of the sintering process of silver nanoink is described. This is a process of importance for making printable electrical
circuits on paper. What we found in this study was the required sintering power and indications that percolation pathways were formed. The dispersion matrix, that holds the particles in ink form, was found to be carbonized due to the heating in the sintering process.

In paper IV we present the method to decorated carbon nanotubes with gold nanoparticles and used this composite in paper V to form carbon nanocages with controllable size. Finally as described in paper VI, we decorated MoS2I6 with gold nanoparticles and then linked these particles to DNA-chains as a demonstration of biosensor capabilities.

The in-situ TEM probing method that was used in the work presented in this thesis was shown to be of high value for to characterizing and manipulating at the nanoscale, especially for individually items. Real time imaging and other analysis methods such as electron diffraction combined with the use of the STM as probing tool has been shown to be of great value.

Nanomaterials

In nanotechnology size matters, and it is often the small scale that determines the physical properties. If all three dimensions are reduced into the nanometer range, materials starts to behave differently as compared to with a bulk sample. For example, it is well known that silicon, heavily used in the electronic industry, is a good photo and electroluminescent material if made into nanoparticles with a size of approximately 2 nm. This is a property that does not exist in bulk and was previously unknown.

Reducing two of three dimensions, a nanowire or nanotube is formed. This provides a bridge between the nanoscale world and the macroscopic world, because one of its dimensions remain unchanged and can be macroscopic in size, while the material still contains some nanoscaled properties. After the discovery of the carbon nanotube, new fields of research opened, and other nanotubes were found built from materials such as transition metal-chalcogenide, -oxides, or -halogenides, or based on boron, silicon or pure metals.

The most important methods for growing nanotubes are sulfurization, decomposition of precursors crystals, template growing methods,
precursors assisted pyrolysis, misfit rolling and direct synthesis.\[13\] Beside nanotubes, solid nanowire may also be synthesized. The most common methods to produce nanowires are by different types of template methods to direct the growth or by growing directly from the vapor phase. In the vapor-solid-liquid (VLS) methods, catalytic particles form a liquid alloy with the substrate, followed by vapor condensation into the alloy, resulting in the growth of a nanowire. A similar growth process can also be achieved from a solution-liquid-solid mechanism. Solvothermal and solution phase methods are other types of techniques for growing nanowires.\[14\]

Mo$_6$S$_3$I$_6$ Nanowires

The high interest in nanomaterials, especially one dimensional structures like nanotubes and nanowires have resulted in search for new and other types nanotubes and nanowires besides the carbon nanotubes, which otherwise has received most of the attention. Mo$_6$S$_3$I$_6$ nanowires are one of these new materials.

One field of interest in one dimensional material, is the use of nanotubes and nanowires as field emission sources. Therefore, general characterization and especially electrical transport studies of new materials are vital as part of the process in turning the material into an useful product.

Transition metal chalcohalide molecular nanowires, such as the Mo$_6$S$_3$I$_6$, are an offspring of the research done on MoS$_2$ and WS$_2$ nanotubes\[15\] which led into the direction of MoS$_{2-x}$I$_y$ compounds, a material which turned out to be problematic to synthesis in any larger quantities.\[16\] However this, in search for more efficient and easier synthesis, led to the discovery in 2004 of the molecular nanowires of type Mo$_6$S$_{9-x}$I$_x$ (4<x<6).\[17\] Now applications of Mo$_6$S$_3$I$_6$ such as vapor- and bio-sensors has been shown\[18\] and they can be assembled into more complex structures.\[19\]

These nanowires are synthesized in an one step process by taking molybdenum metal foils, sulfur powder and iodine all placed together in a sealed evacuated quartz ampule. The ampule is heated slowly to 1070 °C, kept at this temperature for 72 hours, and then slowly cooled down. The produced material consist of bundles of nanowires that
at a macroscopic view resembles fur or a fine brush. This material is produced and supplied by the Mo6 company[20] and we usually use it without further treatment. A review describing the research done up to date on these transition metal chalcogenide nanowires is written by Dragan Mihailovic.[21]

Structure determinations, from atomic pair distribution function (PDF) analysis together with X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) has resulted in describing the MoS2k as being of P63 space group with the atoms positioned as seen in figure 1 and 2. The height of the unit cell is 1.197 nm. These nanowires self assemble into bundles with a wire to wire distance of 0.958 nm.[22–24] These bundles can, compared to carbon nanotubes, easily be dispersed in both polar and organic solvents down to individual nanowires.[25,26] Nanomechanical studies by atomic force microscopy (AFM) indicates a high tensile modulus of 430 GPa in combination with a low shear modulus of 0.45 GPa.[27] These are properties suitable for lubricants which also has been tested with interesting results.[28] These semi-metallic nanowires, both individual bundles and networks, shows poor conductivity (<1 S/m), however, it can be improved by some order of magnitude by annealing in a furnace.[29–31] Quasistatic and frequency dependent electrical studies has also been done.[32] One interesting property is the field emission capability and this has been tested successfully, but sudden current jumps that improve the overall performance has been observed.[33–35] Other studies such as sound propagational gives a sound velocity of 1630 m/s for the material.[10]

We used in-situ TEM probing to analyze the electrical properties of individual bundles as well for electromechanical resonance experiment to analyze the mechanical properties of the material.

**Silver Nanoparticle Ink**

Printed electrical conductive tracks on paper requires a conductive ink and metal containing inks, especially inks containing metallic nanoparticles are suitable for this. The ink itself, directly after print, conduct poorly and therefore a sintering step is required, however it is unclear how the sintering process actually proceeds at the nanoscale level and if the dispersion agent is involved in the sintering process or just evap-
INTRODUCTION

Fig. 1: The close packing of the MoS$_2$I$_6$ wires forming a bundle as observed by TEM (a). (b–d) shows ADF STEM images viewed along high symmetry directions. Inset images are from simulations. Figure from Nicolosi et al. [24]

Fig. 2: The structure of the MoS$_2$I$_6$ nanomaterial. Blue) Molybdenum, Red) Iodine, Yellow) Sulphur. As produced, the nanowires stack themselves in hexagonal patterns in which several wires forming ropes or bundles. The height of the unit cell is 1.197 nm and the wire to wire distance is 0.958 nm.
orates.

Other types of silver ink consist of small flakes of silver, which unfortunately is unsuitable for inkjet printing due to highly specific physicochemical demands such as viscosity, surface tension, adhesion etc. and most of the regular inks for inkjet printers are also water based inks.

During sintering, the silver particles fuse together resulting in an increase of conductivity. Nanoparticles of silver can be sintered at much lower temperatures down to 100 °C\textsuperscript{[36]} due to its nanoscaled size. Bulk silver have a melting temperature of 960 °C but nanosized (<20 nm) particles has a lower melting temperature as a result of higher surface area to volume ratio. Figure 3 shows the melting temperature as function of particle diameter.\textsuperscript{[37–39]} The actual printing, depending on quality, can be done with standard commercial inkjet printers. The sintering process in furnace is not suitable because of substrate shrinkage, non area specific, time consuming process and undesired gas emission from substrate and therefore other more selective methods have been developed such as electrical-, microwave-, and laser-sintering.\textsuperscript{[36,40–42]} Earlier results show that when the particles fuse together, a highly porous structure is produced and that the peculation pathways obtained might contribute to the major part of the conductivity increase.\textsuperscript{[36,43]}

To make an ink out of nanoparticles, several techniques exist, but water based solutions are preferred, making the ink more environmental friendly, however the amount of silver nanoparticles in aqueous

![Graph](image)

Fig. 3: The melting temperature for gold and silver as a function of particle diameter according to the Gibson-Thomson model.
solutions are limited (0.1 wt%) and different kinds of stabilizing agents is required to prevent agglomeration and to obtain a stable dispersion of the particles. To fulfill these demands silver nanoparticles has been dispersed into an ink with polymeric-, nonionic-, ionic-surfactants, and carboxylates as stabilizers.[43-49] The actual nanoparticles, made out of transition metals as the ones used in inks, are most commonly produced by: (i) transition metal salt reduction, (ii) thermal decomposition, (iii) photochemical methods, (iv) ligand reduction and displacement from organo metallics, and (v) electrochemical synthesis.[50]

Using the in-situ TEM probing method, we analyze a small sample at the nanoscale during electric sintering. Directly showing the sintering process of individual nanoparticles. The ink that we use is the product Silverjet DGP-40LT-15C from Advanced Nano Products Co. Ltd.[51] It contains 36 wt% silver nanoparticles with a diameter of 59±2 nm. The particles are dispersed in a polar solvent of triethylene glycol monoethyl ether, see figure 5.

CNT-Au, Mo₆S₃I₆-Au Composites, and Carbon Nanocages

The combined properties of carbon nanotubes or nanowires and metallic nanoparticles is useful and leading to many novel applications.[52-55] A review on the subject is available.[56] Gold nanoparticles are especially important as they may be linked to DNA and other organic compounds. These composites can be used in more complex systems such as nanoelectronics and biosensors.[57-59] However the methods for making these nanowire nanoparticle composites are either complicated or with low yields. Nanoparticles may also function as templates for growing other

![Fig. 4: in-situ TEM probing on silver nanoparticle ink, here seen to sinter (over time a to d) due to electric current throughput. Arrow indicates formation of carbon.](image)
types of nanostructures in which size control is a vital parameter.

Carbon nanotubes are made out of folded graphite sheets and depending on roll up direction, see figure 6, semiconducting or metallic tubes are formed, the metallic version shows ballistic conductance properties. Single-walled tubes are about 1 nm in diameter and for multiwalled types much larger. Methods to deposit metallic nanoparticles onto carbon nanotubes are usually done by (i) wet chemical methods, (ii) self assembly, (iii) electrodeposition, and (iv) physical vapor deposition. The decoration of carbon nanotubes with gold nanoparticles, can be done either by indirect covalent linkage, non covalent bindings, or by directly deposition without the use of indirectly linking by other molecules or groups. Directly deposition is done by chemical reduction of gold salt, by solvated metal atom dispersion, or with the use of surfactants.

We have chosen to mix multiwall carbon nanotubes and MoS2 nanowires with sodium citrate in combination with ultrasonication. This led to shell formation on the nanotubes or nanowires that serves as substrate for the growing of gold nanoparticles in a reduction process when HAuCl4 is added to the solution. These composites were then individually characterized by in-situ TEM probing. The melting behavior by electrical heating were studied. This was specially interesting, since with a carbon source present, such as the carbon nanotUBE, carbon can be deposited onto the nanoparticles, forming nanocages.
INTRODUCTION

Fig. 5: Triglycol monoethyl ether or 2-(2-(2-Ethoxyethoxy)ethoxy)ethanol is the dispersive agent used in the silverink from Advanced Nano Products Co. Ltd. Ref. [51].

Fig. 6: Illustration on how the carbon nanotubes are built up of a folded graphite sheet. Depending on direction, the sheet is rolled up and zigzag- or armchair-type of carbon nanotube are formed.
METHODS

Transmission Electron Microscopy

The transmission electron microscope or for short TEM, is built around the same principle as an ordinary light microscope, and was invented during the 1930. Electrons are used instead of photons as in the light microscope. The electrons are generated in the gun at the top of the microscope, accelerated downwards the column, focused by different types of electromagnetic lenses and projected at an electron sensitive fluorescent screen, and if something is placed into the beam path, at the proper place, a magnified projection can be seen at the screen. The standard light microscope can magnify 1500x but the electron version goes up to 800.000x. A better value of performance is resolution, which is ≈1 µm for the former and ≈0.3 nm for the latter.¹

The transmission electron microscope is built around an evacuated standing column with the electron source, the gun, at the top. Figure 7 on page 14 shows the various parts of a transmission electron microscope. Due to the use of electrons, the system is evacuated and this is accomplished by a high vacuum system with a resulting pressure of 10-50 µPa. Specimen exchange is done by an airlock mechanism leaving the major part of the vacuum system unchanged during specimen replacement.

¹Data from a JEOL-2000FX, a microscope built during 1980, modern aberration corrected types have sub ångström resolution.
Fig. 7: The transmission electron microscope is built around a evacuated standing column with the electron source, the gun, at the top. After the electrons are generated and accelerated by the gun, they travel downwards the column through the sample and through different electromagnetic lenses that contributes to the magnified projection of the sample visible at the fluorescent screen, which the transmitted electrons hit at the bottom of the column.
Electron Gun, Condenser, and Deflection Coils

The "light source" in a transmission electron microscope is an electron gun. Compared to the standard light microscope in which the source is placed at the bottom, the gun is placed at the top of the column. The electrons emitted into the vacuum are either thermionically emitted, Schottky emitted, or by field emission. The two latter ones are modern techniques and gives higher brightness and less energy spread of the emitted electrons, see table 1. Thermionic emission means that the filament is heated to such high temperature, that the electrons can overcome the work function $\Phi_w$ and enter the vacuum. In field emission a very high voltage potential is used instead, to decrease the width of the potential barrier, allowing the electrons to tunnel into vacuum. Schottky is a combination of both the methods. We use a lanthanum hexaboride crystal (LaB$_6$) thermionic source which has slightly better performance over tungsten hairpin filaments. The assembly of the filament in the microscope is slightly different between a thermionic source and field emission source, in which the latter requires an extra anode at high voltage, see figure 9.
The gun accelerates the electron downwards through the column. The accelerating voltage used for this is usually between 100 keV to 200 keV but there are special very high voltage systems up to MeV. In our experiments 160 keV is the default operational mode.

Tab. 1: Performance data of various types of electron emitting sources. Cathode temperature $T_c$, work function $\Phi_w$, emission current density $j$, gun brightness at $E=100$ keV $\beta$, energy spread $\Delta E$, and operating vacuum $p$. Reimer and Kohl [80].

<table>
<thead>
<tr>
<th></th>
<th>Thermionic W hairpin</th>
<th>Thermionic LaB$_6$-crystal</th>
<th>Schottky ZrO/W tip</th>
<th>Field emission cold or heated W tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>2500-3000</td>
<td>1400-2000</td>
<td>1800</td>
<td>300 or 1500</td>
</tr>
<tr>
<td>$\Phi_w$ (eV)</td>
<td>4.5</td>
<td>2.7</td>
<td>2.7</td>
<td>4.5</td>
</tr>
<tr>
<td>$j$ (A/m$^2$)</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td>$10^6$</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>$\beta$ (A/m$^2$sr)</td>
<td>$10^9$</td>
<td>$10^{10}$</td>
<td>-</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>$\Delta E$ (eV)</td>
<td>1.5-3</td>
<td>1.2</td>
<td>0.3-0.7</td>
<td>0.2-0.7</td>
</tr>
<tr>
<td>$p$ (Pa)</td>
<td>$10^{-3}$</td>
<td>$10^{-4}$</td>
<td>$10^{-8}$</td>
<td>$10^{-9}$</td>
</tr>
</tbody>
</table>

Fig. 9: The two types of electron sources in the gun. Thermionic (left) and field emission (right).

The condenser lens system focus the electron beam on the specimen and adjust the beam illuminating area so that it will be equal in size to the viewing area, to maximize the intensity so that it is high enough for viewing even at high magnifications and to make the intensity level even over the hole area. This is accomplished by two electromagnetic
lenses, C1 and C2. An aperture for selecting only the central part of
the beam, deflector coils for beam translation and stigmator coils to
compensate for astigmatism is also included in this part of the system.

Objective Lens, Specimen and Magnifying

The objective lens is positioned right beneath the specimen in the middle
of the column and is the most critical part of the microscope, even though
it only magnifies (M) 20-50 times. At this lens it is vital that spherical and
chromatic aberrations are minimized and to correct for this, stigmator
coops are used together with beam shifting and beam tilting coils to align
the beam so that the beam is aligned and passes through the very center
of the lens. For the following lenses this problem is minor due to the fact
that these kind of errors is proportional to the aperture size as \( a^3 \) and
the aperture size is demagnified dramatically downwards the column
according to the relation \( a = a_0/M \) and therefore can be neglected.\(^8^0\)
The objective aperture itself is interchangeable in several diameters, 20,
50, and 80 \( \mu \text{m} \) for the JEOL-2000FX microscope. By selecting different
sizes of apertures contrast can be improved, a smaller aperture excludes
more diffracted electrons that otherwise will tend to disrupt the image
in transmission contrast.

The specimen is located right above the objective lens. The most
common method is to have a side entry sample holder, see figure 16,
that is inserted into an airlock mechanism for evacuation, then slide into
position above the lens into the goniometer, which provides tilting and
positioning of the specimen. Beside the standard holders that only have
tilting or rotating capabilities of the sample, there are several types of
special holders for heating or cooling experiments, or advanced ones
with nanomanipulating probes. For standard imaging the samples are
placed on a grid of copper mesh. These grids can be made out of
different materials and covered with different types of very thin films,
like carbon films.

The lower section of the column contains the intermediate lens stage,
these lenses (usually three lenses) magnifies the intermediate image
from the objective lens, or the diffraction pattern found in the focal plane
of the objective lens. When doing electron diffraction, field limiting
interchangeable apertures are available (30, 200, and 300 \( \mu \text{m} \)). These
apertures are used to select only the diffracted beams that comes from a region of interest at the specimen.

**Projection Stage, Screen and Digital Imaging**

At the bottom of the column is the projection lens that project the now magnified image onto a fluorescent screen. When the projected electrons hit the screen a green colored image is generated. To record an image photographic techniques have been used earlier, but now several types of digital imaging systems are available. In our experiments we use a very simple setup of a digital camera placed in front of the screen as seen in figure 8. This allow us to record images digitally, however it also has movie recording capability that are of great value when doing in situ probing experiments. During movie recording, high compression algorithms are necessary for reducing file size. We use the DivX codec.

**Imaging Technique**

The transmission electron microscope can in most cases be operated in seven main ways:

- Conventional imaging, the bright- (BF) and dark-field (DF) modes.
- Selected area electron diffraction (SAED)
- Convergent beam electron diffraction (CBED)
- Z-contrast imaging
- Energy dispersive X-ray spectroscopy (EDS)
- Electron energy loss spectroscopy (EELS)

Some transmission electron microscopes also have a scanning beam unit allowing for scanning electron microscopy operation (SEM) and scanning transmission electron microscopy mode (STEM). Beam paths for the different modes is shown in figure 11 at page 22.

In conventional imaging, scattering contrast is used to produce an image of the specimen. Electrons are either transmitted unscattered through the sample, absorbed or scattered at different angles. In bright
field mode the transmitted electrons are collected and then projected at the viewing screen. This shows an image in which the parts of the specimen that the electrons passed through unscattered appears bright, while the parts of the electrons that were scattered or absorbed appears dark, due to the contribution of less electrons in the final image. Best contrast is usually achieved by selecting an small enough aperture so that as many scattered electrons are excluded as possible, this however at a cost of reduced intensity. Different specimen thickness for the electrons to pass through or different elementals also result in change of the intensity of the projected image at the screen, hence a thicker specimen or heavier atoms in specific region of the specimen lowers the intensity from that region. All these different intensities are then summed and contribute to the whole image. If the specimen is a crystalline material, diffraction contrast is also present and depending on orientation of the crystal in relation to the incident beam Bragg diffraction gives contrast enhancements of crystal planes, boundaries, and defects.

Selected area electron diffraction (SAED) can be done at region of interest of the sample. The field limiting aperture provides selection of the region of interest and the intermediate lens is used to focus on the focal plane of the objective lens which in turn produces a diffraction pattern of the crystal at the screen. The tilting mechanism of the goniometer provides tilting of the crystal in one direction. Two tilting directions or rotation are necessary when analyzing diffraction patterns and this is provided by special types of sample holders that are especially used for this purpose. Due to the nature of the electromagnetic lenses the
image is rotated when magnification or operational mode of the TEM are changed. Therefore to be able to make correlations of the ordinary BF/DF imaging and the diffraction pattern, the image rotation must be taken into consideration. This rotation shift can be determined with a known crystallite sample like MoO₃.

The dark field mode is the reverse of the bright field mode. By selecting the diffracted beam of electrons, either by shifting the objective aperture or tilting the incident beam the unscattered beam is excluded and the scattered beam projection of the sample is seen at the screen, see figure 13. This technique is especially useful when it comes visualize crystal interfaces.

The convergent beam electron diffraction method (CBED) uses the prefield of the objective lens as a mini condenser lens system. This permit for a much smaller nanosized electron beam than in the default operational mode. The beam is converged at different angles onto the specimen showing an electron diffraction image, but instead of dots, several small disc shaped images are seen. With the convergent beam technique information from very small regions can be obtained that otherwise is not possible with the SAED method and this method also provides information from the third dimension of the crystal, not just the two dimensional projections that otherwise are seen in conventional electron diffraction.

By letting a nanobeam incident on the sample and then study the high angle electron scattering, high resolution imaging of atoms is possible but this requires an annular dark field detector. This method is called high angle annular dark field imaging (HAADF), or z-contrast and is used in combination with the STEM mode.

The energy dispersive X-ray spectrometry (EDS) method uses a X-ray detector attached to the side of the TEM column next to the specimen. When the specimen is illumined with the electron beam, characteristic X-ray from elements can be analyzed by the detector giving information on the elemental composition of the specimen.

The (EELS), or electron energy loss spectrometry method collects the transmitted electrons and measure their energy loss. This is done in a spectrometer placed at the bottom of the column. Information on local elemental composition is obtained from EELS spectra.
Phase Contrast

The techniques described above belongs to conventional operation mode of the TEM, in which contrast is archived by summing up different contributions to intensity. Theoretically, information is lost when deselection of the scattered electrons are made from the conventional bright field image and atomic resolution is impossible. Due to the wave behavior of the electrons the scattered and unscattered electron waves can then be used to interfere which each other so that their respective wave is super positioned, this is called phase contrast. With phase contrast it is possible to achieve much higher resolution than in the conventional mode. However, due to the complexity of the wave interference, computer simulations and modeling are required to fully interpret the observed image, but then atomic resolution is possible.

More on Diffraction Theory and Crystal Lattices

In a diffraction experiment an incident wave is directed onto a crystal. This beam will interact with the crystal according to Bragg’s Law, equation 1, which relates the beams incident and diffracted angles $\theta$ to the crystal lattice spacing $d$, for a given wavelength $\lambda$ of the beam, figure 12.

$$2d \sin(\theta) = \lambda$$

The beam could either consist of photons, like X-rays, or electrons. Depending on what type of beams used, penetration depth is different. X-rays have a tendency to travel very far through a crystal and therefore powder X-ray diffraction (XRD) is a commonly used method in which powder of the specimen is pressed into a pellet. The diffracted X-rays are recorded on a half spherical photographic film which give rise to the typical XRD spectra. Electron beams do not travel far into a crystal, some hundred nanometers at most, if electron beam energies typical used in electron microscopy are used. One benefit by using electron beams, is that they are much easier to focus to a small spot than X-rays which allows for individual diffraction analysis single small grains.

Crystals can be built up from several basic geometries. There are fourteen types of them, but of seven basic structures: Triclinic, Monoclinic, Orthorhombic, Tetragonal, Cubic, Trigonal, and Hexagonal struc-
The imaging modes of the transmission electron microscope. For simplicity only one of the condenser and intermediate lenses are shown.
Fig. 12: Geometry of the Bragg relation showing the increase in ray length path for one of the rays, result in, at specific angles, constructive and destructive interference.

...
formed by the electron beam will be rotated at some degree relatively to the magnetic field strength of the lens. Changing magnification level therefore always produce a rotation of the image. Because the field strength is changeable in the lens, focus of specimen can be done with fixed lenses and adjusted field strength, compared to the glass lens in light microscopy which is of fixed strength and therefore has to be moved.

The specimen is located between the pole pieces of the objective lens and only a very small space is available due to optimization of performance. Keeping the pole pieces as close to each other as possible is necessary in order to minimize spherical aberration. By selecting a smaller aperture the spherical aberration can be reduced to some degree, but with loss of intensity instead.

To describe how well the beam is focused in an magnetic lens, the disc of least confusion $d_s$ can be used and it is given by the expression:

$$d_s = 0.5MC_s(\alpha)^3,$$

where $M$ is the magnification, $\alpha$ the aperture angle of the lens and $C_s$ is the spherical aberration constant (1-2 mm).\[^{[8]}\]

To decrease $C_s$, has been the main developments of TEM and this had led to a reduced pole piece gap as one of the outcome, however the latest TEM’s now have implemented different types of $C_s$ corrector units to compensate for this error making the pool gap size reduction less important, because with the $C_s$ unit sufficient resolution is achieved anyway.

Chromatic aberrations in magnetic lenses means that electrons with different wavelengths, due to energy spread in the gun or from inelastic
scattering when passing through the specimen, will refract at different angles in the lens according to the Lorentz forces velocity dependency. Figure 14 shows illustrations on spherical and chromatic aberration for glass lenses, which illustrates the concept. Energy filters can be used to filter the electrons from the gun so that monochromatic electrons are used instead which lessens the blurring effect of chromatic aberration.

Astigmatism is when the lens refracts the beam differently in the horizontal plane versus the vertical plane. This can be corrected with a magnetic quadrupole lens. By changing the electric current in the quadrupole lens so that different magnetic pairs produce different strength of the magnetic field, beam deflection is also achieved. Beam deflection is used when aligning the beam to the optical center of the microscope lens system for example.

Fig. 14: Spherical aberration error shown for a regular optic lens (left). Depending on the rays radial distance to optical center, different focus is achieved, an aperture takes away the beams with largest error. Chromatic aberration (right) error gives different focus for different wavelength.

Fig. 15: The different refractions of an output from a perfect-lens cylindric-lens system (left) shows the astigmatism aberration, red solid line is in vertical plane and red dashed line in plane. Both with different focus points. With an electron beam this is corrected with a quadrupole lens (right).
The different type of TEM sample holder used for in situ probing (above) compared to a standard type of holder (below). The in situ holder consists of a piezo driven probe that allows both coarse motion up to some millimeter in range and fine movement with nanometer precision by the piezo element alone.

Detailed view of the inertial sliding mechanism which provides the coarse motion. Fine movement of the probe is accomplished by the piezo element alone. A conducting wire makes electrical contact to the hat, allowing biasing of the sample. The sample itself is usually glued with electrically conductive epoxy to a gold wire of 0.25 mm diameter and slide into position in a metallic tube with electrical connection at the opposing side (left) of the probe.
In-situ TEM Probing

Inertial Slider Probe

In this thesis the work was done using an in-situ TEM probe. The design is based on the scanning tunneling microscope (STM) a small probe unit that scans across the surface of the specimen, following its contours and thereby making a mapped image of the surface with atomic resolution. To actually move the STM tip at such fine level, piezoelectric ceramics are used. These ceramics contracts or expand in size due to the direction and amplitude of an applied voltage and they can be manufactured to customized shape. The tube shape, and its special electrode cutting of the piezo that we use here, is driven by a high voltage (150 V) system and its operational range is several micrometers with nanometer precision. Figure 18 shows a drawing of this assembly. Because the piezo system alone can not make any larger movement than a few micrometer, a coarse motion configuration is needed. Here we use the inertial sliding principal in which a rapid movement can cause an object, lets say a cup of coffee, to slide on a piece of paper at your desk, if instead the paper is moved slowly the cup stays fixed to the paper. By using this "kicking" technique of slow and rapid movement of the piezo ceramic the probe hat that is lightly attached to the sapphire ball, best seen in figure 17 on page 26, can slide into different positions. By using this "kicking" approach in several directions, coarse and fine motion is achieved in three dimensions by the same system.

Fig. 18: Illustration of the inertial slider probe. The 3 mm sapphire ball makes the spider looking head able to slide and be positioned in three dimensions. At its back the high voltage piezo ceramics are isolated from the head. A separate wire connection (not shown) to the head allows for biasing of the specimen.
Software and Electrical Configuration

In our experiments we needed a flexible and adjustable system, easy to configure for different upcoming new tasks. To solve this, LabView from National Instruments was chosen. This allowed us to combine computerized measurement boards together with the firewire camera for correlated measurements and video recording. Labview is a software development platform and is mainly used in a graphical programming environment, figure 19, but it also have C library and matlab extensions. A PXI system contains the signal acquisition boards. Two PXI-6229 16 bit multifunction boards control the probe and generate bias voltage to the specimen for electrical measurements. When resonance studies are made, AC signals are used and this is handled by a PXI-5401 12 bit signal generator board. As a current meter, to measure the sample current we used a PXI-4071 26 bit digital measurement board. Signal adoption was done by a built electronic interface box which also handle the high voltage supply for the piezo. Figure 20 shows the interface electronics.

Specimen Preparation

For in-situ TEM probing, specimen preparation is usually easy to accomplish. A similar type of gold wire, as the one used for the tip is used for the specimen but instead placed at the opposite position to the tip in the holder. To attach nanowires to the top of the gold wire, electrical conductive epoxy glue is used. A gold wire with a diameter of 0.25 mm is cut at appropriate length, and a 45° cut guarantees a tip sharp enough for the experiments. The glue is mixed, then let to dry until its surface is slightly sticky, if it is to wet it will completely soak the gold wire when it is dipped into the glue which is undesirable. After this stage, the gold wire is dipped into the nanomaterial to be studied, carbon nanotube powder or fibrous MoS$_2$I$_6$ nanowire material for example, then let to completely dry. Thereafter the gold wire is inserted into the metallic tube at the opposite side of the probe, see figure 17. This will give a specimen with several hundreds of nanowires attached to the surface of the gold wire which allows for several individual measurements before specimen change of the TEM is necessary. Several nanowires will point in the wrong direction by this method, but there will always be, due to the vast number of them, at least some nanowires that goes in the right direction and are suitable for probing.
In-situ TEM Probing

Fig. 19: View of the graphical programming environment of the LabView, the type of development software that we use in our system setup.

Fig. 20: The interface electronic that connects the probe with the PXI system. Down right one can see the two high voltage power supply units. Top right is the home made circuit board together with the high voltage operational amplifiers that are attached to the black heat sink. Left in image is three green circuit boards connecting by cable the PXI-system.
Measuring Electrical Transport Properties

In situ electrical measurements on a nanowire can be achieved with the in situ probe. Inside the TEM during operation the probe is aligned to the nanowire. Due to the two dimensional projection of the TEM, height differences between the probe and the nanowire is problematic to estimate and a workaround for this is to tilt the sample holder 45° back and forth during the approaching of the probe to the nanowire. When the distance to the nanowire is close enough, focusing technique can be used for height differences and for final alignment. By holding a small bias applied between the tip and nanowire, contact establishment is easily observed by measuring the current.

When contact is made, electrical characterization of the nanowire can be done. The software allows for IV characterization and biasing of the sample up to 150 V. Current is measured in the range from sub microampere up to tens of milliamperes.

Due to the two probe nature of the system, contact resistance is an unknown variable. To give an estimate of the contact resistance a procedure by repeatedly making resistance measurement with the probe alongside the nanowire can be utilized. A fitting model can then be used on the data of the resistance vs. length plot, where the intercept at zero length gives the contact resistance value, see figure 21.

![Contact Resistance Determination](image)

**Fig. 21:** Example of contact resistance determination by several measurements along the length of a carbon nanocone, the intercept gives a contact resistance value of 5±1 kΩ. Due to the conic shape a nonlinear resistance function is obtained.
Annealing of Nanowires and Melting Nanoparticles

When the nanowires are electrically heated, the known input power to the system can be used for model the temperature of the nanowire according to equation 3, [2]

\[ \kappa A \frac{\partial^2 T}{\partial x^2} dx - 2\pi r \sigma (T^4 - T_0^4) dx + \frac{RI}{L} dx = 0 \]  

(3)

Where \( R \) is the resistance of the wire, \( I \) is the electrical current, \( T \), the temperature of the wire, \( T_0 \), surrounding temperature, \( A \) is the cross section area, \( L \) is half the length of the nanowire, \( \kappa \) is the thermal conductivity, \( \sigma \) is the Stefan Boltzmann constant. Because the probe conduct two probe measurements only, contact resistance is usually an unknown variable and depending on situation, high contact resistance might mask the real input power of the nanowire. There are solutions to compensate for this error, and besides the solution mentioned above, gold nanoparticles could be attached to the side of the nanowire and then calibration of the model with the known melting temperature of the nanoparticles is possible. Figure 33 shows such a case when gold nanoparticles are melting.

![Graphs showing temperature modeling of a heated nanowire.](image1)

Fig. 22: Graphs showing temperature modeling of a heated nanowire. Due to increase energy loss as black body radiation, at high power levels the temperature curve flattens out (left). The nanowires are attached to two heat sinks by its ends due to the probe contacts and therefore a temperature profile is given along the wire, at high temperature this curve flattens out at middle (right).

When a nanowire is heated to a certain temperature it will start to melt. The semi metallic MoS\(_2\) I\(_6\) nanowires conduct poorly and therefore high voltage (tens of volts) are being applied to produce high enough current for annealing. When these nanowires transform, the electrical conductivity goes up several orders of magnitude and to prevent burn off by the high voltage still being applied, the nanowire is placed in series with a current limiting resistor \( R_s \), that limits the maximum current according to the relation \( I_{max} = \frac{U_{bias}}{R_s} \). For the MoS\(_2\) I\(_6\) nanowires 100 k\( \Omega \) to 300 k\( \Omega \) is suitable current limiting resistance.
During in situ probing of nanomaterial selected area electron diffraction provides a useful tool when analyzing the annealing progress. Real time imaging of the diffraction pattern gives information on the actual ongoing coarsening process. Figure 24 shows a MoS$_2$ nanowire material transformation, due to electrical heating of the nanowire, followed by a crystal growth process.

The grains in a single phase polycrystalline material are generally oriented in several random directions. Depending on the orientation to each other, the interfaces between them might be more or less favorable. A special case, is if the grain boundaries free energy is independent of the orientation of the grains relative to each other, then the boundary tensions in a cusp interface between three adjacent grains, $\gamma_{12}$, $\gamma_{13}$, and $\gamma_{23}$ must balance according to the equation 4, were $\theta_1$, $\theta_2$, and $\theta_3$ are the angles for the intercept of the three boundaries.

$$\frac{\gamma_{12}}{\sin \theta_3} = \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{23}}{\sin \theta_1}$$

(4)

If the free energy for each of the three grain boundaries also are equal then $\theta_1 = \theta_2 = \theta_3 = 120^\circ$. If these conditions are satisfied then a
metastable equilibrium between the grains are possible, and the grains forms hexagon surfaces. Grains that holds the criteria of 120° at its cups, but have a total number of sides on one plane that are not equal to six, will form curved edges that are concave respective convex depending if the number of sides are less than or more than six. During an annealing phase these grains will either shrink respectively grow in size, see figure 25. This is called grain coarsening and begins in metals at about half their melting temperature and is considered a slow process compared to the phase transformation process.\textsuperscript{[83]}

Fig. 25: If all interfacial energies are equal and all intercept angles of the grain boundaries are 120°, then depending on number of edges is more or less than six, the grain either grow or shrink during annealing.
Electromechanical Resonance of Nanowires

**Fig. 26:** The MoS$_2$-based bundle will come into electromechanical resonance at specific frequencies from the alternating electric field between specimen and probe tip. (a) is when 143 kHz signal is used (no resonance) and (b) when 142 kHz signal is used (resonance). The dark field up to the left is the opposing probe tip and the scale bar is 3 µm.

Resonance studies are commonly used in beam bending theory to determine material properties such as shear and tensile modulus. The material to be analyzed is forced into vibration and the vibration frequency is measured. Knowledge of the resonance frequency $\nu$ make determination of the tensile modulus $E$ possible by using the Bernoulli Euler equation 5, with equation 6 as solution, where $\beta$ is a constant and for the first oscillating mode $\beta = 1.875$. The tensile modulus $E$ can then be determined by measuring the resonance frequency $\nu_1$, the length $L$, and area $A$ together with the knowledge of density $\rho$ for the material. $I$ is the moment of inertia, and $w$ is the beam deflection.

\[
\frac{EI}{\partial^4 w}{\partial x^4} + \rho A \frac{\partial^2 w}{\partial t^2} = 0 \tag{5}
\]

\[
\nu = \frac{\beta^2}{8\pi L^2} \sqrt\frac{EI}{\rho A} \tag{6}
\]

In the in situ probing method, the nanowire is forced into resonance by applying an alternating electric field between the substrate and the probe tip. Increasing the frequency of the electric field will bring the nanowire into oscillation at specific frequencies, see figure 26. This method has been applied by others in situ TEM on nanowires,[84–87] in situ TEM on curved nanowires,[88] in situ SEM on nanowires,[89] to mention some of the studies. For vibration of carbon nanotubes a review is available.[90]
When measurements are made on bundles of nanowires, the Bernoulli Euler equation will usually not give the tensile modulus for the nanowires but instead the bending modulus of the bundle. This since the interaction forces between each nanowire in the bundle, usually are small and therefore the resulting bending modulus will be much smaller than the tensile modulus for the nanowires. For example, Mo$_2$S$_3$, have a high tensile/shear ratio and therefore the bending modulus of the bundles will be much lower than the tensile modulus of the individual nanowires.

Theoretical calculations on this type of method when an electric field is used to bring the nanowire into resonance, predicts that at high field strength of more than 0.5 V/nm the obtained modulus might be with an high error of uncertainty of more than 10%, compared to the true value and if the nanowires length to diameter ratio is more than hundred. In our experiments field strengths of 0.1/nm or less is used.

Another problem with this method is that the clamping point is usually of uncertain strength and the clamp points real location is difficult to determine, obstacles might block the view at the clamp point or the clamping point might be positioned slightly down into the glue that was used to fix the nanowire to the probe tip. This will also make it difficult to measure the length of the free nanowire end, a 10% uncertainty in the length gives 10%-20% uncertainty in the determined tensile modulus. A bad compared to a good clamping point with high stiffness gives another 10% uncertainty in the modulus.

The in situ resonance method has also been applied by others to measure the work function of nanobelts. Equation 7 states that the total force $F$ that contributes to the amplitude of the nanowire forced into oscillation at a frequency $f$ by an alternating electric field $V_{ac}$ is also governed by the differences of the work function for the nanowire $\phi_{NW}$ and the opposing gold probe $\phi_{Au}$. By applying a DC offset $V_{dc}$ to the electric field this difference between the work functions can be canceled and if done so, the oscillating amplitude of the nanowire goes down to zero. The offset voltage can then be used to directly measure the work function of the nanowire by using the knowledge of the opposing probes work function. $\alpha$ and $\beta$ are constants.

\[
F = \beta(Q_0 + \alpha(eV_{dc} + V_{ac}\cos(2\pi ft)))^2
= \alpha^2\beta[(\phi_{Au} - \phi_{NW} + eV_{dc})^2 + e^2V_{ac}^2/2] + 2eV_{ac}(\phi_{Au} - \phi_{NW} + eV_{dc})\cos(2\pi ft) + e^2V_{ac}^2/2\cos(4\pi ft) \tag{7}
\]

We have tried to use this methods but with inconclusive results, in which we found a nanowire probe distance dependency of the oscillating amplitude of the nanowire.
SUMMARY AND OUTLOOK

Summary of Appended Papers

Paper I: Joule heating of Mo$_5$S$_3$I$_6$ nanowires

In this paper we, using the in-situ TEM probing method, characterized the electrical properties of the Mo$_5$S$_3$I$_6$ nanowires. Measurements were done on individual bundles. Measurements on fifteen samples that were 20-1000 nm in diameter and one to several hundred µm in length showed that the electrical conductivity at the beginning was below 1000 S/m, but after transformation and annealing conductivity went up several orders of magnitude to $1.8 \times 10^8$ S/m. The highest current density, before failure, for the wires were $8 \times 10^6$ A/cm$^2$.

During the Mo$_5$S$_3$I$_6$ nanowires transformation, it was observed that the wires straighten out when a solid metallic molybdenum wire was formed. This transformation took place in the beginning of the overall process and happened instantly. During this process the diameter of the nanowires were reduced by 30-60% and this figure agrees with the more compact structure of metallic molybdenum.

The newly formed metallic nanowire contains small grains of molybdenum crystals and by continued electric heating of the wire, these grains annealed into bigger ones until single grains covered the hole diameter of the nanowire.

Figure 27, shows the transformation process from the Mo$_5$S$_3$I$_6$ nanowires to single crystalline molybdenum nanowires as function of conductivity and annealing power.

Paper II: Electromechanical resonance of Mo$_5$S$_3$I$_6$ nanowires

In the second paper we studied the mechanical properties of the Mo$_5$S$_3$I$_6$ nanowires bundles. Previously measurements of individual bundles were made by Kis et al.$^{[27]}$ using AFM.
SUMMARY AND OUTLOOK

Fig. 27: The transformation of Mo$_x$S$_2$I$_y$ nanowires bundles (A) to polycrystalline molybdenum nanowire (B) followed by annealing to single crystalline nanowire (C and D). Scale bar in (A) is 50 nm and in (C-D) 100 nm. The graph shows the corresponding increase in electrical conductivity and annealing power input. The drop at 300 s is due to a decrease in bias for diffraction studies.
The frequency determination in these electromechanical resonance experiment is very accurate due to the sharp resonance curve and low damping factors as shown in figure 28.

![Figure 28](image)

Fig. 28: Q value determination curve (right) indicates high Q values of the experiments with low damping factors (right).

<table>
<thead>
<tr>
<th>$E_{b\text{in situ}}$</th>
<th>$E_{t\text{sound}}^{[10]}$</th>
<th>$E_{t\text{AFM}}^{[27]}$</th>
<th>$E_{t\text{theory}}^{[27]}$</th>
<th>$G_{\text{theory}}^{[27]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9±3.0 GPa</td>
<td>3.8±0.75 GPa</td>
<td>430 GPa</td>
<td>45 GPa</td>
<td>0.45±0.10 GPa</td>
</tr>
</tbody>
</table>

The bending modulus for the MoS$_2$I$_6$ nanowires were determined by the in-situ TEM probing method to 4.9±3.0 GPa. The major part of the resonance frequencies was found in the range 100 kHz to 300 kHz. The collected results from the resonance studies can be seen in figure 29. The spread of the measured values was large, but the major part was in the range 1-10 GPa. The determined value for the bending modulus is more than an order lower than the tensile modulus from the AFM experiments$^{[27]}$. Since the nanowires are assembled into rope bundle structures, this is not a surprising result, because a bundle consists of weakly interacting nanowires where slipping between the nanowires easily occur.

Table 2 gives a comparison of results obtained from others and calculations of modulus by sound propagation measurements done for the material. The high difference between our measurements and the AFM study$^{[27]}$ may be explained by the rope-bundling of the MoS$_2$I$_6$ in which a bundle with larger diameter will have a lower module.$^{[94]}$ Our bundles were one order of magnitude larger than the ones in the AFM
study.

![Graph showing bending modulus vs. diameter](image)

**Fig. 29:** The bending modulus from the experiments plotted as function of bundle diameter. The amplitude oscillation direction is either planar and orthogonal to the view projection plane of the bundle.

**Paper III: Sintering of silver nanoparticle ink**

In the third work we studied the sintering process of conductive silver nanoparticle ink. Normally after printing a sintering step by heating in furnace is used to improve conductivity of the printed circuits but here, we by electrical heating, sinters the sample.\(^{[30]}\) During the electrically sintering we monitored the process in situ at the nanoscale.

![Images showing sintering process](image)

**Fig. 30:** During sintering of the silver nanoparticle ink, carbonization of the solvent was found to take place, leaving a carbon net behind after that the silver evaporated away.
During electric heating of the silver nanoparticle ink, the dispersion agent was carbonized followed by evaporations of the nanoparticles (a to d). Resistance and sintering power as function of time (e) for three experiments with corresponding marks (a to d) of TEM images above. Plot of resistance versus the number of particles melted away (f). If one assumes contact resistance of 15 kΩ, from the intercept, then the resistance of the net at 5 kΩ agrees to the resistance of a graphite structure of similar size.
SUMMARY AND OUTLOOK

Two processes was found to occur, first a slow sintering process of improving conductivity, as seen by the plot in figure 31e, and TEM images in figure 4a,b at page 10, followed by a quick jump in conductivity which is probably due to a carbonization process of the dispersive agent. The similarities between the resistance curves in figure 31 towards a common phenomena such as carbonization and not to curing of high ohmic contacts and the arrow in figure 31a indicates that due to the spacing between the particles no continuous metallic contact exist which further supports the carbonization theory.

The actual carbonization process occurs before the particles evaporates at a power level of 1 µW to 100 µW and power densities of 0.1-10 mW/µm³. The carbon net shaped structure left behind is more durable than the silver nanoparticles, thus it have a higher electric current threshold before failure. A plot of the numbers of particles melted away as function of resistance gives an estimate of the resistance of the carbon net which is 5 kΩ and is of the same order as a graphite structure of similar size would have.

Paper IV: Simple and efficient gold nanoparticles deposition on CNT

In this paper we developed a new and simple method for producing gold nanoparticles deposition onto carbon nanotubes. This is done by premixing different amounts of carbon nanotubes with a sodium citrate solution, followed by ultrasonication for 5 min. The mixture is diluted to a 4% solution by distilled water followed by heating to the boiling point and during stirring different amounts of HAuCl₄ was added, depending on amount of coverage and size of particles needed. The solution is kept boiling for 5 min followed by separation and washing of the carbon nanotubes, and is done by centrifugation at 6000 rpm. During the premixing phase sodium citrate, shells formed on the carbon nanotubes, and later during the injection of HAuCl₄ these tubes serves as substrate for the reduction of the gold salt being added. By different concentrations of HAuCl₄, the size of the nanoparticles is controlled. A high density of nanotubes, reduces the coverage rate of the nanoparticles.

Paper V: Carbon nanocages grown by gold templating

The carbon nanotubes with deposited gold nanoparticles, presented in paper IV, were probed with the in-situ TEM method.

When the CNT-Au composite is heated in situ it was found that, due to the carbon in the carbon nanotube carbon cages were being formed
around the gold nanoparticles, see figure 33b. Because the nanoparticles have a controllable size, the size of the cages can also be controlled.

Another result is that because the melting temperatures of metallic nanoparticles is a known parameter, observation of the melting process of the attached nanoparticles to another materials surface can be used as a tool for temperature estimation and therefore makes it able to calibrate temperature models by calculating the otherwise undetermined contact resistance. By continual electric heating of the carbon nanotube with the attached cages to its surface it was found that the cages melted away at a temperature of 3800 K. This temperature was calculated by the
SUMMARY AND OUTLOOK

modeling technique described above.

Paper VI: Mo₆S₃I₆-Au composites: synthesis, conductance, and applications

By linking gold nanoparticles to the surface of the Mo₆S₃I₆ material the electric resistance could be tuned. Mo₆S₃I₆ nanowires has in the unmodified state resistance in the range of tens of MΩs. When different amounts of particles were attached to the nanowires surfaces the resistance were in the range of 0.1-1 MΩ. The reason for this increase in conductivity is however unclear, several mechanisms are possible. One could be that the gold nanoparticles improves wire to wire contacts, or the particles themselves could bridge the sulfur bonding at the nanowires surface, which otherwise is of poor conductivity.

Besides conductivity improvements, gold linking are widely used for bio molecule connections. Here we used thiol groups to bond to the the gold nanoparticles that are attached to the nanowire surface. The thiol groups links to the ends of single stranded DNA chains that in a second step were hybridized with a fully matched sequence.

During the thiol step the resistance was found to decrease and later to increased again during hybridization. This is due to the conductance differences between single stranded DNA and double stranded DNA. This resistance change could be used for and implemented in different biosensor applications.

Tab. 3: Measured electric current in Mo₆S₃I₆ sample at different stages of DNA linking: without DNA, with single stranded DNA (ssDNA), and double stranded DNA (dsDNA). Bias voltage was 5 V. IV properties, not shown here, are ohmic.

<table>
<thead>
<tr>
<th>Process stage</th>
<th>Exp. 1 (µA)</th>
<th>Exp. 2 (µA)</th>
<th>Exp. 3 (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo₆S₃I₆-Au</td>
<td>22.2</td>
<td>14.4</td>
<td>14.8</td>
</tr>
<tr>
<td>Mo₆S₃I₆-Au-ssDNA</td>
<td>14.2</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Mo₆S₃I₆-Au-dsDNA</td>
<td>17.3</td>
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</table>
Conclusions and Outlook

In this thesis in-situ TEM probing experiments have been presented on several types of nanomaterials, proving its versatility. In situ measurements of electric transport properties of individual building blocks give detailed information about the system, and often key properties of the material. Other methods, such as electromechanical resonance, permits measurements of mechanical parameters of the material at the same time, showing the flexibility of the system. Different types of in situ studies of processes, such as the transformation process of the MoS2I6 material also show the diversity of the system.

This thesis is about in-situ TEM probing and a logical outlook at this subject would therefore be on the next generations of probing equipment. The in-situ TEM probing of today basically consist of the imaging of the TEM combined with some movable probe able to do basic electrical measurement tasks. One project would be to implement more measurement tools into the system and two such tools would be an AFM system as well as an optical system. The AFM allows force measurement and the optical system would give access to several spectroscopy methods. The release of the Cs correcting units for TEM mean that the size restriction of the pool piece gap can be loosen, sub ångstrom resolution is provided anyway, and this will provide more space for more tools within the TEM objective lens.

On a longer time scale an outlook would be the capabilities of several probes with more of assembling possibilities. For building more complex devices in situ.
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APPENDIX TECHNICAL DETAILS

The appendix consists of data tables, recipes, circuit drawings, problem discussions and suggested improvements of the equipment.

Transmission Electron Microscopy

Electron Beam Energy and Wavelength

<table>
<thead>
<tr>
<th>Accelerating voltage</th>
<th>Non relativistic wavelength</th>
<th>Relativistic wavelength</th>
<th>Relativistic velocity</th>
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<td>80 kV</td>
<td>4.34 pm</td>
<td>4.18 pm</td>
<td>1.51·10⁶ m/s</td>
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<tr>
<td>100 kV</td>
<td>3.88 pm</td>
<td>3.70 pm</td>
<td>1.64·10⁶ m/s</td>
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<tr>
<td>120 kV</td>
<td>3.54 pm</td>
<td>3.35 pm</td>
<td>1.76·10⁶ m/s</td>
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<tr>
<td>160 kV</td>
<td>3.07 pm</td>
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<td>1.94·10⁶ m/s</td>
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<td>200 kV</td>
<td>2.74 nm</td>
<td>2.51 pm</td>
<td>2.08·10⁶ m/s</td>
</tr>
</tbody>
</table>
APPENDIX TECHNICAL DETAILS

Beam Alignment Procedure for JEOL-2000FX

1. Read the manual it is good, this is just supposed to be a quick guide.

2. After high tension and filament has been turned on according to local procedures. Remove all apertures: condenser-, objective-, and field limiting-apertures.

3. Set magnification to 4000X and spot size to 3 then make the beam as small as possible by reducing brightness and center it on the screen with the shifting coils. Set spot size to 1, make the beam small again and re center the beam with the gun shifting coils. Iterate procedure until no beam deflection are seen.

4. Change the brightness of the beam so that it covers the screen then insert condenser aperture at appropriate size, center the aperture so that it correlates with screen center.

5. Make the beam small by turning down brightness and make the beam circular with the condenser stigmators.

6. Focus on specimen at magnification 25kX, then by using the objective lens wobbler, adjust the current center with the objective stigmators, the screen should expand and contract uniformly and central to the screens center.

7. Focus the specimen at 100kX and with the high tension wobbler adjust voltage center with the objective stigmators, the screen should expand and contract uniformly and central to the screens center, the binoculars are of great use at this stage.

8. Iterate procedures by this order if necessary. Final tweaking of the objective stigmators is needed for images with magnification larger than 50kX.
Sample Preparation Technique and Recipes

To make very fine tungsten tip by etching, the following recipe can be used.

1. Prepare a solution of 16.8 g KOH pellets in 100 ml deionized water.
2. Cut a piece of tungsten wire and put the positive electric connector onto it then dip it down 1 mm into the solution.
3. Set negative bias in the solution.
4. Set the power supply to 10 V and current limiter at 2 mA.

To glue samples onto a gold wire, the following recipe can be used.

1. Mix conductive epoxy, we use Circuit Works CW2400, thoroughly. Do not mix a to small amount of it, because it is hard to get proper mixing otherwise.
2. Let to dry until the surface is hard and sticky.
3. Cut gold wire at 45° angle with a pair of scissors.
4. Using tweezers, dip the gold wire into the glue and then dip the wire into the sample material to be tested.
5. Let to dry completely before insertion in holder and TEM.
6. Check the resistance level of the conductivity glue by measuring on a dried spot on paper with a multimeter from time to time to check that the glue is properly conductive.
Electronics and Circuit Drawing

Technical Details of the PXI system

The interface electronics, that connects the PXI-system with the inertial slider probe, adjust the signal-levels by using APEX PA84 (high voltage) operational amplifiers. They adjust the 10 V output signal of the 6229 PXI-DAQ boards to 150 V that drives the piezo and bias of the specimen. The potential over the series resistor that limits the maximum amount of current allowed to flow through the specimen and the potential over the specimen are measured by two INA128 instrumental amplifiers. The resulting output signal from the instrumental amplifiers are connected to the 6229 DAQ board. The electronic circuit drawing are shown in figure 34.

We used a PXI-system from National Instruments to control the in situ TEM probe. Timing is important in the measurement system, but was a bit tricky to implement. The 6229-DAQ board of the PXI system forbid update of one or several channels if one of the channels are active doing sampling, however, all signals must simultaneously be updated. For example, the board that drives the piezo element can not do separate parallel tasks like bias ramping, i.e. IV measurements of the sample, even if there is one output channel left over on the board. Thus the other three channels on the board are locked. This results in strange errors messages, that do not point to the problem. The best solution is to move bias signals to a separate board, and this is the reason for our use of two 6229 boards. There are other ways to solve the timing, for example, using a real time operating system, such as the National Instruments LabVIEW Real-Time, that can be used for embedded controllers, but care must be taken to choose proper PXI boards, for example our PXI oscilloscope and signal generator are not compatible with this system. We use Windows as the operating system with the shortest time length of 1 ms, but off course the sampling rates on the 6229 board is much higher (250 kS/s).

Digitalization of the BSE signal of a JEOL-2000FX with ASID

A comment for someone who has an old TEM with a scanning unit (like the JEOL 2000FX):

If the transmission electron microscope is equipped with a scanning unit (ASID) together with a backscatter detector that allows for scanning electron microscopy (SEM) operation, then the SEM image produced by the system can be exported and digitalized.

The signal from the backscattering electron detector includes a pream-
plifier which adjusting signal levels to standard signal conditions. By letting the ASID panel scan the beam over the sample in SEM mode, this signal could be captured directly by the DAQ board of the PXI system. However, a sync signal is also needed and this signal is available externally to be used by the EDS unit. For JEOL 2000FX: proper jumping of the circuit board in the ASID unit, at the scan generator board pin SG6 and 605, is required and then the sync signal can be imported into the PXI system.
Fig. 3: Circuit diagram of electronic interface between FN1 system and probe.
Tab. 5: Data of the Mo$_5$S$_3$I$_6$ and other materials. Superscripts of "in situ" marks obtained results presented in this thesis. The electrical data for graphite is given for the in plane direction.

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<tr>
<th>Material</th>
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<th>Conductivity</th>
<th>Density</th>
<th>Speed of sound</th>
<th>Melting Point</th>
<th>Tensile modulus</th>
<th>Shear modulus</th>
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<tr>
<td></td>
<td>(Ωm)</td>
<td>(Sm$^{-1}$)</td>
<td>($10^3$ kgm$^{-3}$)</td>
<td>(ms$^{-1}$)</td>
<td>(K)</td>
<td>(GPa)</td>
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<tr>
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<td>1.43</td>
<td>1630±160</td>
<td>430 [27]</td>
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