Fabrication, functionalization and electrical conductance modulation of nanoparticle based molecular electronic Nano-devices

ISHTIAQ HASSAN WANI
Over the years many techniques have been proposed for the purpose of the formation of electrically conducting metal-molecule-metal junctions. One such technique utilizes gold-nanoparticles (AuNPs) that could assist in contacting small molecules between large gaps. The ideal device structure then comprises of one nanoparticle and two molecules that are aligned as electrode1-molecule-AuNP-molecule-electrode2.

In present work these AuNP-molecule hybrids were fabricated inside sub 20 nm sized nanogaps between nanoelectrodes. The nanogaps were fabricated by milling of thin gold wires using focused ion beam. The tuning of the ion dosage resulted in the tuning of the gap size and the smallest nanogap of 2.3 nm was achieved.

The nano molecular electronic device (nanoMoED) platform comprised of the AuNPs that were assembled inside the nanogaps via dielectrophoresis. Two types of the AuNPs were used that were different from each other due to their functionalization chemistry. The low bias resistance $R_{LB}$ of the nanoMoED platform was (i) reduced as compared to the nanogaps (ii) remained stable in toluene and air, and (iii) was reduced when exposed to the electron beam.

The nanoMoED platform was functionalized with various molecules using the molecular place exchange method. The successful functionalization resulted in the reduction of the $R_{LB}$. The smallest value of the $R_{LB}$ of the nanoMoED devices was achieved when the inserted molecule was not only highly conducting but also its length was same as the initial spacing between the AuNPs.

The nitrogen dioxide (NO$_2$) molecules reduced the $R_{LB}$ of the nanoMoED devices that were made with 4,4'-biphenyl dithiol. The theoretical simulations showed that this reduction was due to the induced states at Fermi energy of the junction. The nanoMoED devices made with 1,8-octanedithiol showed conductance switching between two levels because of different geometries of the Au-S contact. This switching vanished when these devices were exposed to NO$_2$ and a strong enhancement of signal to noise ratio was observed.

On the basis of these results this thesis suggests possible routes for the fabrication of highly conducting nanoMoED devices as well as elucidates the possibility of using the nanoMoED devices for gas sensing applications.

Keywords: Molecular electronics, gas sensor, hybrid materials, place exchange, random telegraph signal

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ISSN 1651-6214
urn:nbn:se:uu:diva-347161 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-347161)
This thesis is dedicated to my mother Nasim Akhter and my father Ghulam Hassan, my whole family and especially to my (late) grandfather who dedicated his life for education. After all, dedication is to my wife Shamaila and my two little princesses Zoonia and Shiza.

“I begin with an idea and then it becomes something else...”

Pablo Picasso (1881-1973)
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Fabrication of reproducible sub-5 nm nanogaps by a focused ion beam and observation of Fowler-Nordheim tunneling.  

II Designing sterically demanding thiolate coated AuNPs for electrical characterization of BPDT in a NP-molecule-nanoelectrode platform.  

III Investigation of the factors affecting the fabrication of highly conducting NP-molecule junctions inside sub 20 nm molecular electronic devices  
(Manuscript in preparation)

IV Sub 20 nm metal-conjugated molecule junctions acting as a nitrogen dioxide sensor  
(In submission)

V Nitrogen dioxide induced modulation of random telegraph conductance signal through gold-octanediethiol junctions.  
I. H. Wani, A. Orthaber, S. Hassan M. Jafri, A. Grigoriev, R. Ahuja and K. Leifer  
(In submission)

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Unpublished results
Chapter 3, Figure 3-9: SEM imaging performed for visual characterization of nanoMoED platform and its effect on the electrical properties of the platform.

Chapter 4, Figure 4-7: Transition voltage spectroscopy (TVS) of nanoMoED device 2

Chapter 5, Figure 5-4: current versus time response of nanoMoED device 2 at 150mV applied bias in air (green) N2 (blue) and NO2 (red).

Chapter 5, Figure 5-6: Comparison of response times of original data (upper figure) and rate of change calculated data (lower figure).

Appendix
Author’s contribution to articles

I. Carried out the nanogap fabrication experiment, data analysis and contributed to the preparation of the manuscript.

II. Carried out nanogap fabrication, trapping of gold nanoparticles and place exchange with 4,4’-biphenyldithiol. The SEM imaging of the devices and the relevant literature review were also added to the manuscript.

III. Carried out nanogap fabrication, trapping of gold nanoparticles and place exchange with 4,4’-([2,2’-bithiophene]-5,5’-diyl)dibenzeneethiol (0TBT) and nTBT (n=1,2,3) molecules. Prepared the manuscript.

IV. Carried out nanogap fabrication, trapping of gold nanoparticles, place exchange with 4, 4’-biphenyldithiol, performed gas sensing experiments. Performed all SEM, electrical characterization and data analysis. Prepared the manuscript.

V. Carried out nanogap fabrication, trapping of gold nanoparticles and chemical synthesis of molecular junctions via deprotection step. Performed gas sensing experiments. Performed all SEM and electrical characterization. Prepared the manuscript.
Also Published


III. H. Li, S. Wambua, D. Lakshya, I. H. Wani, S. Hassan. M. Jafri, F. Vonau, L. Simon, and K. Leifer. Defect engineering on graphene stiffness in cryogenic and room temperatures by focused ion beam irradiation. (in manuscript)

IV. Enhanced gas sensing performance of ZnS-CdS heteronanowires functionalized graphene gas sensor

H. Li, I. H. Wani, A. Ashok, Y. Han, S. H. M. Jafri, K. Leifer (Journal of physics; conference series)

V. Fabrication of sub 20nm molecular electronic devices by conduction tuning with place exchange in bridge junction platform.

S. Hassan M. Jafri, A. Hayat, I. H. Wani, A. Orthaber, A. Wallner, H. Ottosson, K. Leifer (In manuscript)

VI. Electrical Characterization of Ultrathin Films of ZnS-CdS Hetero-Nanowires by Langmuir-Blodgett Assembly in Nanoelectrode Platform and Observation of Light Induced Current

A. Ashok, H. Li, S. Hassan M. Jafri, I. H. Wani, A. Dalui, D. Sarma, S. Acharya and K. Leifer (In manuscript)

Conference contributions

I. Synthesis of nanoscale electronic devices by molecular place exchange reactions in the nanoparticle nanoelectrode bridge platform.

II. Making of functional devices by exchange of stopper ligand with conducting molecules in the nanoparticle-nanoelectrode bridge platform. 


IV. Focused ion beam based highly resistive and reproducible sub-5nm nanogaps in thin gold wire. European Microscopy Congress 2016: Proceedings (2017) 

S.H.M. Jafri, H. Li, I. H. Wani, K. Leifer.

Acknowledgment of contribution
The author duly acknowledges
All the collaborators who have worked and obtained results that are part of this thesis.
All who have at any part contributed to the understanding presented herein.
The Erasmus Mundus Experts consortium for providing the financial support

A request
Since large proportion of this thesis is not published. Kindly acknowledge if you consider it for your work.
Definitions

- Nanogaps; these are gold nanoelectrodes that are separated by approximately 20 nm.
- Protected AuNPs: These are gold nanoparticles functionalized by ω-thiol protected α,ω-alkanedihtiol. Protection group is triphenylmethy. The size of these AuNPs is 4.9±1.1 nm
- Stopper AuNPs: synthesized in one phase, these NPs have two types of ligands on the surface. Alkane monothiol chain and stopper molecule. These AuNPs with variable concentrations of stopper and alkane monothiol can be synthesized. Size of these AuNPs is 6.3±0.7 nm when stoppers are 5% and remaining ligands are 95%.
- nanoMoED; Nano molecular electronic device
- NanoMoED Platform; this is the device stage when above mentioned nanoparticles are trapped inside the nanogaps. Trapping of both types of nanoparticles is accomplished by dielectrophoresis. At this stage the nanoparticles are chemically isolated from each other because one end of each ligand is protected to bind to the gold surfaces. Chapter 3 describes the fabrication of nanoMoED Platform
- NanoMoED device; this is stage of device synthesis when both ends of molecules are chemically linked to gold surfaces. Chapter 4 describes the synthesis of nanoMoEDs.
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<td>Atomic Force Microscope</td>
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<td>AuNP</td>
<td>Gold nanoparticle</td>
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<td>BPD T</td>
<td>4,4’-biphenylthiol</td>
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<td>Computer aided drawing</td>
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<td>CP-AFM</td>
<td>Conducting Probe-AFM</td>
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<td>EBL</td>
<td>Electron beam lithography</td>
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<td>FIB</td>
<td>Focused ion beam</td>
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<td>HDT</td>
<td>1,6-hexanediethiol</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>IETS</td>
<td>Inelastic electron tunneling spectroscopy</td>
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<td>LB</td>
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<td>nanoMoED</td>
<td>Nano Molecular Electronic Devices</td>
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<td>1,8-octanediethiol</td>
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<td>OM</td>
<td>Optical Microscope</td>
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<td>PE</td>
<td>Place exchange</td>
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<td>Peak Force QNM</td>
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<td>STM</td>
<td>Scanning tunneling microscope</td>
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<tr>
<td>TBT</td>
<td>Thiophene-benzene-thiophene</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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1. Introduction

Since 90s, a new class of organic-inorganic hybrid materials systems consisting of gold nanoparticles (AuNP) that are linked to each other via organic molecules that are terminated with thiol (-SH) anchor groups has emerged as an alternative to be used for electronic devices.\(^{(1-3)}\) The use of this hybrid system as an electronic material is attributed to (i) the possibility to explore the physical properties of organic molecules, (ii) introduce organic molecules as component in electrical circuits, (iii) miniaturize the size and reduce the costs of electronic components, and (iv) address challenges in electrically connecting single and few molecules with measurement instruments.

Molecular electronic devices containing AuNPs bridged with organic molecules are versatile considering the possibility of changing the interlinking molecule via different methods e.g., molecular place exchange reactions.\(^{(4, 5)}\) Such molecular electronics devices can be fabricated in different geometries such as 1D nanoparticle-molecule wires between nanometer spaced metal electrodes and/or 2D nanoparticle-molecule networks between micrometer spaced electrodes with various interlinking molecules.\(^{(6)}\) The synthesis of such NP assisted molecular electronics devices with different molecules leads to the observation of vibrational, optoelectronic and thermoelectric properties.\(^{(3, 5-10)}\)

The work presented in this thesis is a continuation of the work that has been being carried out in Uppsala University related to molecular electronics in general and related to gold nanoparticle-molecule hybrid materials synthesized inside sub 20 nm spaced electrodes, specifically. Previously, it has been demonstrated that (i) the metallic electrodes that are separated by less than 20 nm nanogaps can be fabricated using focused ion beam (FIB) milling, electrochemical deposition and electromigration methods, (ii) the gold nanoparticle of size \(4.9 \pm 1.1\) nm can be prepared in a way that one end of the 1,6-hexanedithiol (HDT) or 1,8-octanethiol (ODT) molecule can be attached with the surface of gold nanoparticle while the other end is protected using triphenylmethyl (trityl) group, (iii) then these AuNPs can be assembled inside the FIB milled nanogaps using dielectrophoretic trapping technique and the protection group can be subsequently removed for the purpose of connecting the molecule between surface of two AuNPs which results in formation of metal-molecule contacts, (iv) the vibrational signatures of the molecule can be observed by performing inelastic electron tunneling spectroscopy (IETS).\(^{(9-13)}\) The stability of the FIB milled nanogaps and the
metal-molecule junctions has been investigate in air and various liquid environments.\(^{(14)}\)

In this thesis, the focus was on understanding the phenomena that determine the fabrication of gold nanoparticle-organic molecule hybrid systems inside sub 20 nm spaced nanoelectrodes and their resulting low bias electrical resistance. Both the synthesis and characterization of low bias electrical resistance of AuNPs-organic molecule was performed at room temperature and at standard atmospheric pressure. It is presented here that (i) size of the nanogaps that are fabricated using focused ion beam milling is tunable, (ii) the two methods for synthesis of metal-molecule junctions that were applied have different implications in determining the low bias resistance of synthesized devices. These methods are conceptualized as protection-deprotection and molecular place exchange and (iii) external environment affects the low bias electrical resistance. The results point to the first ever application of such nanoparticle based molecular electronic junctions which is gas sensing at the example of nitrogen dioxide (NO\(_2\)).

1.1 Using single and few molecules as functional units in electronics

The idea of using molecules as functional units in electronics has led to a vast interdisciplinary research area that is called ‘molecular electronics’.\(^{(15, 16)}\) During the same time period as fabrication of electronics devices using semiconductor technology started, the idea that such devices can be fabricated with atoms and molecules using bottom-up approach was introduced. It was first introduced by Arthur Von Hippel in 1956 and the term ‘molecular electronics’ was first used by US air force Colonel C.H. Lewis in late 1950s during a molecular electronics conference.\(^{(17, 18)}\) This approach was promising but to make electrical connections to the single molecule had proven to be a challenge.\(^{(15, 19-21)}\) At present, the advancement in technology and development of modern tools and equipment has made it possible to manipulate even single atoms.\(^{(22)}\) Single atoms and molecules are visualized, contacted to electrodes and characterized.\(^{(23)}\)

Major contributions to the knowledge in the field of molecular electronics came in early 1970s when first; Kuhn et al., prepared Langmuir Blodgett LB films with molecules of various lengths, sandwiched them between asymmetric metal electrodes and then measured and reported conductivity as a function of molecular length (figure 5 from reference \(^{(24)}\) reeproduced in Figure 1-1) of the as prepared thin films.\(^{(24)}\) This was the first ever experimental result. After this in 1974, the first ever theoretical result, which is also understood to be the ‘kick start’ of molecular electronics field, happened through a famous study by Mark A. Ratner and Arieh Aviram. They
proposed a theoretical model of the molecular diode. Their molecular diode was a donor molecule and an acceptor molecule separated (coupled) by an 'insulating' bond. That molecule could assist the transmission of electrons asymmetrically with respect to the applied voltage.\(^{(25)}\)

![Logarithmic dependence of current density on the length of the SAM. Image reproduced with permission from Journal of Applied Physics](image)

**Figure 1-1:** Logarithmic dependence of current density on the length of the SAM. Image reproduced with permission from Journal of Applied Physics

For the purpose of making a molecular electronic device, an individual molecule or few molecules are contacted between, for example, gold electrodes. The contacting is accomplished by using suitable terminal groups, for example, thiol (-SH) on each end of the molecule. The terminal groups are also called anchor groups because they anchor the molecule with the electrodes via either physisorption or chemisorption. In an individual molecule when in ground state, the electrons fill the energy levels/orbitals up to certain energy and the orbital with the highest energy that is occupied by electrons is called highest occupied molecular orbital (HOMO). The next available energy level i.e. orbital higher in energy than the HOMO level, which is empty is called lowest unoccupied molecular orbital (LUMO). Upon contacting with the metallic leads the Fermi level of the electrodes falls somewhere between the HOMO-LUMO energy gap. Transmission of electrons from one electrode to the other depends upon Fermi energy difference between the two electrodes, Fermi energy difference between the electrode and the nearest molecular orbital and the coupling strength between the molecule and the electrode.
When both electrodes are at the same chemical potential, electrons cannot flow in one direction and net current is zero Amperes. Upon application of potential difference to the electrodes, an energy window is created which is manifested by the difference of the Fermi level of the electrodes which is shifted. Now, the electrons can transmit across the electrodes. This transmission is assisted by the molecule. The transmission can happen either through the HOMO–LUMO gap if the Fermi level is situated away from the HOMO or LUMO levels or transmission can happen on the HOMO or LUMO levels if the Fermi level of matches any of the levels. In the former case the transmission is defined as direct tunneling while in the latter case transmission is called resonant tunneling.

Tremendous efforts have been made to bring this concept, “molecules in electronic circuits” into practice during the last few years. Various experimental platforms have been invented for the electrical characterization of single or a few molecules. The invention of the scanning tunneling microscope (26, 27) has marked the major breakthrough regarding experimental platforms. This platform was then used for characterizing individual molecules by a technique called scanning tunneling microscope break junction (STM-BJ). (28, 29) Invention of other experimental platforms for the purpose of studying properties of molecules has continued. (16)

For the purpose of elucidating the study presented in this thesis which is motivated by the ‘applied’ molecular electronics idea, the platforms and techniques that are available today can be categorized into two subcategories. Moveable electrode/s platforms and fixed electrodes platforms. Examples of moveable experimental setups (30) including STM-BJ, (28) conducting probe atomic force microscopy (CP-AFM) (31, 32) and mechanically controllable break junction (MCBJ) (33, 34). These techniques require at least two metallic electrodes where one or both electrodes are moveable and where at least one of the electrodes is in nanometer dimensions. While nanometer (nm) and sub nm dimensions of electrodes ensure that the single molecule is in the metal-molecule-metal junction, the movability of electrodes ensures that contact between molecules can be repeatedly made and broken hundreds of times. That means that many molecules can be measured in one experiment but one molecule at a time and then the results can be analyzed together to yield statistically significant data. For example a distinction between conductance behavior that was observed using STM-BJ technique for bithiophene and biphenyl molecules that were terminated with thiol on each end is discussed in reference (35). The movable electrode/s platforms are excellent to develop the understanding of the electronic properties of the molecules but these are laboratory setups and lack their applicability in applied electronics devices. For applied molecular electronics devices, the electrodes are preferably required to be positioned rigidly on the substrate. Various devices and platforms that fall under this category have been proposed. Electromigration break junction, (36, 37) electrochemical...
deposition junctions\(^{(38, 39)}\) and focused ion beam (FIB) milled nanogaps \(^{(13, 14)}\) are typical examples.

Among the above mentioned platforms all except FIB milled nanogaps have demonstrated their potential for characterizing single and few molecules. FIB milled nanogaps that are fabricated between metallic nanoelectrodes impose a size constraint on contacting molecules. The size of the nanogaps that are fabricated using FIB milling of metallic wires is controlled by the spot size of the ion beam. The spot size of Gallium ion beam at 30 keV energy is as small as 5 nm. This implies that the size of the nanogaps cannot be equal to the length of the molecules of interest and the molecule cannot bridge the nanoelectrodes.\(^{(40)}\)

To correct for the mismatch between the molecular length and the size of the nanogap, an alternate method is available. This method utilizes metallic nanoparticles as intermediate contacting sites. This is described in the next section.

1.2 Nanoparticle-molecule junctions as molecular wires

Typical molecules that are used during the study in this thesis are dithiolated-alkanes and dithiolated-phenyl molecules of length which is less than 2 nm. Since these molecules cannot bridge the nanogaps that are made by focused ions beam (FIB) milling because of size mismatch as shown in Figure 1-2(a), there is an alternate method which aids to the formation of molecular wires. This method utilizes metallic nanoparticles as intermediate contacting sites. The nanoparticles are placed between large gaps i.e., gaps larger than the combined size of the nanoparticle and molecule as shown Figure 1-2(b). The molecules can contact between the surfaces of the nanoparticle and electrodes.

![Figure 1-2. Nanoparticle assisted bridging of nano-electrodes with molecules (a) a molecule of length smaller than the size of the separation between nanoelectrodes cannot bridge them (b) nanoparticle can facilitate the bridging. (Image not drawn to exact scale)](image-url)
Insertion of nanoparticle brings about an advantage i.e., because of the nanoparticle, it becomes possible that the molecular wires can be formed between those metallic electrodes that are separated by a size which is larger than the length of the molecule. In this situation the molecular functionality can be utilized. But this advantage introduces many additional effects that need consideration. For instance, it is well understood that gold in bulk form is a conductor and possesses free electrons which can be directed under the effect of electric field but the gold as nanoparticle does not remain conductor. A certain amount of energy known as single electron charging energy is needed by an electron to jump on to a gold nanoparticle. This charging energy \( E_c \) depends on the capacitance of the nanoparticle \( C \) as \( E_c = e^2/2C \) where \( e \) is charge on an electron. The capacitance \( C \) of a nanoparticle is given by \( C = 4\pi\varepsilon_0\varepsilon_rR \) where \( R \) is the radius of the nanoparticle, \( \varepsilon_0 \) is dielectric permittivity of the free space and \( \varepsilon_r \) is relative dielectric permittivity of the material. This implies that smaller the \( R \) of the NP, smaller will be its capacitance and hence larger will be the single electron charging energy. This is also known as Coulomb blockade. The effect of Coulomb blockade is apparent in low temperature electrical measurements where a certain voltage also called threshold voltage of conductance is needed before conduction could begin.

Use of nanoparticles also imposes additional challenges during the fabrication of nanoparticle-molecule junction based electronic devices. For instance, in addition to inserting molecules between clean gold surfaces one requirement arises that methods for assembly of nanoparticles between electrodes need to be investigated. Similarly another challenge is faced when inserting the molecules between NP surfaces: nanoparticles contain various ligands on the surfaces which are introduced during synthesis and these ligands may introduce steric effects which hinder the insertion of new molecule.

Many researchers have used nanoparticle molecule junctions for the purpose of making electronic devices. It has been demonstrated so far that the nanoparticle-molecules junctions can be formed between metallic electrodes in various geometries i.e., 1-D molecule-NP wires, 2-D molecule-NP networks and 3-D molecule-NP structures. It has been demonstrated that it is possible to change the interlinking molecules between gold nanoparticles via place exchange.

We in Uppsala University intend to fabricate the nanoparticle-molecule junctions between electrodes that are rigid and separated by sub 20 nm spacing.
1.3 Metal molecule junction as gas sensor

The main contributors which cause contamination of the environment are particulate matter (PM), ground level ozone (O$_3$), NO$_X$ (oxides of nitrogen), sulfur dioxide (SO$_2$), carbon monoxide (CO), heavy metals (Pb, Hg, Cd, As, Ni) and organic compounds like benzene (C$_6$H$_6$). These contaminants pose serious hazards to health of human and other animal species, plants, crops and the climate.(45) Among these contaminants NO$_X$, and specifically nitrogen dioxide (NO$_2$) which is generated from combustion process (both domestic and industrial) and exhausted from automobiles and industries, causes health problems like respiratory illness (lungs infection and asthma)(45, 46), eutrophication and acidification of all ecosystem.(45, 47) Concentration of these contaminations is monitored using the gas sensor technology. Sensors for these contaminants have become essential part of industry, environment monitoring and protection protocols and household.

A sensor is a device that is able to convert a variation of any quantity or property into useful output signal. The device, whose electrical property/properties can vary in accordance with the changing physical environment around it, is specifically termed as sensor. Gas sensors are characterized by monitoring change in any representative physical property of the sensing device upon interaction with, for example, redox gas. In electrical gas sensors the physical property which is monitored is resistivity or conductivity. If Figure 1-3 represents electrical gas sensor placed in gaseous environment; then upon changing the gas environment (arrow head points to this change) conductivity of the sensor changes.

So far many different types of sensors for the sensing of NO$_2$ have been developed. Devices based on semiconductor(48), metal oxides(49), carbon nano-materials (graphene, rGO, carbon nanowires and nanotubes)(50, 51),
2D materials like phosphorene(52), polymer compounds(53), metal-oxide and other nano-composites(54, 55) and nanoparticles(8) are in continuous development for the purpose of achieving better sensor performance. Making sensors with molecules is possible because conductance of molecular junctions is sensitive to environment. Theoretical investigations of electron transport through metalloporphyrin suggest that depending upon the connection, electron transport happens through metallic center or the porphyrin ring. In the former connection, if a diatomic gas molecule adsorbs on the metalloporphyrin, the electron density in the metallic center changes and hence the resistance changes.(56) Similarly binding of the cations with the lone electron pair of nitrogen atom in quinolinedithiol (QDT) molecule induces states at the Fermi energy level of the system and hence resistance drops.(57) Oligothiophenes show increased conductance because of the lowering of the LUMO level towards the Fermi energy upon surrounded by water molecules.(58) Similarly crown ether bridge anthraquinone molecule shows a change in conductance upon binding of alkali ions. This change is due to lowering of the LUMO level towards the Fermi energy which is due to charge transfer from ions to the molecular wire. With the size of the alkali ions charge transfer increases and resonance energy is lowered which leads to increased conductance.(59)

One important advantage of miniaturization of gas sensors is the possibility to probe the single molecule interactions. This is in contrast to probing single molecule interactions using bulk devices. For bulk, large surface area and large volume devices, single molecule detection is possible by (i) diluting the gas to sub parts per billion levels (ii) applying specific signal analysis techniques. Whereas, devices made at the bottom end of the nanoscale consist of one or few sensing elements and hence many molecules of the gas can only interact with one or very few sensing elements. This makes it possible to understand the gas detection at the elementary level of the device structure.

1.4 Motivation
The nano molecular electronics devices (nanoMoED) platform provide alternate route for fabrication of metal-molecular junctions. T. Blom developed the nanoelectrode platform(60) and S. Hassan M. Jafri(61) demonstrated that this nanoelectrode platform can be used to characterize molecules and nanoparticles. It has been shown that nanoMoED devices can be fabricated using alkanedithiol molecules and that single molecule characteristic can be observed using the nanoMoED platform when stable chemisorbed junctions are formed in the junction.(10) The next level is to bring this nanoelectrode-nanoparticle platform for characterization of other short chain molecules as well as demonstrate the functions of newly inserted molecules.
With the increasing length of the exponential graph of Moore’s law,(62) the need to adopt alternate technologies for building electronic components is growing. To add a single data point on this graph, besides other economic and political factors, reduction in size of the device, decrease in power consumption by the device, enormous increase in computational speed of the device and reduction in cost is required. Any of the aforementioned factors needs to be scaled at a pace defined by power law and this is where conventional semiconductor technologies, which did put the first point on this graph, are being questioned for; if the size can be reduced further to next few Å? If the power consumption can be (at-least) kept constant? Is it possible to increase the computational speed during the coming couple of years? Whether cost of devices can be maintained while augmenting other factors? And so on.

While many different technologies and technological materials have provided possible answers to these questions, the graphene ‘solution’ was most entertained, well which is now being questioned for itself. We chose to work on searching the answer to above questions using a technology whose aim is to build electronic and opto-electronic components and devices using molecules as basic functional unit. Motivated by this alternate method for fabrication of electronic devices, the idea was to try the various possibilities that exist for the creation of molecular junctions. This alternate method i.e., to fabricate electronic components with molecules was promising because the molecule is the smallest entity that can perform electronic and opto-electronic functions.(17, 63) But at the same time this idea came with unforeseen challenges. The biggest challenge which remained was to contact the molecule between electrodes and one of the many sub-questions was how to reduce the electrode spacing between electrodes so that the length the molecule and spacing between the electrodes becomes compatible. We chose to use nanoparticles that can compensate for the size mismatch as shown in Figure 1-1. The choice was very suitable but then as explained earlier the nanoparticles introduce their semiconductor nature to the electrical properties of the molecular junctions. Hence we extended our focused on investigating the electrical resistance of the molecular junctions that are assisted by nanoparticles. The phenomenon that could affect the electrical properties of the junctions could be internal to the device or the external environment and hence we made efforts to investigate the both.

1.5 Aims and objectives of the thesis

The objectives of this thesis have been designed based on the aim that, understanding the factors that affect the electron transport across metallic electrodes when they are bridged with short organic molecules and nanoparticles. This aim lead us to seek answers for following (i) how small a nanogap
can be fabricated using focused ion beam method, (ii) How different molecules can be inserted between nanoparticles and electrodes, (iii) What factors affect the direct tunneling resistance of molecule-nanoparticle junctions that are fabricated inside sub 20 nm spacing between nanoelectrodes, and (iv) How the direct tunneling of electrons through the molecule-nanoparticle junctions is affected when the environment near the junctions changes.

1.6 Structure of thesis

The remaining chapters of this thesis are organized in following order. Chapter 2 describes research methodology that was followed for fabrication of Nano molecular electronic devices (nanoMoED) and highlights the useful instruments. Chapter 3 covers that conceptual knowledge about the elements of nanoMoED platform i.e., fabrication of sub 20 nm gaps between nanoelectrodes and assembly of gold nanoparticles inside the nanogaps to fabricate the platform. In Chapter 4, methods for synthesis of the molecular junctions are discussed. Experimental results of electrical characterization are cross-compared to elucidate the important factors that had the determining effect on the electrical properties of resulting nanoMoED devices. In Chapter 5, the very effects of environmental gases on the charge transport through nanoMoED devices are discussed.
2. Experimental methods and instruments

Fabrication of the nanoparticle-molecule metamaterials inside electrodes that are separated by ≈20 nm gaps would result in a device whose electrical properties are governed by single and few molecules. This device is called nano molecular electronic device (nanoMoED) from here onwards. This chapter describes the specific methods and instruments which were used to fabricate and analyze these nanoMoEDs.

For the purpose of fabrication of these components, both top-bottom lithography and cutting methods as well as bottom-up physical manipulation and chemical synthesis methods were used. Figure 2-1 elaborates the split between these two procedures.

Figure 2-1: Nanogaps are fabricated by top-down approach whereas NNMB resistors are prepared starting from nanogaps and chemicals as raw materials and applying Bottom-up synthesis approach.

First the nanogaps that are separated by a distance which is less than 20 nm are fabricated by using top-down methods. P-doped silicon substrate, gold
(Au) and chromium (Cr) metals are the raw materials. After this bottom-up methods are used to fabricate nanoMoEDs. For this purpose nanogap, gold nanoparticles and application specific molecules are raw materials. The reason for using both approaches is that neither the top-down nor the bottom-up approach can alone be successful for the fabrication of these devices.\(^{(64)}\)

### 2.1 Steps of fabrication

Each of the two methods is further subdivided into steps as shown in Figure 2-2. Top-down method comprises of electron beam lithography (EBL), Photolithography (PLi) and focused ion beam milling steps. Bottom-up methods comprise of physical manipulation of gold nanoparticles to trap them inside nanogaps and chemical linking of molecules to gold surfaces for the formation of molecular junctions.

**Figure 2-2: Depiction of process flow for fabrication of nanoMoED**

In the subsequent sections each of the steps are described briefly. First the methods and instruments for top-down block and then methods and instruments for bottom-up block that are shown in Figure 2-2 will be discussed.

#### 2.1.1 Top-down methods and instruments

*Electron beam lithography*

Interactions between electron beam and organic materials are utilized to perform Electron beam lithography. This is one preferred method, which is used to pattern features at the nanometer scale. It is a mask-less technique extensively used for direct writing of patterns on materials like poly(methylmethacrylate) (PMMA). The first ever patterns written using this method were 14nm wide lines separated by 100 nm.\(^{(65)}\) State of the art of electron beam lithography is that features with less than 5 nm resolution can be patterned.\(^{(66)}\) The equipment and materials that are required in this step are (i) an electron beam (e-beam) forming instrument with beam deflection circuitry such as scanning electron microscope SEM (ii) a suitable substrate on which patterns are structured (iii) an e-beam sensitive resist which is ex-
posed to the e-beam for writing process and (iv) chemicals for developing the patterns.

For making the nanoelectrode patterns, EBL was carried out following the procedure demonstrated earlier. Briefly revisited here, the procedure is as follows. First ≈150 nm thick layer of PMMA was spin coated on ultra clean Si/SiO₂ substrate. Thickness of SiO₂ layer on Silicon was ≈285 nm. PMMA acts as positive electron beam resist in which chemical bonds can be weakened upon exposure to the e-beam. The patterns to be designed were drawn using computer aided drawing (CAD) software. These CAD drawings require being adapted to the software environment of e-beam scanning and deflection system. Standalone systems are available for carrying out the EBL, but general purpose SEMs and TEMs still have a wide user base for standard and also very special purpose EBL. We used FEI’s XL30 environment scanning electron microscope (ESEM). Electron beam was focused at energy of 30kV, its line dose (µC/cm²) was optimized to avoid over exposure or under exposure and then optimized e-beam was scanned on the PMMA resist according to the patterns in the CAD drawing. After scanning, the patterns were developed by immersion in 1:3 solution of MIBK: IPA for 1 minute followed by immersion/rinsing with pure IPA for 1 minute.

**Metallization**

The developed patterns on the substrate contain the resist on the entire surface except the regions exposed to e-beam. These regions are filled with conductor material (gold/Cr) using physical vapor deposition technique. For this purpose, the sample was mounted on a circular plate which is then hanged inside the chamber of PVD system. Gold does not adhere to SiO₂ so at first, a 3 nm layer of either titanium or chromium was deposited which acts as adhesion layer between gold and SiO₂. This layer was deposited at a deposition rate of 3 Å/sec. After depositing the adhesive layer of Ti or Cr, a 70 nm thick layer of gold (Au) was deposited on all the samples at a deposition rate of 4 Å/sec.

Metallization completes with metal lift-off. For this purpose the wafer was placed inside Acetone for lift off. After waiting for few hours, it was taken out from acetone, placed in isopropanol (IPA), a brief sonication was performed for 10-15 seconds and then rinsing with IPA was done again. Figure 2-5(a) shows the SEM image of one of the EBL wire made with gold.

**Scanning Electron Microscope SEM**

For performing the electron beam lithography, FEI’s XL30 environmental scanning electron microscope (ESEM) was used. Its environmental feature was not used during EBL. So here a general description of Scanning electron microscope (SEM) is presented here for the purpose of information about working of SEMs.
SEM is the most convenient tool to directly visualize the Nano objects. *Figure 2-3* (left) is camera image of one of the scanning electron microscopes in micro structure laboratory at Ångstrom laboratoriet, Uppsala. It is Zeiss Merlin which one of the most advanced SEM in its family. *Figure 2-3* (right) is the schematic diagram of a typical SEM.

![Zeiss Merlin scanning electron microscope with Aztec EDS/EBSD]

All elements are installed inside a column at vacuum pressures. Vacuum is maintained in the column so as not to contaminate the column and path of electrons. Electrons can be ejected from the electron gun by either heating the filament or by applying electric field to it. In the former case phenomenon is called thermionic emission and in the latter case phenomenon is field emission. Wehnelt cylinder surrounds the filament; it has a small opening and is at negative potential. Anode is at high positive potential and lies below the Wehnelt cylinder. The placement of the three elements, the filament, Wehnelt cylinder and the anode is such that negative electrostatic potential of Wehnelt cylinder suppresses the electrons from most part of the filament and anode attracts and accelerates the electrons down the electron column which are ejecting from the filament. The electrons then pass through a set of electromagnetic lenses and apertures. Condenser lens forms the beam and causes the electrons to converge and form small beam diameter. Aperture is a small physical opening which blocks the off axis electrons. Objective lens focuses the beam on the sample. Scanning coils scan the electron beam on the sample in raster scan fashion. There is a set of detectors inside SEM which detect the electrons coming from the sample, send this signal to electronic circuitry and image is produced. Electrons for image production in SEM are a consequence of interaction between electrons in the incident beam and sample. The images in this thesis are mostly taken by using secondary electron (SE) detector inside the beam column. It is called inlens detector. Three types of secondary electrons are produced when primary incident electron beam interacts with the sample. SE1 and SE2 are from the sample i.e., SE1 is produced by the primary beam and SE2 is produce by SE1. SE3 is pro-
duced from inside of the chamber for example, the chamber walls. Position of the inlens detector is such that the signal to noise ratio is maximized as SE3 cannot reach it.

**Photolithography**

For electrical characterization of nano-entities inside nanogaps, the devices need to be contacted to probe needles which are of µm dimensions. For this requirement of contacting nano-objects to micro probe needles, gold pads of µm dimensions are deposited on the ends of the EBL lines with the help of photolithography.

Photolithography was invented and conceptualized for printing purposes by Alois Senefelder in 18th century. This technique has been a major contributor to the progress and miniaturization of devices in semiconductor industry and research since 5 decades or more.

Figure 2-4 is simplest picture conceptualizing the process of photolithography. Inverted image of the patterns is made on light transparent material with chromium. Chromium blocks the light (UV) while other regions let it pass. Substrate on which patterns are to be ‘printed’ is coated with photore sist whose chemical bonds are broken or weakened upon exposure to light (UV). The regions of the resist which are exposed to light are later developed chemically and are then ready for next process which is deposition of metal.

![Figure 2-4: Photolithography](image)

Contact pads on the ends of the EBL lines were patterned using the above mentioned method. First 5-6 um thick layer of photoresist (AZ 4562) was deposited on the wafer by spin coating. After putting 2-3 ml of resist, the wafer was spun at 1000 rpm for 3 seconds and then at 4000 rpm for 45 se-
conds. After spin coating with photoresist, baking was performed on a hot plate at 90 °C for two minutes. Patterns of contact pads were transferred on to the photoresist using mask aligner and UV exposure. Patterns of large contact pads were aligned on the edges of EBL lines and then exposed to UV for 30 seconds. Developing of the photolithographic patterns was performed in 1:4 mixture of AZ400k:H₂O for 4 to 5 minutes.

For the purpose of performing UV light exposure Karl Süss MA6/BA6 double sided exposure instrument was used.

Metal deposition or metallization was done using the physical vapor deposition (PVD) as described earlier. Only difference here was that the thickness of gold layer was 150 nm. Figure 2-5 shows all images which are taken after metallization. Figure 2-5(b-c) show the optical microscope (OM) image and camera picture respectively of the patterns after photolithography. At the completion of lithography there could be residual resist on the surface of the wafer. Plasma stripper Tepla 300 was used to clean wafer surface.

Evaporator used for physical vapor deposition of materials was Lesker PVD 75. Gold was deposited by resistive evaporation technique. In this technique high current is passed through the material that heats the materials to cause evaporation. The chromium/titanium material was deposited using electron beam evaporation technique. In this technique a focused beam of high energy electrons falls on the material to heat it and cause evaporation.(68)

Figure 2-5: Lithography (a) SEM image of thin gold wire made with EBL (b) OM image of one of the electrodes from the column of figure (c) which shows 12 individual electrodes.
Focused ion beam milling

A very versatile method called focused ion beam (FIB) milling (69) was used to cut nanogaps smaller than 20 nm and larger than 2 nm. We set the upper size limit while the lower limit on size was imposed due to science of FIB instrument and FIB sample interactions. The principal is that the high energy ions with large momentum (~1836 times more than that of electron) when collide with atoms of the material, the momentum transfer of ions to atoms of the material causes knocking out of the material atoms and hence digging of target material occurs. The ion beam spot size in the FIB/SEM dual beam system is >5 nm at 30keV energy when the beam current is 1pA. The milling resolution is generally larger than the spot size because this resolution depends on both, the ion beam diameter and the physical processes during the focused ion beam sputtering.

The wafer containing thin gold wires that were prepared during lithography step was taken to the focused ion beam apparatus for the purpose of milling nanogaps. Gallium ion beam was aligned at 1pA current and 30kV acceleration voltage. Nanogaps were milled in the approx. middle of individual gold wires by sputtering with ion beam. For ion dosage of more than $5 \times 10^{10}$ ions/cm complete sputtering of the gold material in the exposed region occurs. Figure 2-6 shows example of focused ion beam milled nanogap.

Figure 2-6: A typical nanogap of size smaller then 20nm fabricated with focused ion beam milling.

FEI Strata DB235 FIB/SEM/EDS/Cryo dual beam instrument was used for the purpose of milling nanogaps. Focused ion beam formation is accomplished by the beam generation and manipulation structure as shown in Figure 2-7. Liquid metal ion source (LMIS) where molten Gallium wets the tungsten needle and application of negative voltage at the extractor electrode extracts the ions. These ions move along the column accelerated by the voltage with acceleration voltage between 5 to 30keV. The beam passes through
apertures which control beam current and determine probe size. A condenser lens focuses the ions into probe and objective lens focuses the probe onto the sample. All lenses in the ion column are electrostatic lenses as opposed to electromagnetic lenses in the electron column. Similarly for deflection of the ion beam on the sample for scanning purposes is done with the help of electrostatic lenses called octopole.(70) Sample is housed on a stage whose motion can be controlled around 5-axis namely x, y, z, tilt and rotation.

Figure 2-7: focused ion beam formation and manipulation system (a) camera image of FEI Strata DB235 FIB/SEM dual beam system (b) inside the ion column.

2.1.2 Bottom-up method and instrument

The nanogaps in the previous step, now serve the purpose of the locality where the Nano-entities need to be assembled. Gold nanoparticles were trapped inside the nanogaps using dielectrophoresis. After this the molecules are contacted between gold surfaces.

Dielectrophoretic trapping of the gold nanoparticles

After cutting the nanogaps dielectrophoretic trapping(71) of AuNPs is carried out by (i) electrically connecting the nanoelectrodes to the AC signal source (ii) making suspension of functionalized AuNPs in toluene (iii) putting 6-10 μl of this suspension on the nanoelectrode (iv) applying 1 V_{p-p} Electrical signal with a frequency 1 MHz for 50-60 seconds. The instrumentation for this step is shown in Figure 2-8. This polarizes the AuNPs and creates dielectrophoretic force which is responsible for, in this case, positive dielectrophoresis and causes diffusion of the nanoparticles towards region of high electric field. The field is strongest inside the nanogap so the nanoparticles move towards the nanogap. After this the contacts are removed and
access solution is removed by thoroughly rinsing the sample surface with DI water and blow drying with N₂ blås.

Figure 2-8: trapping of gold nanoparticles (a) setup for dielectrophoretic trapping (b) AC signal source

Contacting molecules
Contacting of molecules to the gold surfaces is a chemical reaction and was performed in liquid environment. Major requirements were that (i) the target molecules be dissolved in suitable solvent (ii) the environment to be kept oxygen free. The solvent that was used is toluene. To maintain the oxygen free environment flow of Argon gas was maintained throughout the reaction. The reaction was carried out in a three neck flask shown in Figure 2-9.

Figure 2-9: Chemical reaction was carried out inside three neck flask.

2.2 Characterization methods and instruments
Many methods and instruments have been used during the device fabrication process. Those methods and instruments are described in this section.
**Characterization of the patterns after lithography**

Since the EBL patterns are very small in dimensions so SEM characterization was preferred. Visualization of patterns can also be done in optical microscope (OM). SEM that was used is described earlier. Optical microscope that was used is Olympus AX70.

![SEM image of optimized pattern and OM images of the patterns resulting from overdose and under-dose respectively](image)

**Characterization of the FIB milled nanogaps and nanoMoEDs**

After fabrication, the nanogaps were characterized by (i) visual inspection in SEM (ii) electrical characterization. SEM characterization can provide the information about size and morphology of the nanogap. Electrical characterization can tell about the size and cleanliness of the nanogaps.

Electrical characterization was performed using Agilent b1500a semiconductor parameter analyzer coupled to Karl Süss probe station. Figure 2-11 shows the instruments and setup. The device under test (DUT) is placed on the sample stage and probe needles that are connected to Agilent b1500a are connected to the contacts on the DUT. The probe station is housed inside a Faraday cage that when closed, isolates the internal environment from any electromagnetic interference. Also the base of the probe station is resistant to vibrations and hence this setup becomes very useful for electrical characterization at ambient conditions.

By electrical characterization the technique which is referred to is called low bias voltage resistance measurement. In this technique, two ways Current-Voltage (I-V) sweep measurements are performed. The applied Voltage is swept between 0V and positive maximum voltage and then back to 0V. Similarly voltage is swept between 0V and negative maximum voltage and then back to 0Volts. Then the ratio of voltage and corresponding measured current (i.e., resistance) is calculated for both positive and negative voltage sweeps. Average of the resistance values that are calculated where I-V graph
is linear gives the value of resistance which is then called low voltage bias resistance. The low bias resistance is ‘translated’ as tunneling resistance.

Figure 2-11: Electrical characterization setup. Karl Süss probe station (main figure). The insets in green boxes show the Stage and probe needles (left inset in green box) and Agilent b1500a semiconductor parameter analyzer (right inset in green box).

Characterization of the nanoparticles and molecules
The size of the nanoparticles was characterized using transmission electron microscope, Scanning electron microscope, UV –Vis absorption measurements.

The transmission electron microscopy (TEM) was performed using Tecnai F30 in bright field mode. TEM was used to measure precise diameter of the nanoparticles and precise spacing between the nanoparticles. Scanning electron microscopy (SEM) imaging was done as described in section 2.1.1. The SEM imaging was useful for the visual characterization of nanoparticles. In most of the images shown in the manuscripts and this document the SEM was operated in analytical mode, energy of the electron beam was 15 kV and inlens secondary electron detector was used.
The UV-Vis absorption measurements were performed using the Perkin Elmer’s Lambda 35 Spectrometer. In this instrument the wavelengths in the UV, Visible and IR range are produced using two sources of light, a Deuterium and a Halogen lamp. A monochromator and beam splitting setup will filter the signal produced by the sources into single wavelength. This wave then passes through the sample and is received at the detector. The detector then shows the loss of signal in the sample in the form of absorbance spectrum.

Gas sensing instruments and methods
Figure 2-12 shows the custom made gas sensing chamber. Same has been use before to investigate the NO$_2$ sensor properties of Graphene. Its volume is 154 cm$^3$. It is housed on a stage which is electrically grounded and its motion in 3-axis can be controlled via micro-manipulators.

![Figure 2-12: Instruments for gas sensing](image)

It has six custom made openings. One opening acts as gas inlet and one act as gas outlet. Two of the openings were used to insert metallic probes which are connected to electrical measuring instrument through low noise, high performance cables. One opening was used to couple light from optical light source via optical fibers. Sixth opening was not used and kept sealed during the experiment. There is a transparent lid which is used to seal the chamber from top while performing the gas sensing measurements. Figure 2-13 shows the simulation of rate of rise of concentration when input concentration is
100 ppm. Brooks 5878 mass flow controller is used to control the speed of various gases flowing into the chamber. It is calibrated for N\textsubscript{2} which means that the flow rate NO\textsubscript{2} will be factor of 0.78 slower than the apparent reading. At a flow rate of 100 ml/min, it should take approximately 450 seconds before the NO\textsubscript{2} concentration could increase to 99% of 100 ppm.

![Figure 2-13: gas sensing chamber (a) volume (b) simulation of rate of rise of concentration](image)

To perform current time measurements Keithley 6430 sub femto amp source meter was used. Keithleys’ customized software for controlling the hardware to perform fixed voltage bias sourcing and current measurement is utilized. All the measurements presented in this chapter are taken with 10 PLC and two consecutive data measurements are spaced by 0.625 sec.

### 2.3 Summary

The useful instruments and methods that were applied during the study in this thesis are described in this chapter. The fabrication of the nanoMoED devices requires use of both the top-down lithographic and cutting methods as well as the bottom-up synthesis methods hence these methods were described in different sub sections. Analytical methods and instruments are discussed in a separate section. The electrical characterization of the nano-MoEDs was performed at ambient temperature in air as well as N\textsubscript{2} and NO\textsubscript{2} atmospheres. For the purpose of performing gas sensing experiments, a custom made gas sensing chamber and associated circuitry is also discussed.
3. Elements of an nanoMoED Platform

In order to establish metal-molecule junctions, the macroscale metallic contacts must be contacted with the nanoscale molecules that are typically smaller than 5 nm and larger than an atom. Instead of connecting µm sized contact pads directly to 1 nm sized molecules, in the multiscale nanoMoED devices, we choose to move stepwise, in particular from the µm scale down, to the 1 nm scale. In the nanoMoED device, on a Si/SiO₂ substrate there are three basic entities, housed in a way to act as a two terminal molecular electronic resistor. These entities are nanometer spaced electrodes, gold nanoparticles and functionalizing molecules.

Before introducing the functionalization with molecules a platform which can host molecules is fabricated. This chapter describes the platform which is, gold nanoparticles trapped inside small nanogaps separating the metallic electrodes as shown schematically in Figure 3-1.

![Figure 3-1: The nanoMoED platform; Electrode 1 (source) and electrode 2 (drain) are made of gold and the nanoparticles (red spheres) are trapped between nanogaps by dielectrophoresis.](image)

In section 3.1, the nanogaps fabrication is discussed. Section 3.2 deals with the nanoparticles that are used in present study. Section 3.3 describes the fabrication of Platform. Chapter concludes with describing the characterization methods that are applied to the platform.
3.1 Metal electrodes separated by thin insulating barrier

For a molecule to be contacted between metallic electrodes there are two major requirements: (i) the spacing between the electrodes should be well-matched to the size of the molecule and (ii) the molecule should have suitable terminal groups on each side which can chemically bind with metallic electrodes. End groups are also called anchor groups.

Theoretical background

The understanding of the nanometer spaced electrodes and charge transport across them is the basis for understanding the electron transport through nanogaps bridged with molecules. The understanding of the electron transport across such nanogaps that are separated by thin insulating film was first proposed by John G. Simmons in 1963 by analyzing the situation of symmetric electrodes separated by thin insulating region. (73)

Figure 3-2(a) depicts the situation when the applied bias voltage is 0 V and Figure 3-2(b) shows the right electrode at positive bias voltage.

![Figure 3-2: Metal electrodes separated by insulating medium with a barrier height $\Phi$ (a) representation when applied bias ($eV$) is $\approx 0$ V, (b) lowering of the Fermi level of right electrode by `$eV$' when positive voltage is applied $0 < eV < \Phi$ and (c) reduction in the barrier length `$d$' when applied voltage is greater that barrier height $eV > \Phi$ and $\Phi_L$ is for left electrode.

Here $\Phi$ is mean barrier height which depends upon applied bias voltage `$eV$', `$\psi$' is work function of the metal electrodes, `$d$' is the length of the and `$\eta$' is
the Fermi level of electrodes. The probability of an electron tunneling across
this barrier from left to right electrode is calculated using WKB approxima-
tion
\[ D(E_x) \approx e^{-A\sqrt{(\eta + \Phi - E_x)}} \]

\[ \text{Where } A = \frac{2\beta d}{\hbar} \sqrt{2m} \]

Here ‘\( \beta \)’ is introduced as a correction factor which is approximately equal to
unity. Using this approximation, the current density equation derived by
Simmons is reproduced in equation 3.2
\[ J = \frac{e^{2\sqrt{2m\Phi}}}{4\pi^2 \hbar^2 \beta d} \Phi e^{-A\sqrt{\Phi}} \left( e^{-A\sqrt{\Phi + eV}} - (\Phi + eV) \right) \]

This is the general form of the current voltage relationship for the case under
discussion. From this result Simmons derived the voltage dependent current
density relationships for three cases of applied voltage bias i.e. 0 V and small
voltages, intermediate voltage and high voltage.

At 0 V and for small voltages such that \( eV \approx 0 \), the barrier height does not
depend on voltage and current density is calculated to be a linear function of
voltage.
\[ J = vV \left( \frac{e^{2\sqrt{2m\Phi}}}{4\pi^2 \hbar^2 \beta d} \Phi e^{-A\sqrt{\Phi}} \right) \]

For intermediate voltages when ‘\( eV \)’ is less than barrier height Simmons
showed that current density is calculated as (74)

\[ J = J_L(V + \gamma V^3) \]

\[ \text{where } \gamma = \frac{(Ae)^2}{96\Phi_o} - \frac{Ae^2}{32\Phi_o^2} \]

Here ‘\( \Phi_o \)’ is barrier height at V= 0 Volts. This equation describes the nonlin-
ear dependence of current on applied voltage when \( eV < \Phi \).

For higher values of applied voltage larger than the mean barrier height,
that is \( eV > \Phi \) the current density is
\[ J = \frac{2.2e^3F^2}{8\pi \hbar \Phi_L} \left( e^{-\frac{8\pi\sqrt{2m\Phi_L}^3}{2.96eF}} \right) \]
In equation 3.5, ‘F’ is the field strength in the dielectric layer which is given by \( F = V/d \). Field strength in the dielectric region changes linearly and slowly with voltage.

The Simmons’ model sets up a tool box for understanding electron transport across nanometer spaced tunnel junctions. We made use of this formalism to understand and extract the value the size of the smallest nanogap which was fabricated using focused ion beam milling technique. This is described next.

**FIB milled nanogaps (PAPER-I).**

In chapter two, the general procedure for fabrication of nanogaps was described. It begins with electron beam lithography for depositing thin gold wires, then photolithography for structuring the contact pads on the ends of gold wires is done and finally using focused beam of gallium ions is used to cut gaps in approximately middle of the thin gold wire.

A focused ion beam instrument can be used for the fabrication of rigid gaps between electrodes with size less than 10 nm. The ion beam spot size in the FIB/SEM dual beam system is \( \approx 7 \) nm at 30 keV energy when the beam current is 1 pA. The milling resolution is generally larger than the spot size because this resolution depends on both, the ion beam diameter and the physical processes during the focused ion beam sputtering. If specific locations on the sample are targeted the milling resolution can be enhanced. For example it is understood that at the grain boundaries the material of the sample is sputtered faster than at other regions and hence differential sputtering can cause enhancement of the milling resolution.\(^{(75, 76)}\) Figure 3-3(b-e) shows the nanogaps size tuning achieved by controlling the ion dosage and manifested by the differential sputtering effect.

Size of the nanogaps was tuned by controlling the ion dosage i.e., number of ions falling per unit area. The complete cutting of the nanowire was obtained for more than 50 ions falling per Å. Higher ion dosage than 50ions/Å resulted in larger size of the nanogap. Gap can be reduced further by utilizing the interactions between the ion beam and the local sample morphology. By precisely tuning the ion dose and taking into account the differential sputtering of the material from grain boundaries to the lattice, nanogaps with a width of less than 5 nm are fabricated. The smallest gap size of 2.3 nm is achieved at an ion dosage of \( 5 \times 10^{10} \) Ions/cm.

Inspection of the cut gaps is done by two methods (i) observation in HRSEM and (ii) measuring electrical continuity between contact pads by performing current voltage (IV) sweep measurements. With this ion dosage range, the sputter yield is estimated to be 1.5-2 Au atoms/ion when ion beam is at an incident angle perpendicular to the gold surface.
Figure 3-3: Size tuning of the nanogaps size with the help of tuning of the ion dose. (a) uncut gold nanowire made with EBL (b) an undercut line when ion dosage was $4.6 \times 10^{10}$ ions/cm (c) ion dosage of $5 \times 10^{10}$ ions/cm opens a small gap (d) ion dosage of $6.7 \times 10^{10}$ ions/cm increased the gap size (e) nanogap fabricated with ion dosage of $9.3 \times 10^{10}$ ions/cm (f) tilted image of nanogap shown in figure (c) shows the smallest gap size < 5nm achieved at 50G ions/cm ion dose which is also understood to be due to the differential sputtering phenomenon.

SEM imaging is a vital method for visual characterization of Nano objects but when feature size reduces below 5nm, use of the SEM characterization is limited. For the purpose of estimating the size of the smallest nanogaps, the
electrical characterization is done whose results are then evaluated using the Simmons model.

The electrical characterization of these nanogaps is done by performing the two-way current-voltage (I-V) sweep. The applied voltage is swept between ±600mV and the resulting current is measured. In the Figure 3-4(a-b), the I-V curves of a bigger nanogap and the as prepared smallest nanogap are shown, respectively. When the nanogaps get larger, the measured signal approaches the noise of the system. The resistance of the gaps that are larger than 20 nm width is more than 1000 TΩ. The smallest nanogap which was fabricated in the present work shows field emission tunneling. This is a consequence of the applied voltage being higher than the potential barrier (see Figure 3-2(c)). Three regions of the IV curve namely, linear region is observed at low applied voltage bias which is a characteristic of direct tunneling, the knee point is observed at intermediate voltages. At higher voltage, field emission was observed. This region is also described as Fowler Nordheim region characteristic of tunneling at voltages higher than the barrier height. The use of Simmons equation that are described above resulted in estimated effective gap size of 2.3 nm and the effective barrier height of 0.8 eV. The fact that these estimated values are very small is understood to be because of (i) the effect of image potential (ii) probable adsorbed contaminations which could exist because the measurements were done at non-UHV conditions and (iii) the non-uniform surface of the electrodes as shown by the SEM images. These three have been reported as the possible cause of lowering of the barrier height.\(^{(36, 77-79)}\)

![Figure 3-4: I-V characterization of empty nanogaps. (a) IV sweep for nanogaps of size >20 nm (b) IV sweep for nanogaps of size <5 nm adopted from reference (76) with permission from Applied Physics Letters.](image-url)
3.2 Gold nanoparticles, properties and their functionalization with organic ligands

In previous section it was described that with the FIB milling method the smallest visible separation between electrodes can be ≈5 nm and theoretically estimated separation can be ≈2.3 nm. A molecule of length 5-15 Å cannot bridge this gap. Placing an intermediate site which can assist the bridging process is a viable solution and gold nanoparticles are the suitable choice of intermediate site. Suitability of AuNPs is justified in the nano-MoED devices because of many reasons.

First, the motion of the gold nanoparticles can be directed under the effect of electric field due to the phenomenon called dielectrophoresis. Dielectrophoresis is a widely used method for the separation of particles from the solution. Application of alternating electric field can cause displacement of the electrons in the nanoparticle which results in the polarization of the nanoparticle. The polarized nanoparticle can then move along the electric field gradient ‘∇E’. The equation 3.1 describes the dielectrophoretic force ‘FDEP’ that acts on the nanoparticle of radius ‘r’ suspended in a medium of dielectric constant ‘εL’ when it gets polarized. In our nanoMoED devices the electric field is maximized in the nanogap and gradually decreases going away from the nanogap. That means the polarized nanoparticles move towards and get assembled in the nanogap.

\[
F_{DEP} = 2\pi r^3 \varepsilon_L \text{Re} \left( \frac{\varepsilon_p - \varepsilon_L}{\varepsilon_p - \varepsilon_L^*} \right) \nabla E^2
\]  

(3.1)

This assembly of AuNPs is called dielectrophoretic trapping.

Second, the thiol terminated organic molecules can be anchored on the gold surface and molecular junctions can be formed (to be discussed in section 4.1.2). Hence one end of the dithiolated organic molecule can connect to gold electrode and the other end of the molecule can contact with the nanoparticle surface which results in the formation of molecule-nanoparticle bridge between electrodes.

Third, gold nanoparticles of size less than 100 nm and larger then 2-3 nm have band structures different from bulk metal as well as molecules and individual atoms. The energy levels are not entirely distinct like molecules and not overlapped like bulk metals. Instead the energy levels split with very small difference. Energy levels in these particles have very small separation in energy i.e., ≤ 5 meV. This implies that at ambient temperature, with 25 meV energy of electrons, the electron transport behavior of gold nanoparticles can be approximated as a conductor.

The approximation of the nanoparticles as conducting, in our nanoMoED devices needs more discussion. As discussed in section 1.2, energy greater
than the charging energy \( E_c \) is required by an electron to hop on and off a nanoparticle. This charging energy depends on size \( R \) of the NP as well as the dielectric constant \( \varepsilon_r \) of the surrounding medium (the functionalizing ligand shell). Larger the size of the NP and higher the relative dielectric constant of the surrounding medium; smaller will be the charging energy. It has been observed in many experiments that the effect of charging energy is not observable at room temperature unless the size of the AuNPs reduced to \( \approx 1 \text{ nm} \).\(^{(80)}\) It is also argued that the effects of charging energy require the condition: \( E_c \gg 10k_B T \).\(^{(41)}\) Similarly the ligands on the surface of a AuNP reduce the injection barrier for electron to tunnel on to an NP. Hence the charging energy is reduced as compared to that of a bare nanoparticle in vacuum. This reasoning qualifies the approximation and we assume that the gold nanoparticles in our nanoMoED devices serve the sole purpose i.e. act as interconnects between molecules and assist the molecular-bridging of the nanogaps that are larger than the length of the molecules used.

Two types of gold nanoparticles are used in this thesis. These two types differ from each other with respect to the functionalization chemistry. These are called (type 1) \( \omega \)-thiol protected \( \alpha,\omega \)-alkanedihtiol coated gold nanoparticles and (type 2) sterically demanding thiolate coated gold nanoparticles. Figure 3-5 shows the schematic representation and SEM images of each type of AuNPs. Figure 3-5(a) describes that for type ‘1’ the AuNP surface is occupied by alkanedithiol molecules in two ways i.e., backbiting configuration labelled ‘1’ and standing configuration labelled ‘2’.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure35.png}
\caption{Two types of gold nanoparticles. (a-b) type ‘1’ and (c-d) type ‘2’.
}
\end{figure}
In the study of reference (11) it has been shows that majority of the ligands are in backbiting configuration. Chemistry of the standing ligands is such that one ‘S’ end of alkanedithiol molecule chemically links to AuNP while other ‘S’ is protected hence these AuNPs are also called protected AuNPs. Figure 3-5(b) shows the HRSEM image of protected AuNPs.

Type 2 nanoparticles are discussed in Paper-II. Figure 3-5(c) represents these nanoparticles. Surface of these nanoparticles is occupied by two types of ligands i.e., alkane monothiols labelled ‘1’ and alkyl thioacetate with tris-[(para-tert-butyl)phenyl] methyl phenyl end group labelled ‘2’. Figure 3-5(b) is high resolution image of these AuNPs. Due to bulky end group these AuNPs acquire a name stopper AuNPs.

There are obvious differences between these two types of AuNPs. First, the average size of Stopper AuNPs is 6.3±0.7 nm which is larger than average size of protected AuNPs 4.9±1.1 nm. Second, all ligands on the stopper AuNPs surface are not lying down while on protected AuNPs surface every 3 out of 4 ligands are lying down on the surface via both ‘S’ ends chemically linking to gold. Another important difference is that the protection group on the stopper AuNPs ligands cannot be easily removed but the protection group of the protected AuNPs ligands can be removed by acid treatment. (9)

Localized Surface Plasmon Resonance (LSPR)

By using the gold nanoparticles in our study, we benefit from another property. The optoelectronic properties of gold at the nanometer length scale can be used for understanding the process of chemical synthesis of nanoparticle nanoelectrode molecule bridge devices. At this size scale the phenomenon of localized surface Plasmon resonance (LSPR) is of greater importance and measurement of this phenomenon can inform about difference between nanoparticles with different ligands. (81)

LSPR is characterized by the oscillations of all electrons in a nanoparticle (NP) upon excitation by electromagnetic waves. This happens because NP size is smaller than the wavelength of light as well as smaller then penetration depth of the light in gold as shown in Figure 3-6.
Upon excitation by light all electrons mechanically oscillate between opposite ends of the NP hence oscillating polarization is created. Frequency of this oscillating polarization is characteristic of LSPR and is quantized. With changes in size of NP this frequency shifts.(82)

In the Figure 3-7, are shown the UV-Vis absorption from the two types of AuNPs. Absorbance peak around $\lambda = 520$ nm is characteristic of this size of gold nanoparticles. It also signifies that nanoparticles are well separated from each other.

![Figure 3-7: absorbance spectra of two types of AuNPs. Figure (a) is adopted from reference (11) and represents type ‘1’ i.e., $\omega$-thiol protected $\alpha, \omega$-alkanedihtiol coated gold nanoparticles and (b) represents type ‘2’ or sterically demanding thiolate coated gold nanoparticles.](image)

### 3.3 Characterization of trapping step

With dielectrophoretic trapping technique; nanoparticles were trapped inside nanogaps. Trapping of type ‘1’ nanoparticles has been performed and extensively studied.(9, 11) To know if the trapping of nanoparticles is accomplished the first choice is to perform electrical characterization. It is done using Agilent b1500a semiconductor parameter analyzer. Two-ways current-voltage (I-V) sweep measurements are performed. Then the resistance is calculated by taking average of the ration of Voltage and current between 75mV and 125 mV applied bias range. After performing the trapping step Figure 3-8 shows the SEM image where AuNPs of type ‘2’ are trapped inside nanogaps through dielectrophoresis.
Trapping of the nanoparticles results in reduction of effective tunneling distance because now electrons does not require to tunnel across from left to right electrode through vacuum. Rather it can hop from left electrode to nanoparticles to nanoparticles and then to the drain electrode. This reduction in effective tunneling distance results in higher current in trapped devices as compared to empty nanogaps.

**Effect of SEM imaging on electrical properties**

Electron microscopy is most valuable and straight forward method to visualize features at the length scale of the features of the nanoMoED platform. Especially SEM imaging is very useful because of ease of experiment and details of nanoMoED platform which it provides.

It gives direct evidence of nanoparticles in the gap. But this technique has its demerits also. Figure 3-9 shows the SEM characterization. Trapped nanogaps are the nanoMoED platforms which are fabricated by dielectrophoretic trapping of the type ‘2’AuNPs. In the IV comparison column blue curves are current voltage sweep measurements performed before doing SEM imaging and red curves are I-V sweep measurements performed after SEM imaging. Energy of the electron beam is 15keV. I-V measurements
show that after SEM imaging higher current is conducted through the platform. More than two orders of current is conducted at similar voltages. This detrimental effect on the nanoMoED platform due to SEM imaging is understood as follows. The nanoMoED platform contains organic species in the form of ligands which are coated on the nanoparticles surfaces. Also while trapping the solvent molecules (AuNPs are dissolved in toluene) may easily sit in the nanogap. With the cleaning techniques which can be applied after trapping step it is not possible to make sure that these organic contaminants are removed completely. SEM imaging of the platform which has these organic contaminations is considered to result in carbon deposition. This carbon deposition could be the cause of the observed decreased resistance.

3.4 Summary

The nanoMoED platform, which is nanoparticles trapped inside nanogaps, is described in this chapter. Fabrication of nanogaps between nanoelectrodes is performed using focused beam of gallium ions. Tuning the ion current resulted in smallest nanogaps achievable with this technique whose size was estimated to be 2.3nm using Simmons model. Two types of gold nanoparticles which are fundamentally different in their functionalizing chemistry are described in their trapping in nanogaps is performed using dielectrophoretic trapping technique. Chapter concludes with describing the characterizing techniques which can show signatures of trapped nanoparticles. It is seen that SEM imaging has detrimental effect on the resistance of the platform.
4. Synthesis of molecular junctions; nanoMoED devices

Molecules are chemisorbed on to the metal surfaces to form molecular electronic junctions. In the previous chapter, two types of gold nanoparticles were discussed and it was shown that both types of AuNPs can be trapped inside the nanogaps for the purpose of fabrication of the nanoMoED platform. In this chapter, synthesis of the molecular junctions in the nanoMoED platform is discussed. The nanoparticle-nanoelectrode bridge, based on such chemisorbed junctions on both end of short chain organic molecule will be called nanoMoED device. There are two chemical approaches that can be used to synthesize molecular contacts i.e., (i) in situ deprotection of the protected ω-thiol of the α,ω-alkanedithiol ligand when type ‘1’ AuNPs are trapped inside the nanogaps (9, 11) and (ii) ligand exchange of the functionalizing molecule from the nanoparticle with target molecule.(83, 84) Type ‘2’ AuNPs allow formation of molecular junctions via ligand exchange approach only.

Figure 4-1: nanoMoED devices contain molecules bridging the nanoparticles and electrodes.
The rest of this chapter is organized as follows. First, the understanding of the metal molecule junction and transmission of the electrons across such junctions is discussed. After this, the synthesis of molecular junctions using the three molecules shown in Figure 4-1 is described. In the end evaluation of the results of synthesis of molecular junctions in nanoMoED devices prepared using various molecules is presented.

4.1 Molecular junctions

When an organic molecule contacts between metal electrodes, various phenomena affect the transmission of electrons across the molecular junction from one electrode to the other. To understand those phenomena, the application of the Simmons model (section 3.1) is limited because that model does not take into account the strength of the contact between the metal and the molecule. A modified model that is inspired by the Landauer approach (85) need to be considered for understanding the electron transmission across metal molecule junctions.

An isolated molecule which is at least larger than an atom does contain discrete molecular orbitals which are a consequence of overlap between atomic orbitals. The molecular orbitals are filled up to the highest orbital called highest occupied molecular orbital (HOMO) and the next empty orbital which is higher in energy then the HOMO is called lowest unoccupied molecular orbital (LUMO). The energy separation between highest occupied and lowest unoccupied orbital is called HOMO-LUMO energy gap. Both, the energy position of the HOMO and/or LUMO and the energy gap between them are of particular interest in molecular electronics and determine the electron transport properties of the molecules connected between metallic electrodes.

When a molecule is connected between metallic electrodes, its electronic structure is altered, manifested by the interaction between energy states from electrode and states from molecule. Figure 4-2(a) represents the energy diagram of a molecule connected to metallic electrodes at 0 V bias Voltage. The Fermi level lies typically between HOMO and LUMO of the molecule. (86) Figure 4-2(b) shows the broadening \( T = T_L + T_R \) of levels of the molecules which is a consequence of overlap between states from the electrode and that of molecule. This broadening is large for strong coupling. In this situation when voltage of 0 V is applied, no net current flows across electrodes because both electrodes are at same chemical potential.
This situation changes when a bias voltage (eV) is applied. The Fermi level of the right electrode is lowered with respect to the left electrode when positive voltage is applied to it as shown in Figure 4-3.

An energy window with magnitude ‘eV’ is created. Hence electron can flow from left to right electrode.

The quantification of voltage dependent current which could flow in the situation depicted in Figure 4-3 can be done following the Landauer approach. In this approach the total conductance of any sample can be considered as sum of the transmission of individual conducting channels in the sample

$$G = G_o \sum_{i=1}^{n} T_i$$  \hspace{1cm} \text{(4.1)}

Here $G_o = 2e^2/h$ and ‘$h$’ is Plank’s constant and ‘$i$’ is for i-th transmission channel. For a single perfectly transparent channel value of transmission function is 1 and current in equation 4.1 equals $7.748 \times 10^{-5}$ S. This value is called the conductance quantum and is the highest value of the conductance.
which a quantum channel can acquire. For a metal molecule junction, the
states from the molecule that overlap with states from the electrode result in
the transmission function which depends on energy and voltage. Also only
those states that lie inside the energy window defined by the Fermi level
difference between two electrodes contribute to the conduction. Hence cur-
rent is given by

\[ I = I_0 \int_{-\infty}^{+\infty} T(E, V)[f_1(E) - f_2(E)]dE \]  

4.2

Here ‘\( \Gamma \)’ is the Fermi function of the electrodes and ‘\( T(E, V) \)’ is energy and
evoltage dependent transmission function for the metal molecule junction. At
low bias voltages the value of transmission function is constant and no mo-
lecular levels are present for conduction hence the voltage ‘\( V \)’ can be omit-
ted from the transmission function of equation 4.2.

In metal molecule junctions, the orbital hybridization leads to an equilib-
rium situation which is defined by position of the Fermi level of metal elec-
trodes somewhere between HOMO-LUMO gap of the molecule. Depending
upon the energy difference between Fermi level and HOMO or LUMO, the
transport will happen through that respective orbital which is closest to the
Fermi level. The transmission function now depends on the density of states
of the resulting junction which depends on molecular density of states ‘\( D(E) \)’
and broadening ‘\( \Gamma = \Gamma_L + \Gamma_R \)’ of the levels due to hybridization as described
by equation 4.3

\[ \frac{1}{\pi} T(E) = D(E). \frac{\Gamma_L \Gamma_R}{\Gamma} \]  

4.3

The results of the electrical characterization that are presented in this chapter
were intended to investigate direct tunneling or low bias electrical tunneling
resistance.

4.1.1 Insulating and conducting molecule.

The insulating or conducting character of a molecule is defined by localiza-
tion or delocalization of electron pathways, respectively.\(^{(87, 88)}\) Alkane
chains are considered as insulating molecules due to (i) the localization of
electrons and (ii) the large HOMO-LUMO gap. These molecules have been
test beds for studying various transport properties of molecules but lack their
applicability in applied molecular electronics to date.

However, conjugated molecules like benzene which contain pi-orbitals
that are overlapping and hence electrons are delocalized over the whole ring
are considered to be conducting. In addition, the HOMO-LUMO gap is
smaller as compared to alkane molecules and hence the resonance situation
can be achieved at lower voltages and thence these molecules are considered better candidates for molecular electronics. The molecules used to make nanoMoED devices are shown in Figure 4-1.

Molecule 1 is 1,8-octanedithiol. This molecule is an insulator in the molecular electronics context. It possesses large HOMO-LUMO gap of \( >6 \) eV, electrons are localized in \( \sigma \)-bonds. Upon formation of metal-molecular junction, the energy difference between the Fermi level of electrode and conducting molecular orbital is large \( >2.5 \) eV.\(^{(89, 90)}\)

Molecule 2 is 4,4'-biphenyldithiol. This molecule is considered conductor in the molecular electronics context because it has a HOMO-LUMO gap of \( \approx 3 \) eV, which is small as compared to alkane molecules. It has delocalized electrons in overlapping \( \pi \)-bonds. Upon formation of metal molecule junction, the energy difference between Fermi level of electrode and conducting molecular orbital is small \( \approx 1 \) eV.\(^{(91-94)}\)

Molecule 3 is 5,5'-diphenyl-2,2'-bithiophene whose conductance is understood better if its structure is considered as two phenyl rings connected at each end of bithiophene molecule to the electrode surfaces.\(^{(35)}\) When connected between gold electrodes, the phenyl rings of the molecule introduce states which result in lowering the energy difference between HOMO of the molecule and the Fermi level of the gold electrode as described in reference \((95)\). In this reference, the authors discuss alkoxythiolated diphenyl-2,2'-bithiophene molecular junction and demonstrate that the HOMO level is positioned at \( \approx 0.3\)eV from the Fermi level of gold. This argument describes that the molecule 3 is more conductive as compared to molecule 2 even though this molecule is longer.\(^{(96, 97)}\)

### 4.1.2 Electrode material-anchor group pair and properties

The coupling of a molecule to the electrodes happens through its terminal (anchoring) groups. For this to happen the choice of electrode material as well as anchoring groups of molecules is crucial because this determines the creation, long term stability, physical and electrical properties of the molecular junction.\(^{(98)}\) The choice of material of electrode is based on, at least, following requirements (i) that it is chemically inert (ii) that it is mechanically stable at operating conditions and (iii) that it allows chemical link between molecules for creation of molecular junctions. Detailed information about choice of electrode materials to be used in molecular electronics can be found in sections 2, 3 and 4 of the review in reference \((99)\). Here, is highlighted the use of gold (Au) as electrode material is highlighted. Gold, in bulk form, is chemically inert due to its unique electronic structure. Also, its oxides and sulfides are not stable because they have positive heat of formation.\(^{(100)}\) This fulfills the first requirement. The second requirement that it needs to be mechanically stable is not ideally fulfilled by gold because its surface atoms are mobile. A better choice will be platinum whose atoms are
more stable. The third requirement which is chemical synthesis of molecular junctions via chemical bonding is fulfilled by gold because it can form gold thiolate bond with thiol anchor group of molecules. Further, the FCC structure of gold nanoparticles and Au(111) and Au(100) facets can be utilized for creating molecular junctions.\(^{(101)}\)

With gold as electrode material the anchor groups which have been studied extensively are thiol (SH), amine (NH\(_2\)), methyl sulfide (SMe) and pyridyle (Py). \(^{(102-105)}\) Among these anchor groups, thiolate results in highest conductance because of lowest injection barrier for electrons, highest coupling strength with gold electrodes and the longest mechanical stability of the junction. Detailed information about the anchor groups and choice of electrode materials is available in comprehensive review of molecular scale electronics\(^{(99)}\) and whose section 7.1 contains extensive information about electrode material-anchor group pairs.

In present work, the molecules which have been used to form metal molecule junctions were terminated with thiol (SH) anchor group which results in gold thiolate bond. We also used (di)thiolated molecules when sulfur was protected by either acetyl (SAc) or trimethylsilyl (TMS). Before insertion into between gold surfaces the protection groups were removed so that gold thiolate contact can be formed.

4.2  Formation of metal-molecule junctions in nanoMoEDs

The two methods that were chosen to bind molecules with the gold surfaces for the purpose of the creation of molecular junctions in the nanoMoED platform are (i) protection then deprotection and (ii) molecular place exchange.\(^{(84)}\)

4.2.1  Method (I); Protection then deprotection

This method is detailed by S.H.M. Jafri et al.\(^{(9, 10, 76)}\) They investigated the creation of molecular contacts using 1,6-hexanedithiol and 1,8-octanethiol using this method. These molecules terminated by (SH) prior to creation of molecular junctions were used to functionalize gold nanoparticles. One thiol end of the molecules was connected to gold nanoparticle via Au-S bond while the other thiol end of the molecule was protected by a triphenylmethyl (trityl) group. After trapping these nanoparticles inside the nanogaps the devices were immersed inside deprotection solution (solution of 5mL trifluoroacetic acid, 5mL DCM and 0.5 mL triethylsilane for 20 minutes) which cleaved off the trityl protection group and thence the mo-
lecular junctions between gold surfaces were created by linking the bare ‘S’ from the alkane molecule with gold.

4.2.1.1 Molecular junctions made with 1,8-octanediithiol; nanoMoED device 1

Type ‘1’ AuNPs that are functionalized with ω-thiol protected α,ω-octanediithiol (ODT) ligands, were trapped in the nanogaps by dielectrophoresis. Two ways current-voltage (I-V) sweep characterization was performed before and after deprotection step. Figure 4-4 shows the IV response before and after deprotection of 1,8-octanediithiol i.e., cleaving of the triphenylmethyl group from thiol. Deprotection resulted in reduction of low bias resistance by more than two orders of magnitude. This result is consistent with previously reported results.(9) Low bias resistance is another terminology for direct tunneling resistance which happens when applied voltage is less than the difference between Fermi level of the electrode and conducting molecular orbital.

The Figure 4-4 also shows that keeping the deprotected nanoMoED devices in toluene for 150 hours did not have considerable effect on the low bias electrical resistance (PAPER V).

Previously Jafri et al., in reference (14) reported the variations in size and low bias electrical resistance of the empty nanogaps and the variations in low bias electrical resistance of the nanoMoED devices when trityl group was removed from ODT. They stored these nanogaps and deprotected nanoMoED devices in air and various liquids over the period of 4 weeks. It was reported that the nanogap size remains stable in toluene while electrical
resistance of the deprotected nanoMoED devices decreased in toluene. The effect of toluene on the nanoMoED platform which is shown in Figure 4-4 was not reported. Here this result signifies that only after treatment with deprotection solution, the low bias electrical resistance changes. This reduction in low bias resistance after deprotection step is a consequence of the formation of chemisorbed metal molecule contacts which reduce the charge injection barrier at the metal-molecule contact. Hence higher current is observed.(9) It has been shown that after deprotection the nanoparticles were bridged with specific molecule either HDT or ODT. The low bias resistance of the devices was calculated in reference (9) to be (i) with HDT 0.2GΩ and (ii) with ODT 2GΩ.

The result that the nanoMoED devices made with longer molecule (ODT) showed one order of magnitude larger resistance as compared to devices made with shorter molecule (HDT) can be understood as a consequence of the fact that after deprotection the physical spacers between nanoparticles are only molecules either HDT or ODT, so longer molecule introduces longer physical separation between nanoparticles and hence reduced probability for tunneling of electrons across the electrodes, at low voltage bias conditions.

4.2.2 Method (II): molecular place exchange

The second approach is called molecular place exchange. It has been applied for the formation of nanoparticle molecule bridge based molecular electronic devices.(3, 5) Place exchange is understood as an associative substitution reaction i.e., leaving of the attached ligand ‘1’ from the surface of the gold nanoparticle when incoming molecule ‘2’ with an anchor group (in present case thiol (SH)) attaches on the surface of the gold nanoparticle, Figure 4-5.

![Figure 4-5: Place exchange of ligands 1 attached to the nanoparticle with incoming molecules 2. (a) Before place exchange and (b) after place exchange.](image)

Surface of the gold nanoparticle affect the place exchange reaction and place exchange is preferentially initiated at the corners and edges on the nanoparti-
The most favorable reaction is between staple gold atoms and terminating thiol end of molecule. That means that the more vertices and edges on the surface of the nanoparticle, higher will be the likelihood that a molecule will attach to the surface.

The type of ligands functionalizing the gold nanoparticle surface may or may not favor the place exchange reaction. For instance, example a ligand which is attached to the surface has three body parts (i) foot (ii) stem and (iii) head. The foot group has no effect on place exchange if both molecules ‘1’ and ‘2’ have the same. Stem group which is one factor in determining the packing of the molecules ‘1’ on the surface of the nanoparticle. If packing is denser then there is more hindrance to place exchange. Head group may or may not affect place exchange. And in addition; the difference in concentration of the attacking molecules with respect to the ligands on the nanoparticle surface is crucial. While performing place exchange in our setup it is clear that the concentration of molecules ‘2’ is far greater then molecules ‘1’.

In this technique, in our work, the target molecules were dissolved in toluene and a 10 mM solution was prepared. The nanoMoED platform devices which contain nanoparticles of type ‘1’ or type ‘2’ trapped inside the nanogaps, were immersed in this solution of the target molecule for 24 to 96 hours. Electrical characterization was performed by doing two-ways I-V sweep measurements before and during place exchange. Test measurements were performed during place exchange i.e., the sample containing the nanoMoED devices was taken out from the place exchange solution after (for example) 24 hours, washed with analytical grade toluene, then blow dried with N₂, then investigated by electrical characterization. After this characterization the sample was again immersed in the solution of the target molecules. If the results of any two consecutive electrical characterization steps do not show a change in resistance, the reaction was stopped and the sample was not immersed in that solution again.

### 4.2.2.1 Molecular junctions made with 4,4'-biphenyldithiol; nanoMoED device 2 (PAPER-II and PAPER IV)

Both types of AuNPs have been used for making nanoMoED devices via place exchange technique. The target molecule 4,4'-biphenyldithiol (BPDT) was dissolved in toluene and nanoMoED platform devices were immersed in the solution for a total of 48 hours. The results obtained, using type ‘1’ nanoparticles and 10mM concentration of BPDT in toluene, are shown in Figure 4-6. Current-voltage (I-V) sweep characterization, green and purple graphs in Figure 4-6 (a) respectively, show that the nanoMoED device conducted approximately ≈2 orders of magnitude higher current after place exchange as compared to trapped nanoMoED platform. The histogram made with the calculated low bias resistances of the nanoMoED platform before (green bar chart) and after place exchange reaction (purple bar chart) is
shown in Figure 4-6(b). Resulting geometric mean resistance of the devices after place exchange is \( \approx 3 \, \text{G}\Omega \).

Similarly, the place exchange reaction was carried out on type ‘2’ AuNPs trapped inside the nanogaps. In reference \((108)\) PAPER II, it was demonstrated that, ratio of alkane-monothiols and stopper ligands on the surface of these nanoparticles can be controlled. Those nanoparticles with 5%, 15% and 30% stopper coverage were trapped inside nanogaps and place exchange with BPDT was carried out. Low voltage bias resistance of the devices after place exchange reaction is summarized in. It was observed that the geometric mean resistance of the nanoMoED platform devices containing 5%-stopper AuNPs after place exchange was \( \approx 1 \, \text{G}\Omega \).

![Figure 4-6: I-V sweep characterization (a) and low bias resistance before (blue) and after (red) place exchange (b) with BPDT. Figure taken from PAPER (IV)](image)

The measured value of nanoMoED devices prepared with BPDT in these experiments is larger as compared to previously reported values in literature. \((91-94, 109)\) This is because there are at least two BPDT molecules and one nanoparticle connected in series between nanoelectrode surfaces. Hence series combination of resistors results in large resistance.

4.2.2.2 Effect of tunable ligand chemistry of type ‘2’ gold nanoparticles on place exchange reaction

The Table 1 summarizes the results of place exchange reaction which was carried out using BPDT molecules when type ‘2’ nanoparticles were trapped in nanoMoED platform. The resistance of the as prepared devices using nanoparticles consisting of 5% stopper ligands is smaller than the resistance of the devices that were prepared with nanoparticles consisting of 15% and 30% stopper ligands. This result is understood as due to the effect of steric hindrance which increases when quantity of bulky stopper ligands increases. Increase in steric hindrance to the incoming BPDT molecules could results in less efficient place exchange and hence measured resistance of nano-MoED devices is smaller when stopper coverage is larger.
Table 1: Effect of increasing the quantity of stopper ligands on the surface of type ‘2’ AuNPs,

<table>
<thead>
<tr>
<th>Type of AuNPs</th>
<th>Low bias resistance after place exchange with BPDT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From reference(108)</td>
</tr>
<tr>
<td>5%-stopper</td>
<td>0.3 GΩ (2 devices)</td>
</tr>
<tr>
<td>15%-stopper</td>
<td>7.9 GΩ (6 devices)</td>
</tr>
<tr>
<td>30%-stopper</td>
<td>6.7 GΩ (4 devices)</td>
</tr>
</tbody>
</table>

4.2.2.3 Probing the energy levels of molecules in nanoMoED devices via transition voltage spectroscopy

Transition voltage spectroscopy (TVS) presents the current versus voltage data in a different graphical way i.e., plotting the $1/V$ on abscissa and $\ln(V/V_0^2)$ on ordinate axis. It is a method that gives valuable information about voltage dependent conductance of molecular electronic junctions.\(^{(110-112)}\) Qualitatively this method can be understood as follows. The Fermi level $E_F'$ of the gold electrodes is shifted in a continuous energy range by applying voltage. This ‘movement’ of the Fermi level effectively scans for the available conduction channels in the connected molecule. The current that is measured while scanning for the molecular orbitals has different features at different positions of the Fermi level with respect to the conducting molecular orbitals. As discussed in section 3.1 three regimes of conduction are described (i) direct tunneling regime, when Fermi level of electrode (due to applied voltage) is below the barrier height $\varphi'$ of the insulating material, (ii) transition regime, when Fermi level and barrier height are equal, and (iii) field emission, when Fermi level is higher than barrier height. The change from direct tunneling to field emission appears as a ‘dip’ in TVS graph. Figure 4-7 shows the TVS for nanoMoED device 2 i.e., device containing BPDT inserted using place exchange reaction.

![Figure 4-7: Transition voltage spectroscopy (TVS) of nanoMoED device 2](image)

This dip is called transition voltage $V_{\mathrm{trans}}'$. The Figure 4-7(a) shows the current conducted by the nanoMoED device 2 when applied voltage is ramped from 0 V to 1 V in steps of 10 mV. This I-V curve is average of three consecutive I-V curves. Nonlinear dependence of current on voltage is
typical of molecular electronic junctions. In Figure 4-7(b) the transition voltage graph is plotted for the averaged I-V response. There is a clear dip in the graph which appears around 0.45 V. This is the transition point on the voltage axis. Below this voltage, the current is conducted via direct tunneling and above this voltage current is conducted via field emission.

When the BPDT is contacted to gold electrodes the theoretical value of \((E_F - E_{\text{HOMO}})\) is 0.96 eV.\(^{(113)}\) In reference \((114)\) authors observed the value of \(V_{\text{trans}} = 0.7\ eV\) for BPDT gold junctions. The value of transition voltage that is extracted from the TVS plot in Figure 4-7 is below the actual energy difference \((E_F - E_{\text{HOMO}})\) for BPDT-gold junction. This is not understood completely. Probably this could be due to the lowering of the work function of gold electrodes in non-UHV conditions\(^{(36)}\) and also could be due to reduction of effective barrier height due to adsorption of organic molecules.\(^{(115)}\) Another reason could be the resonance of Au-S states that are closer to the Fermi level of the gold. For instance, the authors in reference \((90)\) used alkanedithiol-gold junctions and demonstrated that the occurrence of TVS dip at lower than actual energy difference between HOMO and Fermi level is due to the effect from Au-S bond states. These states are located closer to the Fermi level of gold at zero bias as compared to conducting molecular orbital (HOMO) of the ODT and hence the transition point in the I-V response is observed at a lower voltage. Our result needs more study for better understanding.

**4.2.2.4 Molecular junctions made with 5,5'-diphenyl-2,2'-bithiophene; nanoMoED device 3**

This result is published in **PAPER-III**. The Low bias resistance of 16 devices, which was obtained before and after place exchange with 5,5'-diphenyl-2,2'-bithiophene (also called 0TBT) is shown in Figure 4-8. The value of geometric mean resistance obtained after place exchange, extracted from the low bias resistance data of individual devices is 0.082 GΩ.

![Figure 4-8: Low bias resistance after place exchange with 0TBT with inset showing the current voltage relationship of one of the representative devices.](image)

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This value of low bias resistance is smaller than nanoMoED devices prepared with BPDT (nanoMoED device 2). It should be pointed out, that after trapping, the devices may have very different resistances i.e., the resistance histogram spreads over several orders of magnitude. After the place exchange reaction, the devices have a less broad resistance histogram. This is shown in Figure 4-8, where the device resistance after place exchange is only varying by one order of magnitude.

4.3 Spectroscopic study of place exchange

The synthesis of molecular contacts via place exchange is also characterized by studying the localized surface Plasmon resonance (LSPR) from the AuNPs before and after place exchange. LSPR is studied from samples in solution phase where the medium is toluene. After measuring absorbance of stopper-AuNPs solution, BPDT or 0TBT is added to the solution and kept in argon atmosphere. Place exchange is allowed to happen for 15 hours and after this absorption is measured from the sample. Figure 4-9 shows the normalized UV-Vis absorption spectra of the gold nanoparticles before and after place exchange with BPDT (red dashed line) and 0TBT (blue dotted line). The LSPR peak from the stopper-AuNPs before place exchange reaction (around \(\lambda=521\) nm) is red shifted more than 27 nm after place exchange reaction.

![Figure 4-9: LSPR measured before and after place exchange with BPDT (red) and 0TBT (blue).](image)

The red shift in absorbance (\(\Delta\lambda\)) is observed in both cases i.e. \(\Delta\lambda_{\text{BPDT}} \approx 37\) nm and \(\Delta\lambda_{\text{0TBT}} \approx 27\) nm respectively for BPDT and 0TBT as target molecules. This effect has been described Calame et al.(3) According to them this observation indicates the bridging of the nanoparticles with molecules because the ligands contain -SH group on both ends which facili-
state the formation of chemical link with gold. A larger red shift is observed in Figure 4-9 as compared to Calame et al., which could derive from the fact that, in their case the AuNPs are fixed in a matrix whereas in the present samples AuNPs are free to move. Therefore, it is expected that a higher percentage of ligands was exchanged. Furthermore, the LSPR shift observed in the experiment of 0TBT is smaller than the observed in the experiment of BPDT. This result can be qualitatively described as comparatively weaker Plasmon coupling between the AuNPs when the spacer ligand is longer.\(^{(81)}\)

4.4 Deviation from the expected resistance of nanoMoED devices

The results for individual nanoMoED devices that are presented in this chapter point to a very interesting deviation from the expected resistance value. In Table 2 is presented, the summary of the low bias resistances which are measured for various devices and/or taken from literature.

The low bias resistance of nanoMoED device 2 which is synthesized with BPDT is larger than the low bias resistance of nanoMoED device containing same type of AuNPs and 1,6-hexanethiol. This is because the techniques used to make the two devices are different. The nanoMoED device 2 was synthesized using place exchange whereas 1,6-hexanethiol based devices were fabricated via deprotection chemistry. There are differences in the ways the molecules form junctions when one or the other technique for synthesis is applied.

Table 2: Comparison low bias resistance of nanoMoED devices synthesized with various molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Low bias resistance (\times 10^9) (\Omega)</th>
<th>(Synthesis approach)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6-hexanethiol (HDT)</td>
<td>(\approx 0.2)</td>
<td>(I) reference ((9))</td>
<td></td>
</tr>
<tr>
<td>1,8-octanethiol (ODT)</td>
<td>(\approx 2)</td>
<td>(I) reference ((9)) and article ((VI))</td>
<td></td>
</tr>
<tr>
<td>4,4'-biphenyl-dithiol (BPDT)</td>
<td>(\approx 3)</td>
<td>(II) Article-IV</td>
<td></td>
</tr>
<tr>
<td>4,4'-biphenyl-thioli (BPDT)</td>
<td>(\approx 1)</td>
<td>(II) Article-III</td>
<td></td>
</tr>
<tr>
<td>5,5'-diphenyl-2,2'-bithiophene</td>
<td>(\approx 0.082)</td>
<td>(II) Article-III</td>
<td></td>
</tr>
</tbody>
</table>

The deprotection technique results in efficient contacting between molecule and gold surfaces.\((9)\) It is also understood that after complete deprotection only chemisorbed metal molecule junctions exist and only 1,6-hexanethiol is present in spaces between gold nanoparticles. On the other hand, the place exchange technique may or may not result in the formation of chemisorbed contacts between gold surfaces and the anchor group of the molecule. Indeed it has been demonstrated that place exchange depends on the initial spacing between the nanoparticles.\((4, 116)\) If the spacing between the nanoparticles
is larger than the size of the target molecule, then the molecule cannot contact the nanoparticles on its both ends.

A similar reason explains the results under discussion. In PAPER II, the information of type ‘2’ AuNPs is presented. The minimum spacing between the AuNPs was found to be ≈1.6 nm from the transmission electron microscope (TEM) measurements. This spacing is larger as compared to the length of the BPDT molecule connected to gold surfaces (≈1 nm). Therefore, BPDT cannot efficiently bridge between the nanoparticles. The length of the 5,5’-diphenyl-2,2'-bithiophene molecule is 1.6 nm which is compatible with the spacing between gold nanoparticles. Therefore, place exchange reaction with this molecule was more favorable and resulted in comparatively smaller resistance of the devices as compared to the resistance of those devices that were made using place exchange with BPDT.

4.5 The nanoMoEDs with oligo(phenylenethienylene)s series molecules (Paper-III)

These molecules also called nTBT (where n=1, 2 and 3). These are schematically shown in Figure 4-10(a) and are suggested for use in molecular electronics. (117) Formation of nanoMoEDs with these molecules using place exchange method was performed and results of three devices are shown in Figure 4-10(b).

This observation that a longer molecule may result in smaller resistance is not surprising for nanoparticle molecules junctions (4, 116) but requires further discussion when observed in the sub 20 nm nanoMoEDs.

The type ‘2’ AuNPs with 5% stopper coverage were trapped inside the nanogaps. The low bias resistance of the three separate nanoMoED platform devices on which the nTBT place exchange (PE) was performed was; before PE with 1TBT = 4 TΩ, before PE with 2TBT = 3.8 TΩ and before PE with
3TBT = 2.8 TΩ. These values of low bias resistance of the nanoMoED platform are very similar to each other. After place exchange with 1TBT the low bias resistance did not change. After place exchange with 2TBT the low bias resistance was reduced by ≈1 order of magnitude and after place exchange with 3TBT the low bias resistance was reduced by ≈2 orders of magnitude. We propose that this result could be because in nanoMoED devices where electrodes are separated by ≈20 nm, there can be one AuNP of type ‘2’ with size 6.3±0.7 nm and two 3TBT molecules to make a bridge between nanoelectrodes (Similar to Figure 1-2). Therefore, total 4 contacts (Tc) are required. Of these 4 contacts, 2 contacts will be at clean gold surfaces (Pc) and other two will be at the AuNPs. The formation of the contacts at the AuNP side is very less likely because of steric hindrance between nTBT molecules and stopper ligands. The resulting probability \( P = Tc/Pc \) of formation of a bridge between the electrodes with one AuNP and two 3TBT molecules is \( P = 0.5 \). Similarly for 2TBT, \( P = 0.33 \) and for 1TBT, \( P = 0.25 \). This reduction in probability with reducing length of the molecule could possibly be the reason of result of Figure 4-10(b).

4.6 Summary

In this chapter two methods are applied to synthesize molecular junctions in the nanoMoED platform. Results of individual nanoMoED device are cross compared to understand that, the method with which molecular contacts are prepared is one important factor in understanding the low bias resistance of these nanoMoED devices. If applying the deprotection method for synthesis of metal molecular junctions, as prepared nanoMoED devices show resistance which is small for small length of the molecule and vice versa. If using place exchange method for the synthesis of metal molecule junctions, as prepared nanoMoED devices may show opposite resistance versus molecular length behavior. The initial spacing between the nanoparticles determines the junction formation when using place exchange method. This implies that a longer molecule may result in smaller resistance because of its size compatibility with the spacing between nanoparticles. Transition point in the TVS graph of nanoMoED devices prepared with BPDT showed smaller value as compared to theoretical value of \((E_F - E_{HOMO})\). The nTBT molecules showed that in nanoMoEDs their resistance reduces with increasing length. We call the devices prepared with 1,8-octanedithiol as device 1 and devices made with BPDT as device 2 for the purpose of discussions in chapter 5.
5. Electrical resistance of the molecular junctions in NO\textsubscript{2} environment

In chapters 3 and 4, the synthesis of metal molecule junctions in the nanoMoED platform was described. The various factors that determine the tunnel resistance of the as prepared nanoMoED devices and the various factors effecting the tunnel resistance, which are introduced during the device fabrication process were discussed. In present chapter, the focus will be on understanding the effects of external species on the tunnel resistance (low voltage bias electrical resistance) of the nanoMoED devices.

Recall that the nanoMoED platform was name given to that device which contains gold nanoparticles of either the type ‘1’ or the type ‘2’ that were trapped inside the nanogaps using dielectrophoresis. The nanoMoED device ‘1’ was name given to that device which contains metal-molecule junctions that were synthesized by applying protection-deprotection method using type ‘1’ nanoparticles. The molecule that bridged the two gold surfaces was ODT. The nanoMoED device ‘2’ was the name given to that device that has BPDT inserted between gold surfaces using the molecular place exchange method. Both type ‘1’ and type ‘2’ nanoparticles can be used for place exchange method.

In this chapter these three devices i.e., the nanoMoED platform, the nanoMoED device ‘1’ and nanoMoED device ‘2’ will be used to describe how the resistance of metal molecule junctions is modulated when placed in various gaseous environments.

5.1 Current – time (i-t) characterization at low DC bias voltage

Electrical characterization technique used to acquire the results that are presented in this chapter is called current-time (i-t) characterization. In this technique devices are biased with fixed DC voltage and the current flowing through them is recorded. The changes in the environment surrounding the devices can affect the electronic properties of the devices. Thus the change in electronic properties of the devices is reflected in the measured current.

The underlying idea of the current-time characterization experiment can be understood using equations 4.2 and 4.3. According to those equations, the
conductance of a molecular junction depends on density of states of the metal-molecule junction at the Fermi level ‘\(D(E)\)’, the coupling strength between the metal and the molecule ‘\(\Gamma\)’ and the difference between the Fermi levels (eV) of the two electrodes. When devices are biased with low DC voltage that means difference between Fermi levels is fixed and the transmission function is independent of voltage. Upon exposure to different gaseous species there can be changes in the properties of devices. These changes could be reflected in the measured current. For instance, if the magnitude of the measured current changes this will be indicative of change in ‘\(D(E)\)’ of the metal molecule junction at the Fermi level since low voltage is applied.

5.1.1 Current-time characterization in N\(_2\) environment

Current-time (i-t) spectroscopy was performed at fixed voltage bias while the environment around the devices was switched between N\(_2\) and NO\(_2\).

![Figure 5-1: Results of current time (i-t) characterization in N\(_2\) environment for (a) nanoMoED platform (c) nanoMoED device ‘1’ and (e) nanoMoED device ‘2’. In subfigures (b, d and f) are the histograms of current levels obtained from figures (a, c and e) respectively.](image-url)
Figure 5-1 shows the results of (i-t) measurements performed in N₂ environment when the three configurations were experimentally tested. The current-time graph in Figure 5-1(a) is measured from the nanoMoED platform i.e., when the molecules on the trapped nanoparticles are not chemically linking a pair of gold surfaces. In this situation very small current i.e., less than 1pA is observed whose average level does not change significantly. Fluctuations in current are observed and in this case these can be due to shot noise introduced by the system. The signal to noise ratio is 20.87 dB which describes that the signal power is approximately two orders of magnitude strong as compared to noise power. For current levels smaller than 1e-12 A this SNR demonstrates state of the art quality of gas sensor setup and measuring conditions. Figure 5-1(b) shows the histogram of current values for the observed i-t response.

The current-time graph observed from the nanoMoED device 1 is shown in Figure 5-1(c) and the histogram of the observed current levels is plotted in Figure 5-1(d). Among all the presented results this histogram was characteristic of nanoMoED platform. Large fluctuations in current were observed which showed that current fluctuates between 51 pA and 76 pA. The histogram of current levels shows that the current switches between two levels which are separated by 25pA. SNR is less than 10 dB which does not justify the quality of the measurement setup. This low value of SNR is because of noise from the device i.e., switching of current between two distinct levels.

These distinct current levels have physical origin. The first reason which is understood is the contact geometry of 1,8-octanedithiol molecule between two gold surfaces.(12, 118-120) Au-(s)-molecular-(s)-Au junctions can have one of the contact on top site and other contact at hollow site on Au surfaces. Similarly Au-S contacts on both sides can be on atop sites on gold surface. These two contact geometries have different conductances i.e., the conductance in the former geometry of the molecular junction is higher while in the latter geometry it is lower. Similar phenomenon is reported reference (119) which describes the effect of contact geometries on conductance of Au-ODT-Au junctions. Two sets of conductance values have been reported. Here the authors elucidate further that the occurrence of Au-S bonds at the step edges has effect of increased overlap between electrode and anchor group of molecule which reduces the charge injection barrier and hence higher conductance is observed. In reference 28 in addition to effect of contact geometries on conductance, authors also point to gauche defect containing alkanedithiol backbone. This defect results in third conductance value which is lower than the other two conductance values. Effect of conformational changes in the ODT backbone could cause current level switching and this has also been investigated by Paulsson et al.,(121) in their theoretical study. Formation of gauche defects in the ODT backbone is attributed to lower the conductance while all-trans conformation represents higher conductance. Another reason for conductance switching and observation of bi-
binary level switching of current through alkanedithiol molecular junctions is described by Calame et al in reference (122) They attribute the two level random telegraph signal which is observed in their MCB-J based devices to random breaking and formation of Au-S bond. This causes conductance to switch and it will be lower when Au-S bond breaks. In reference (123), authors used a very similar device as the device under discussion and observed similar signal. Electrical characterization of their devices (which contained gold nanoparticle-molecule junctions synthesized inside very small nanogaps between metal electrodes) was performed at very low temperatures. They suggested that the random switching of current through a chain made of electrode-molecule-nanoparticle-molecule-electrode was due to coulomb charging effect of a nearby nanoparticle which was not chemisorbed. Although this could be the possible reason, but since in our devices the binary level switching was observed at room temperature this phenomenon is less likely the cause.

The current-time (i-t) response of nanoMoED device 2 is shown in Figure 5-1(e) and the histogram of current levels is shown in figure Figure 5-1(f). Current maintains at single level with SNR of 28.22 dBs, Apart from better SNR in this device other parameters are qualitatively similar as in Figure 5-1(a). Improved SNR is because in this device molecular junctions exist while in the nanoMoED platform molecular junctions are absent.

It is intriguing that the nanoMoED device 1 conducted the current which was switching between two levels but other two devices showed single level conduction. One reason is described by Lindsay and coworkers.(124) Another reason could be due to the robust chemisorbed metal molecule junctions on both ends of the molecules which exist only in the nanoMoED device 1. On the other hand, in the nanoMoED platform there is chemisorbed metal-molecule link at one side of the molecule while its other end is protected from chemisorption, similarly it was discussed in chapter 4 that BPDT which is smaller than the spacing between the AuNPs, may not bridge the gold nanoparticles completely. Hence, because the metal-molecule links which exists in the three mentioned configurations of these devices are different hence there response is different.

5.1.2 Current-time characterization in NO2 environment

The nanoMoED platform when exposed to NO2 while fixed DC bias was applied to it, did not show change in either the SNR or the average current level. Figure 5-2 shows the current conducted by the nanoMoED platform when the applied bias voltage was 300mV.
Average current remains same both in N\textsubscript{2} and 100 ppm NO\textsubscript{2}/N\textsubscript{2} gas environments. Similarly noise fluctuations of current also have similar amplitude in both gas environments.

The nanoMoED device 1, which contains chemisorbed molecular junctions of ODT with gold surfaces showed current time response at fixed bias voltage as shown in Figure 5-3,

Conduction through this device in N\textsubscript{2} atmosphere is a characteristic random telegraph signal. Switching between two levels is due to the Au-S bond changing position on the gold surfaces.(119-121) Contact of the thiol at the gold step edges results in higher conduction as compared to when thiol contact with gold is on atop position. In nitrogen dioxide environment conduction at higher level gradually diminishes. This effect is attributed to the occupation of under-coordinated sites on gold surface(125) which are thence not available for making contact with ‘S’ end of the molecule.(PAPER V).
For nanoMoED device 2 current versus time measurements performed at fixed bias voltage are performed and Figure 5-4 shows the measured response. Green portions show when device was in ambient air, blue portion shows device in N₂ gas and red portion shows the device in 100ppm mixture of NO₂/N₂. Black line passing through the response curve is moving average line averaged over 255 data points.

Upon NO₂ exposure, current rises and reaches up to ≈62% above baseline value. Qualitatively arguing this observation is indicative of change in density of states of the molecule in presence NO₂. It has been demonstrated in PAPER-IV through DFT calculations that combined transmission spectrum of BPDT-NO₂ shows induced energy states at the Fermi level of Au-BPDT-Au junctions. These induced states are the cause of increased current.

The rising current through BPDT upon exposure to NO₂ resembles typical gas sensor response. To analyze the sensing property, recovery of response to baseline current when NO₂ is stopped is one parameter that describes underlying details of the sensor. Here it is seen that the recovery is initiated with a delay and recovery is not complete while the device is in N₂ atmosphere. Instead the current reduces 50% from maximum value and then stabilizes there. Complete recovery is obtained when the gas sensing chamber is opened and the device is exposed to ambient air. This observation is indicative of strong enough binding between NO₂ and BPDT.

Most of the times when analyte molecules adhere strongly to the constituents of the of any gas sensing device, natural recovery to initial state is either very slow and in present case do not happen. In such situation one way to recover initial state is through external stimulus like heat or UV light. Figure 5-5 shows effect of stimulated recovery. Here two important observations
are (a) recovery to baseline is complete and faster as compared to natural recovery in N₂ atmosphere and (b) reduction of current continues further below the baseline current value. First observation is straightforward to interpret i.e. UV reduces the activation barrier for NO₂ desorption hence fast recovery happens. Second observation could be due to several reasons. Most probable reason is that there could be some trapped solvent molecules in the device which evaporate during UV exposure and hence a different level of current is established as compared to initial state.

Figure 5-5: Stimulated recovery

The results presented in this chapter can be qualitatively described using equations 4.2 and 4.3. For the nanoMoED platform, it was observed that the current does not change when gas environment was changed from N₂ to NO₂. Hence it is inferred that neither the density of states ‘D(E)’ nor the coupling strength ‘Γ’ between metal-molecule junctions is affected. For the nanoMoED device ‘1’ there was no change in magnitude of current in both gases hence ‘D(E)’ of the gold molecule junction at the Fermi level is unaffected. But there was a change in current from binary level switching to single level. This can be understood as change in coupling ‘Γ’ between metal and molecule. Similarly current conducted by the nanoMoED device ‘2’ increased when exposed to NO₂ gas which indicates change in density of states ‘D(E)’ of the metal-molecule junctions at the Fermi level. Noise fluctuation in current that was recorded for nanoMoED device ‘2’ did not change and hence coupling ‘Γ’ between metal and molecule could be unaffected.
5.2 Rapid detection of NO₂

The 64±10% increase of conductance of Au-BPDT-Au junctions in presence of NO₂ molecules is quite significant to consider this device for future gas sensing applications. But one important observation is that it takes on the order of hours for the conductance to increase from base line value to maximum value. A practical device would require that the detection of gas happens rapidly.

For the purpose of rapid detection of the analyte, many studies apply calculation of the ‘rate of change of conductance’ of the sensor data.\textsuperscript{(126-129)} In this analysis method the rate of change of current is calculated manually and then plotted against time. This is shown in Figure 5-6.

![Figure 5-6: Comparison of response times of original data (upper figure) and rate of change calculated data (lower figure).](image)

Here approximately response time \(T_{res} \) of 80 minutes was observed for the current to reach 90% of maximum value (upper figure). Whereas a clear peak in the \(di/dt\) plot of lower figure which is observed after only \(\approx 150\) seconds. The response time in this case \(T_{res}'\) is time between the instant of NO₂ exposure and the instant of occurrence of the peak. The com-
parison shows that \( T_{res}' \ll T_{res} \). Hence this method of analyzing the current-time data gives very small value of response time.

### 5.3 Chapter Summary

Summary of the results which are presented in this chapter is given in Table 3.

Table 3. Summary of results

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Characteristic i-t response</th>
<th>In N₂</th>
<th>In NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanoMoED platform</td>
<td>Single level conduction with SNR ≥ 20 dB</td>
<td>No change in average current and change in SNR not significant</td>
<td></td>
</tr>
<tr>
<td>nanoMoED device 1</td>
<td>Binary level conduction with SNR ≤ 10 dB</td>
<td>Current conducted at single level and SNR improved to &gt;23 dB</td>
<td></td>
</tr>
<tr>
<td>nanoMoED device 2</td>
<td>Single level conduction with SNR ≥ 28 dB</td>
<td>Current rise 64% above baseline and SNR does not change significantly</td>
<td></td>
</tr>
</tbody>
</table>

Current-time (i-t) characterization of the three configurations of metal molecule junctions has been performed at low applied DC bias voltage, in N₂ and NO₂ environments. The current-time (i-t) response measured from the physisorbed configuration that is also called the nanoMoED platform shows the same behavior to both gases. The chemisorbed configuration containing ODT molecules which is also called nanoMoED device ‘1’ shows a change in the signal to noise ratio (SNR) of current when it is exposed NO₂ gas. The chemisorbed configuration containing BPDT molecules that is also called nanoMoED device ‘2’ shows a response to NO₂ gas in the form of rise in current. The response time of nanoMoED ‘2’ is very long. For faster detection, the rate of change of current is calculated numerically which gives value of response time which is almost 2 orders of magnitude smaller. Hence rapid detection of the NO₂ gas molecules can be performed by analyzing the rate of change of a current.
Summary

The story in short
Functionalized gold nanoparticles (AuNP) constitute a hybrid material with the potential to be used in molecular electronic devices. In this thesis, the various factors that affect the transmission of electrons through these hybrid materials are described and optimized with the goal to understand and build a nano molecular electronic device (nanoMoED) that can be used both for measurements in basic science as well as in applications. The nanoMoED device consists of the AuNP-molecule hybrid material placed between sub 20 nm spaced gold nanoelectrodes. The major characterization technique which was applied is electrical measurements. Various materials analysis methods such as spectroscopic and electron microscopy methods were applied.

The thesis consists of three different parts, the fabrication of very small top down structured nanogaps, the use and analysis of place exchange reactions of molecules in the hybrid material and gas sensor measurements.

For the purpose of electrical characterization of molecules, they need to be contacted between metallic electrodes. Physically this contacting is only possible when the electrode spacing and the molecular length are same. We used the focused ion beam (FIB) milling method for the fabrication of the nanogaps between metallic electrodes. With this method the size of the smallest nanogap that could be fabricated was 2.3 nm which is one of the smallest nanogaps fabricated by top-down Nano structuring methods.

Since many conductive molecules used in molecular electronics are ≈1 nm in length, still, this gap size is too big for directly contacting such molecules. To overcome this difficulty, functionalized AuNPs were assembled inside nanogaps. This resulted in reduced spacing between ‘gold’ surfaces. In this case, the spacing between gold surfaces was mainly caused by the functionalizing ligands on the AuNP. In this nanoMoED platform it was possible to insert molecules and fabricate metal-molecule-metal junctions.

In the second part of the thesis, after having fabricated the devices containing the hybrid AuNP-molecule material in the nanogap, in an additional step, the original molecules are exchanged with, in general, more conductive molecules. The procedure is called a place exchange reaction. We could realize this place exchange reaction, having been demonstrated in several micron sized 2D AuNP arrays, in the 20 nm small nanoMoED devic-
es thus enabling us to place a vast amount of molecules into our platform. In a second work, we analyzed the efficiency of and principles ruling the place exchange mechanism as a function of molecule length and resistance, two important factors, determining the properties of the molecule-metal junction. We confirmed using TEM investigation that the spacing between nanoparticles was on average 1.6 nm. Since the BPDT molecule is ≈1 nm long, the 4,4′-biphenyldithiol (BPDT) only bridge the gap, if the NP-NP spacing changes during the place exchange reaction. But the second molecule used in this study, 0TBT molecule has a length of 1.6 nm. In the devices where place exchange was carried out with the 5,5′-diphenyl-2,2′-bithiophene (0TBT) molecule, thus, the molecule could directly bridge the NP-NP gap and as a result, these devices yielded a two orders of magnitude lower resistance than BPDT containing molecules. An additional factor for this high difference in conductivity was demonstrated by DFT calculations that show that the HOMO level of the 0TBT is positioned at the Fermi level of the gold upon contact formation, which decreases the molecule-metal junction resistance further as compared to BPDT. In order to study the length dependence of place exchange more systematically, a series of molecules of the same type, but with different length, 1TBT, 2TBT, 3TBT were moved by the place exchange reaction into the electrode gap. The molecules show only a smaller variation in conductivity. When the molecule length increased, the resistance of the nanoMoED device decreased, which could not only be related to the more efficient molecule bridging of the NP-NP gap but equally due to the fact that less NPs can bridge the gap for longer molecules.

In the third part, the current-time (i-t) characterization of the three configurations of metal molecule junctions was performed at low DC bias voltage, in N2 and NO2 environments. The i-t response was measured for several types of nanoMoED devices, containing A) octanedithiol, B) octanedithiol where the thiol at one end was protected with a thiol group and C) BPDT that was moved into the NP-NP spacing by a place exchange reaction. Whereas the molecules in case A, B were present on the AuNPs after synthesis, the BPDT was moved into the NP-NP spacing by a place exchange reaction. In physisorbed configuration B, the nanoMoED platform showed the same behavior in both gaseous environments. The chemisorbed configuration A showed a switching between two or more current levels when exposed to N2 gas and thus a change in the signal to noise ratio (SNR) of current when it was exposed to NO2 and to N2 gas. In the chemisorbed configuration containing BPDT molecules the nanoMoED devices respond to NO2 gas exposure in the form of rise in current. Using DFT calculations, it could be shown that the current rise upon NO2 adhesion to BPDT can be explained by the insertion of new electronic levels in the BPDT molecule corresponding to new transport channels.
Sammanfattning på svenska

Historien i korthet

Avhandlingen består av tre olika delar, tillverkningen av väldigt små uppifrån och ner strukturerade nanogap, användningen och analysen av molekylernas platsutbytesreaktioner i hybridmaterial och gasmätare.

För elektrisk karakterisering behöver molekylerna vara i kontakt med metallelektroder, fysiskt är denna kontakt endast möjlig när elektrodavståndet och molekylärlängden är samma. Vi tillverkade nanogapen mellan metallelektroder genom att fräsa med en fokuserad jonstråle. Med den här tekniken var storleken på det minsta nanogapet som kunde tillverkas 2,3 nm, vilket är en av de minsta nanogapen som har tillverkats med uppifrån och ner nanostruktureringsmetoder.

Eftersom många ledande molekyler som används i molekylärelektronik är ≈ 1 nm i längd, är denna gapstorlek förstörande för stor för direkttkontakt med sådana molekyler. För att övervinna denna svårighet monterades funktionaliserade AuNP inuti nanogapen. Detta resulterade i minskat avstånd mellan guldtyorna. I detta fällt var avståndet mellan guldtyorna huvudsaklig orsakat av de funktionella liganderna på AuNP. I denna nanoMoEA-plattform var det möjligt att införa molekyler och tillverka metall-molekyl-metallkorsningar.

I den andra delen av avhandlingen, efter tillverkningen av de apparater som innehåller det hybrida AuNP-molekylmaterialet i nanogapen, byts de ursprungliga molekylerna ut mot mer ledande molekyler. Förfarandet kallas en platsutbytesreaktion.

Vi insåg att denna platsutbytesreaktion ägde rum i flera mikronstora 2D AuNP-uppställningar, i 20 nm små nanoMoEA-enheter, således kunde vi
placerar en stor mängd molekyler i vår plattform. I ett andra arbete analyserar vi effektiviteten och principerna för utbytesmekanismen som en funktion av molekylängden och resistansen, två viktiga faktorer som bestämmer egenskaperna hos molekyl-metallföreningen. Vi bekraftade med TEMundersökning att avståndet mellan nanopartiklarna i genomsnitt var 1,6 nm. Eftersom 4,4'-bifenylditioliolen (BPDT)-molekylen är ≈ 1 nm lång, överbrygger BPDT endast gapet om NP-NP-avståndet förändras under platsbytesreaktionen. Men den andra molekylen som användes i denna studie, 5,5'-difenyl-2,2'-bithiofen (0TBT)-molekylen är 1,6 nm lång. I de enheter där platsutbyte utfördes med 0TBT-molekylen, kan sålunda molekylen direkt överbrygga NP-NP-gapet och som ett resultat gav dessa anordningar ett två storleksordningar lägre motstånd än BPDT-innehållande molekyler. En ytterligare faktor för denna stora skillnad i konduktivitet demonstrerades genom DFT-beräkningar som visar att HOMO-nivån för 0TBT är placerad vid guldets Fermi-nivå vid kontaktbildning, vilket minskar molekylmetallförbindningsresistansen ytterligare jämfört med BPDT. För att studera längdberoende av platsutbyte mer systematiskt, flyttades en serie molekyler av samma typ men med olika längd, 1TBT, 2TBT, 3TBT av platsbytesreaktionen in i elektrodgapet. Molekylerna visar endast en mindre variation i konduktivitet. När molekylängden ökade minskade nanoMoEA-enhetens resistans, vilket inte bara kunde relateras till den mer effektiva molekylöverbryggningen av NP-NP-gapet utan också på grund av det faktum att mindre antal NP kan överbrygga gapet för längre molekyler. I den tredje delen utfördes ström-tid (i-t) karakterisering av de tre konfigurationerna av metallmolekylöverbryggningar genom platsbytesreaktioner vid låg DC-biasspänning, i N₂- och NO₂-omgivningar. Responsen mättes för flera typer av nanoMoEA-enheter innehållande A) oktanditiol, B) oktanditiol, där tiolen i ena änden var skyddad med en tiolgrupp och C) BPDT som förflyttades in i NP-NP-mellanrummet genom en platsbytesreaktion. Medan molekylerna i fall A och B var närvarande på AuNP efter syntesen, förflyttades BPDT till NP-NP-mellanrummet genom en platsbytesreaktion. I den fysisorberade konfiguration B, visade nanoMoEA-plattformen samma beteende i båda gasomgivningarna. Den kemisorberade konfigurationen A visade en växling mellan två eller flera strömnivåer när den utsattes för N₂-gas och därmed en förändring i strömförhållandet mellan signal och brus när den utsattes för NO₂ och N₂-gas. I den kemisorberade konfigurationen innehållande BPDT-molekyler svarar nanoMoEA-enhheterna på NO₂-gasexponering i form av ökning av strömnivå. Med användning av DFT-beräkningar kan det visas att de ökande strömnivåerna vid NO₂-vidhäftning till BPDT kan förklaras genom införandet av nya elektrovska nivåer i BPDT-molekylen som motsvarar nya transportkanaler.
Acknowledgments

It is because, together with colleagues in the Electron Microscopy and Nanotechnology (ELMiN) group, colleagues in the department of engineering sciences, collaborators from Chemistry Ångstrom, Collaborators from the department of Physics and astronomy and experts in MSL cleanroom Uppsala that I have been able to do research and write this thesis. All aforementioned, have valuable contributions in the making of this thesis. Not to forget administration, they manage a great working atmosphere, thumbs up!

My dear supervisor, Prof. Klaus Leifer has helped me throughout my PhD. I am indebted by his normal as well as peculiar help and support. Throughout my PhD research, I found that Klaus was consistent, passionate and energetic in all matters related to research work. Together, we have been able to design nice experiments, obtain and understand fantastic results and draw novel conclusions. Today if I have been able to present this thesis, this is all due to unprecedented and peculiar support from Klaus. I am thankful to Klaus for offering the finest review on my thesis. I am also thankful to Klaus for appreciating some prospects of my thesis and initiating work investigations on those.

It was due to my dear co-supervisor Syed Hassan Mujtaba Jafri, who also has been my teacher during undergraduate studies that I came to know Prof. Klaus Leifer and all colleagues here, MSL, Uppsala, Sweden and huge part of the world. I can never forget all the guidance he provided. In addition I should mention that he together with Klaus made a very thorough investigation of my results. This proved to be helpful in the development of understanding.

This thesis document was also finely reviewed by Doc. Henrik Ottoisson. The valuable suggestions and correction from them helped me to reach the goal. I am obliged.

It is always due to fellow PhD students that most of the progress is made in one’s PhD. In ELMiN group I met some of the inherently finest researchers ‘polished’ by Klaus. With respect to the order of research experience in the group, I should mention that Ling Xie, Hu Li, Yuanyuan Han, Hasan Ali, Aqib Hayat, Farnaz Ghajeri, Omer Sher and Tianbo Duan, all have been very nice and supportive. Especially Yuanyuan Han, with her chemistry and spectroscopy measurements contributed to manuscripts and her input constitutes the backbone of this thesis. Aqib Hayat, with transfer of his experience
to me, laid for me the basis for understandings of our nanoMoED. I had high level scientific discussions with Ling Xie and I can say if I know something about microscopy, Ling shares the credit. A one word summary is, “thankyou-ELMiN”.

Not to forget those who had been in the group during my PhD and are now off for their further adventures. I should mention in the order of their contribution to my research that, Anumol Ashok Kumar helped me in understanding microscopy and some chemistry. Tom Thersleff with fantastic sessions on FIB especially during collaboration of FIB Auto-slice and view experiment gave me a take-off moment to the next level in understanding of FIB/SEM system. Olivier Donzel-Gargand while ‘treasure hunting’ by digging on his sample using FIB, made me understand a lot about the FIB instrument. Sharath Kumar has always been a kind and nice support, I will especially remember the work we did together during organization of TEM spectroscopies workshop 2015. I mention also some fantastic colleagues from around the world with whom I worked on Atomic force microscopy. Sylvester Wambua, Antoine Delafosse, Morin Clémence and I did some quality work on AFM. Mikael Anttila and I worked together in ELMiN lab and fine-tuned the electrical measurements.

Through various collaborations I got a chance to work with many nice researchers in our TMV division. Tao and I successfully @destroyed his nano-sphere samples using FIB and published two articles.

I should mention the very valuable contributions of colleagues towards the correction of this thesis document. I pay my special gratitude towards Mariia Pavliuk because she had always been kind and helped me correct the chapter 4, Micheal Palmer helped me to correct the chapter 3 and with his help English level was improved. The most critical help was provided by Oscar Janson who has always been inclined to help. He performed Swedish translation of the thesis summary. Thank you Oscar you came to help at the most critical time. Thank you Celine Robo also, for accompanying during thesis writing. I am also thankful to Petra Olander for being a very nice colleague at the division.

I came to know that Uppsala University hosts some of the top quality researchers. During PhD I got a chance to work with some of them through project collaborations. Their contributions weigh equal to others’ contributions. Most support I obtained from Andreas Orthaber and Anton Grigoriev. I found them as best in what they do and working with them had always been a great desire and advantage for me. Andreas Orthaber has always guided me like a mentor. He provided very detailed and critical review on the results that I showed him. Anton Gregoriev provided me with the best possible theoretical explanation of the results that I showed him. I also recall fine discussions with Vivek Anand Shukla and Tanveer Hussain from the Materials theory group and admit the effect of those discussions was always ‘a food for thought’. I admit that Rabia Ayub had been a kind colleague to
me. Nice discussions with Rabab Naqvi helped me many times. Muhammad Anwar Shameem helped me at times to do chemistry. Johan Oscarsson helped me for learning XPS. I am thankful to Asim Aijaz and I am lucky that you came to Uppsala when I needed some guidance. Thank you for sharing your experiences with me.

Expert scientist at Microstructure laboratory (MSL), Ångstrom laboratoriet have been very helpful. I found that working with the expert scientists like Fredric Ericson, Amit Patel, Victoria Sternhagen, Farhad Zamany, Peter Wirsching, Rimantas Brucas and Jan Åke Gustafsson has made it possible for me to use state of the art instruments. I especially pay my humble gratitude towards Amit, Farhad and Jan-Åke for all the help and support.

The support I received from the administration was valuable. Jonatan Bagge deserves the best acknowledgment for all IT related support and because, “without Jonatan’s help forget about thesis”. I also pay my gratitude towards Sara Rudqvist, Maria Skoglund and Ingrid Ringård for their effective and timely help in all relevant matters.

Some friends outside the department have been very kind and will remain in memories for an indefinite time. We spent a lot of time together and I admit that without these friends time would have been difficult. Thank you dearzzz Yasir Bilal, Shaezi, Izzac Afridi, Bilal, Yadish and all who played cricket together. Many friends especially Osama, Aqib Hayat and Imran Aziz had been kind enough to keep me motivated to pray Namaz in the masjid. I pray to Allah, the Almighty to bless you.

In the end I acknowledge contribution of my family and relatives. My brother Imtiaz Wani and his family, My Sisters Bushara and Sobia and their family all have supported me and my decisions. My parents in M. Yousaf Khan and Shamshad Akhtar and all relatives in law have been very considerate of my needs and requirements and always supported me.

In the end I (and on the behalf of my wife Shamaila and my two daughters Zoonia Ishtiaq and Shiza Ishtiaq) say thank you for providing us magnificent memories in Sweden.

Thank you all!
Ishtiaq Hassan Wani
12th of April 2018
Ångstrom laboratoriet
Uppsala Sweden
This section of the thesis contains supplementary information.

SEM images of typical FIB milled nanogaps and nanogaps size distribution

<table>
<thead>
<tr>
<th>nanogap</th>
<th>Contrast profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE1</td>
<td><img src="image" alt="NE1 Contrast" /></td>
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<tr>
<td>NE2</td>
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<td>NE3</td>
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Typical current-voltage (I-V) response during fabrication of the devices

Stage 1 represents empty nanogaps, stage 2 represents trapping nanoparticles and stage 3 represents nanoMoED devices made after place exchange with 4,4′-biphenyldithiol (BPDT)

Device 1

![Image of I-V plot for Device 1]

Device 2

![Image of I-V plot for Device 2]
**Device 3**

Semi-log I-V plots show characteristic current conducted by the device at different stages of synthesis.

**Device 4**

Semi-log I-V plots show characteristic current conducted by the device at different stages of synthesis.

**Device 5**

Semi-log I-V plots show characteristic current conducted by the device at different stages of synthesis.
Temperature dependent (IV) characterization

After 0TBT was inserted by place exchange

*Original I-V curves*

![Current (A) vs Voltage (V) graph](image)

*Temperature versus low bias resistance*

![Low Bias resistance (Ω) vs T(K) graph](image)
After 3TBT was inserted by place exchange

*Original IV curves*

Temperature versus low bias resistance

Temperature dependence of IV response was not always observed as shown below for 3TBT nanoMoED
Data analysis gas sensing results

Curve fitting of the experimental data. Two exponentials functions with different time constants fit the experimental data as shown below.

Time constants of the two exponentials obtained from all the sensor curves on nanoMoED device 2 show one exponential with a time constant of 10 minutes and the other exponentials with a time constant on the order of hours as shown in histogram below,
The nanoMoEDs made with another molecule

Ferrocenedithiol derivative

This molecule belongs to family of metallocene sandwich compounds.\textsuperscript{(130)}

![Resistance distribution after Trapping the type ‘1’ AuNPs](image1.png)

After place exchange

![Resistance distribution after Place Exchange](image2.png)
Exposure to NO₂ sensing


38. Y. Wu et al., Batch fabrication of gold-gold nanogaps by E-beam lithography and electrochemical deposition. Nanotechnology 24, 235302 (2013).
60. T. Blom, Uppsala University, (2010).
68. D. M. Mattox, Handbook of physical vapor deposition (PVD) processing William Andrew, Incorporated. (2010)).
A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)

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