



UNIVERSITÉ CATHOLIQUE DE LOUVAIN

Ecole Polytechnique de Louvain

CERMIN

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Correlated characterization of hybrid metal-conjugated polymer nanowires

Dissertation présentée en vue de l'obtention du grade de
Docteur en Sciences de l'Ingénieur
par

Loïk Gence

Promoteur:
Prof. Vincent Bayot

Octobre 2010



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Octobre 2010

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Hier et demain. Pensées brèves, Gustave Le Bon

Voici la section préférée des lecteurs. Pour dire vrai, ce sont les seules pages qui intéressent réellement tous les lecteurs et celles qu'il est plaisant de lire et de relire encore. Mais paradoxalement, d'après le petit sondage que j'ai pu effectuer auprès des docteurs fraîchement diplômés de l'UCL, bien que la rédaction de ces quelques lignes signifient clairement la fin de cette période ingrate qu'est la phase de rédaction d'une thèse, ainsi que la fin du statut de thésard, il n'en reste pas moins qu'il persiste tout de même l'angoisse de commettre l'irréparable: oublier quelqu'un dans la liste des gens, des personnes qui ont permis, financé, corrigé ce travail et celles qui ont aidé, encouragé, soutenu et supporté ce travailleur de l'ombre qu'est le thésard...

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Abstract

In recent years, investigators in industry and academia have increasingly tamed the structural and electronic properties of low dimensional materials. Among them, nanowires (NWs) and nanotubes were intensely scrutinized because of their potential use in various applications requiring miniaturization. Besides the well-known CNT, many species of NWs-like nanomaterials can be synthesized from inorganic and/or organic materials and offer an impressive potential in applications ranging from bio-environmental sensing and energy harvesting to ultra-low power electronic devices and high density memories. Nevertheless, the use of single NW in real applications asks for identifying their intrinsic behavior and requires to manipulate and contact them properly.

The aim of this thesis is to contribute to this active research area, focusing particularly on hybrid metal-polymer nanowires made of conjugated polymers (PPy, PEDOT, PANi) and metals (Au, Pt, Ni) with diameters ranging from 30 *nm* to 160 *nm*. In this experimental study, we investigated the electrical and structural properties of several classes of hybrid nanowires (HNW) and HNW arrays.

The first part of this thesis, focuses on the structural and electrical characterization of several classes of HNW arrays. A careful characterization of the metal-polymer interfaces by transmission electron microscopy revealed that the structure and mechanical strength of the interfaces are very different. Variable temperature electrical transport measurements suggested that the three-dimensional Mott variable-range-hopping (VRH) model provides a complete framework for understanding charge transport, including nonlinear current-voltage characteristics and magnetotransport. The diameter dependence of the electrical properties of HNWs suggests that the transport mechanism changes for the 40 nm HNWs samples which exhibit a behavior indicative of the critical regime of disorder-induced metal-insulator transition.

Then, because of the several limitations of the bulk characterization of HNWs (e.g. averaging effects on the measured properties, high contact resistance, no interactions with the environment, ...) we investigated

the integration of single HNW in a planar electronic devices. Advantageously, single HNW measurements allow us to probe the responses of HNWs to different stimuli. Especially, we showed that the electrical properties of mutli-segmented HNWs can be switched chemically from a linear to a rectifying behavior. We proposed a simple model based on Schottky diodes to explain and reproduce the observed phenomenon.

Finally, to gain further insight into the structure-property relationships of these nanomaterials, we developed, fabricated and characterized multipurpose platforms, fabricated via Si micromachining techniques. These microdevices enable the correlation between the structural properties -as observed, for instance, by transmission and scanning electron microscopies - the electrical and thermal properties obtained from the same sample. While these membrane-based microdevices were used for correlated studies of NWs, the extension to other nanomaterials (organic, inorganic, or hybrid films, nanoparticles) is straightforward.

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List of Symbols

Here are the main symbols and acronyms used in the present manuscript.

A^*	Richardson constant of free electron
a	lattice constant
B	magnetic field (induction)
χ_{SC}	semiconductor electron affinity
ΔE_{ij}	energy difference between sites i and j without electric field
H_2O DI	deionized water
ϵ_{SC}	semiconductor permittivity
e	absolute value of electron's charge
$\mathbf{r}$	space vector
$\mathbf{R}_j$	j th site on the lattice
E	energy
E_C	Coulomb energy
E_F	Fermi energy
E_g	semiconductor bandgap
F_0	Critical electrical field
$G(T)$	electrical conductance
$N(E_F)$	density of states at the Fermi energy
λ	mean free path
m^*	effective mass of the carrier
Φ_B	Schottky barrier height
Φ_M	metal work function
$\rho(T)$	electrical resistivity
T_0	Mott temperature
$\mathbf{R}_{ij}$	Hopping range
$\bar{R}_{hop}$	average hopping distance traveled per hop
$\bar{R}'_{hop}$	average hopping distance without electrical field
$\bar{R}'$	average nearest hopping range without electrical field
ξ	localization length
ac	alternating current

$\mathbf{e}_z$	unit vector for the z -direction
f	frequency
$\mathbf{E}$	Electric field
h	Planck constant
I	electric current
K	thermal conductance
κ	thermal conductivity
k_B	Boltzmann constant
$\mathbf{k}_F$	Fermi wavevector
l_B	magnetic length
κ	thermal conductivity
m^*	electron's effective mass
n	areal electron density
$\mathcal{N}$	number of particles
∇	gradient operator
P	electric power
R	electrical resistance
R_0	zero magnetic field resistance
σ	electrical conductivity
T	(lattice) temperature
t	time variable
τ	time constant
V	electric potential difference
$W(T)$	Reduced activation energy
AAO	anodic aluminum oxide
CP	conducting polymer
D	1D: one-, 2D: two-, 3D: three-dimensional
DOS	density of states
EBID/E	electron beam induced deposition/etching
EDX	energy dispersive X-ray
EEI	Electron-electron interactions
EELS	Electron energy loss spectroscopy
EBL	electron beam lithography
FET	field effect transistor
FWHM	full width at the half maximum
GDM	Gaussian distribution model
HNW	hybrid nanowire
HOMO	highest occupied molecular orbital
LPCVD	low pressure chemical vapor deposition
LUMO	lowest occupied molecular orbital

LL	Luttinger liquid
MR	magnetoresistance
MIT	metal-insulator transition
NW	nanowire
NWFET	nanowire field effect transistor
PMMA	polymethylmethacrylate
PA	Polyacetylene
PANi	Polyaniline
PC	Polycarbonate
PEDOT	poly(3,4-ethylenedioxythiophene)
PPV	Poly(p-phenylene vinylene)
PPy	Polypyrrole
PT	Polythiophene
rms	root-mean-square
RT	Room temperature
SAED	selected area electron diffraction
SBH	Schottky barrier height
SCLC	space charge limited current
SC	Semiconductor
TMAH	Tetramethylammonium hydroxide
VRH	variable range hopping
XPS	X-ray Photoelectron Spectroscopy
ZBA	zero bias anomaly

Motivation

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Based on very important scientific discoveries made during the past century, the explosive growth of technology has transformed the world more rapidly and widely than in any previous century. Many technological advances made in the beginning of the 20th century have opened new paths towards scientific discoveries, which in turn led to new technological possibilities. Nowadays, nobody can deny that science and technological advances have considerable impact on our modern societies, and our way of life. Technology is present everywhere in our daily lives: in the way we communicate, in the way we move, in everything we do. Of course, scientific research has also benefited from these intense technological developments.

Nowadays, so-called *nanotechnology* which encompasses many fields of science (e.g. chemistry, physics, medicine) initially opaque to each other, constitutes a trendy and very active research field. Initially proposed by Dexler in the beginning of the 80's [28], the term nanotechnology, now usually refers¹ to the sciences and techniques that enable the engineering of materials at the nanometer scale.

The potential outcomes that should ensue from nanotechnology are so plentiful that not only the scientific community, but also industry and even politicians are all really excited about nanotechnology. Indeed, current leaders of the microelectronic industries see in nanotechnology potential answers to the issues arising from scaling down silicon-based complementary metal-oxide-semiconductor (CMOS) technology (increasing costs, leakage current, parasitic capacitance and resistance, ...).

¹More precisely, nanotechnology can be defined as research and technology development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1-100 nm range [29].

Time is running out, and microelectronic industries are looking beyond conventional manufacturing technology to more exotic materials such as carbon nanotubes (CNT) and graphene, despite general acceptance that the Moore's law could still remain valid with Si-based technology at least during the next decade. This will give time to reach a few more technological nodes, producing functional transistors with gate lengths as small as $L_G \approx 15 \text{ nm}$. This would be achieved by optimizing the transistor structure [30] (multigate-gate transistors, SOI, vertical structures) and fabrication processes [29] (materials, lithography techniques).

Beyond the quest for the materials and technologies that will replace the Si-based technology to produce more efficient electronic devices, other paths are being explored to develop electronic devices with a different philosophy, for several classes of emerging applications which do not require the high performances of the Si-based technology. One of these paths is *organic electronics*.

Organic electronics developed rapidly since the impulse given by the seminal work of Alan Heeger, Hideki Shirakawa and Alan MacDiarmid for which they received the Nobel prize in 2000. The impressive development of organic electronics relies on the versatile properties of organic materials that offer new possibilities for electronic industry. Strikingly, it is known that organic materials exhibit lower intrinsic charge transport efficiency than silicon because of the charge mobility found in organic semiconductors is orders of magnitude lower than typical values found in silicon. However, the interest of organic electronics is somewhere else. First of all, organic materials are much easier to process, as most of these materials offers solution processability, and can be processed at much lower temperature over large areas which drastically reduces the processing costs [31]. Moreover, organic materials are compatible with a multitude of substrates such as glass, plastic or even paper. Therefore, the versatile properties of organic semiconductors allow production of low-cost, flexible, renewable and light-weight applications just like the 31 inch panel displays (3 mm thick) based on organic light-emitting diodes (OLED) thin film² technology, recently presented by LG corporation at the IFA 2010 exhibition³.

While OLED based technology is being introduced into the market, several strategies are being investigated to go beyond and exploit the impressive possibilities offered by conducting polymer nanostructures.

²In such OLED-based panel displays, organic semiconductor-based pixels are arranged in arrays with typical pixel dimensions ranging from tens to hundreds of microns.

³<http://www.ifa-berlin.com>

More particularly, one-dimensional (1D) nanostructures are intensely scrutinized because of their unique structural one-dimensionality and possible quantum confinement effects, but also because they are envisioned, within the framework of the bottom-up approach, as fundamental building blocks for the construction of vast array of innovative applications requiring miniaturization. Indeed, conducting polymer nanowires are expected to be used as the active materials in many sensor applications thanks to their very high specific surface area compared to bulk materials. Also, because of their size, they could be easily integrated into low-weight applications such as intelligent fabrics that could adapt to the environment (by changing shape and color) or for medical purposes, smart clothes could monitor fundamental physiological parameters (body temperature, sweat composition, ...) and even perform drug delivery. The tools offered by nanotechnology make possible to literally tailor the morphology, phase and structure of organic nanomaterials to fit with the envisaged applications [32]. Despite significant advances in synthesis of 1D nanostructures, there is still a lot to be done to fully understand the transport mechanisms and structure-property relationships existing in such organic materials. In particular, while conducting polymers present vast technological opportunities and can be easily combined with inorganic materials, besides pure polymer nanowires, hybrid inorganic-organic nanowires have been scarcely studied.

The main goal of this thesis was to gain insight into the properties of novel classes of hybrid nanowires (HNW) that combine several segments of metals (Au,Pt,Ni) and conjugated polymers polypyrrole (PPy), polyaniline (Pani) and poly(3,4-ethylenedioxythiophene) (PEDOT). These HNWs were produced by the template method which is known to allow very good control over the dimensions and composition of the produced nanowires. The development of the synthesis processes and the production of hybrid nanowires were carried out by Dr. Olivier Reynes and Vincent Callegari, under the supervision of Pr. Sophie Demoustier-Champagne from the FHYN group (UCL/IMCN/BSMA).

In this work, we focus on the structural and electrical properties of HNWs, paying special attention to the metal-polymer interfaces. Variable temperature electrical transport measurements were performed as a function of the electric and magnetic fields, on several classes of HNWs, in vertical⁴ and planar⁵ configurations. We show that HNW arrays measurements corroborate with single HNW measurements and give access to intrinsic properties of HNWs. The three-dimensional (3D) Mott

⁴HNW arrays embedded within polycarbonate template.

⁵Single HNWs deposited and contacted on insulating substrate.

variable-range-hopping (VRH) model provides a complete framework for the understanding of charge transport in HNWs with diameters ranging from 160 to 50 nm, including nonlinear current-voltage characteristics and magnetotransport at low temperatures. Strikingly, a size-dependent transport mechanism was identified for low diameter samples ($\phi < 50$ nm) and was ascribed to the existence of a disorder-induced metal-insulator transition. Finally, we investigated the integration of single HNWs in a planar electronic devices as it allows us to probe the responses of HNWs to different stimuli. Especially, we showed that the electrical properties of mutli-segmented HNWs can be switched chemically.

The manuscript is structured as follows: the chapter 1 is an introduction to the conducting polymer nanowire. After a short introduction to conjugated polymers (CP), the synthesis of CP nanowires and their potential applications are reviewed. In the second chapter, models and related concepts of charge transport which are relevant to derive quantitative information on our samples are reviewed. The end of the chapter briefly reviews the literature dealing with charge transport in CP and more specifically CP nanowires. The analysis of the electrical measurements presented in the next chapters will often refer to models, concepts and equations described in this chapter.

In the chapter 3, we report on the structural and electrical properties of several classes of HNW made of conjugated polymers (PPy, PEDOT) and metals (Au, Pt, Ni), and with diameters ranging from 30 nm to 160 nm. A careful characterization of the metal-polymer interfaces by transmission electron microscopy revealed that the structure and mechanical strength of the interfaces are very different. Variable temperature electrical transport measurements performed on HNW arrays suggested that the three-dimensional Mott variable-range-hopping (VRH) model provides a complete framework for the understanding of the charge transport, including nonlinear current-voltage characteristics and magnetotransport. The diameter dependence of the electrical properties of HNWs suggests that the transport mechanism changes for the 40 nm HNW samples which exhibit a behavior indicative of the critical regime of disorder-induced metal-insulator transition.

Then, because of the inherent limitations of the bulk characterization of HNWs⁶, several techniques for the integration of single NWs into planar devices, were investigated and compared in the chapter 4. To further investigate the structure-property relationships of nanomateri-

⁶These limitations mainly stem from the high number ($N_{HNW} \approx 10^3 - 10^6$) of HNWs measured in parallel which translates into an averaging effect and a distribution of their characteristics (diameter, segment length, interface resistance).

als, we developed, fabricated, and characterized multipurpose platforms, fabricated via Si micromachining techniques which offer a unique tool for studying single nanostructures. These microdevices enable the correlation between the structural properties -as contemplated, for instance, by transmission and scanning electron microscopies - and the electrical and thermal properties of nanomaterials. While these membrane-based microdevices were used for correlated studies of NWs, the extension to other nanomaterials (organic, inorganic or hybrid films, nanoparticles) is straightforward.

Next, in the chapter 5, we come up to our experimental results obtained on single nanowires. The first part of this chapter focuses on low- T transport properties of HNWs based on PPy and Au segments. We show that the electrical transport properties observed on single HNWs measured in a planar configuration are consistent with the measurements of HNW arrays presented in chapter 3 and follows the Mott VRH model. Then the RT tunable transport properties of HNWs are investigated. We show that the electrical properties of tetra-segmented HNWs can be switched chemically from a linear to a rectifying behavior. We proposed a simple model based on Schottky diodes to explain and reproduce the observed phenomenon.

Chapter 1

Conducting Polymer Nanowires

La perfección es una pulida colección de errores

Mario Benedetti

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1.1 Introduction

The electronic industry that was born symbolically with the vacuum tubes, developed quickly since the introduction of integrated circuits discovered in 1958 by Jack Kilby, Physics Nobel Prize laureate in 2000. This development was based on the miniaturization of integrated circuits performed until now by shrinking the size of every component. Since the 1960's the miniaturization has continuously shrunk component size, roughly doubling the complexity of electronic components each year, following the well-known Moore's law [33]. The figure 1.1 exemplifies the huge evolution of microelectronic technology by giving several state of the art devices as a function of time, from the old style vacuum tube to stretchable electronics. This growth was enabled by the development of new technologies and materials together with a better understanding of the intrinsic properties of materials involved in the fabrication process of semiconductor components.

Parallel to the emerging electronic industry, polymer science has also experienced explosive growth, resulting nowadays, in the presence of polymers and especially plastics, everywhere in our environment from clothes to automotive applications. Thanks to the impressive properties of plastics and their numerous advantages compared to metals or wood (excellent mechanical properties, low weight, good processability, low cost), since 1950, the average annual increase in the plastics market has been about 9% and represents 245 million tons in 2008 [34].

While plastics are organic polymers with saturated macromolecules and are generally excellent electrical insulators, conjugated polymers (CP), also called as *synthetic metals*, have alternating double and single bonds that confer unique properties to CP. These *synthetic metals* combine the features of plastics with the ability of to conduct electricity and are promising materials involved in the development of the recent field of organic electronics [35]. Moreover, together with the recent advances in mechanics and materials, synthetic metals have opened a pathway to build integrated circuits that can offer the electrical properties of conventional semiconductors but with the ability to be stretched, compressed, twisted, bent, and deformed into arbitrary shapes [36, 37].

A decade after Heeger, MacDiarmid and Shirakawa received the Nobel prize in 2000 for their pioneering work on polyacetylene (PA), the number of studies devoted to the synthesis and characterization of CP is still increasing as exemplified by the number of publications dealing with CP (roughly 4000 published papers in 2009), given by searching

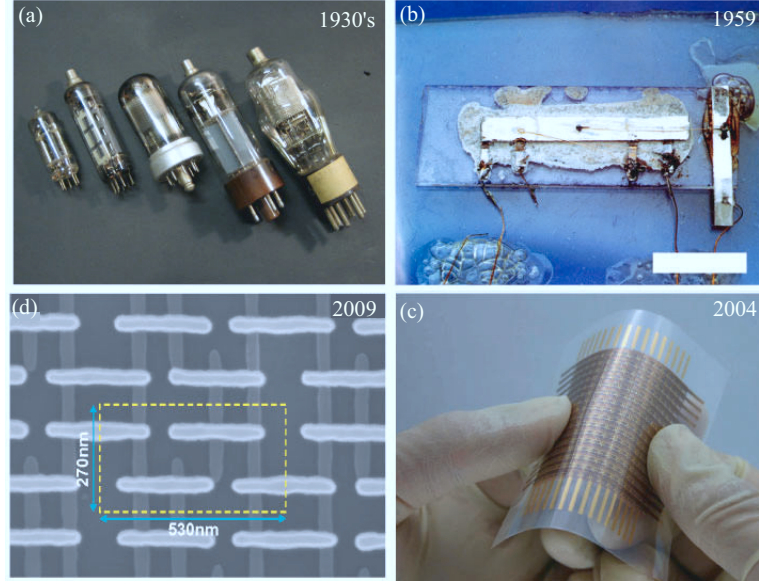


Figure 1.1: (a) Examples of vacuum tubes. (b) Kilby's first integrated circuit (1959). adapted from reference [1]. (c) Flexible large-area Organic-based FET and pressure sensor. Adapted from reference [2]. (d) Top-down SEM image showing a 6-transistors SRAM cell with an area of $0.143 \mu\text{m}^2$. Courtesy of IBM research (2009).

for *conjugated polymer* on the sciencedirect platform ¹.

Since the discovery of the metallic conductivity obtained in PA [38], chemists found multiple paths for producing polymers that conduct electricity with tunable electronic properties. Just by modifying the dopant or the side chain's length the chemists can finely tune the electro-optical properties of CPs as what has been done for inorganic semiconductors. For example, it has been demonstrated that CPs can exhibit a wide range of electrical conductivity σ , from the insulating state $\sigma \approx 10^{-10} \text{ S cm}^{-1}$ to the metallic state with conductivity as high as $\sigma \approx 10^5 \text{ S cm}^{-1}$, reaching the conductivity of metals [39, 40]. While the discovery of highly conducting PA has been a major step for the development of CPs, doped PA has poor mechanical properties (brittle), is unstable in air, and is not easy to process. Hopefully nowadays, the new generation of CPs are stable and easily processable from a wide variety of solvents [3], allowing researchers and engineers to exploit the versatile properties of CPs for producing low-cost, flexible, renewable, and lightweight applications.

¹www.sciencedirect.com

Even though commercial products (thin film transistors, photovoltaic and light emitting devices), based on CPs are already on the market, they are quite simple and characterized by low efficiency compared to the inorganic semiconductor-based devices. This low efficiency is mainly due to the much lower charge mobility found in organic semiconductors ($\mu = 10^{-6} - 20 \text{ cm}^2/\text{Vs}$) which is orders of magnitude lower than typical values found in silicon.

Strikingly, one of the pathways taken for research to improve the efficiency of the CP-based devices is basically the same as that for conventional semiconductors, and consists in decreasing the device dimensions. Moreover This is a general trend in applied physics research that originates from quantum confinement and low dimensionality effects which are expected to bring new and original properties (electrical, mechanical, thermal, optical) to nanomaterials compared to their bulk counterparts. Many studies have demonstrated higher performance for nanostructured CPs over their bulk counterparts and this for various applications such as electrochromics devices, field effect transistors (FET), or chemical sensors [41, 42, 43, 44]. The purpose of this chapter is essentially to introduce the reader to the subject- namely CP nanowires (NW), to present useful concepts and theories as well as a few definitions that will be used through the manuscript. As the number of existing CPs is very high, the choice has been taken to limit their presentation to a few examples, including, the conducting polymers that have been studied and characterized in this work, that is: polypyrrole (PPy), polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT). They will often be used as examples through this introduction. This chapter will be divided as follows. In the first section, the generic paths for CP synthesis are presented and some generalities about CPs are reviewed.

The second section presents the strategies available for achieving the anisotropic growth of CPs nanostructures. There will be described in details the different methods used for synthesizing conducting polymer nanowires (CPNW) in particular. Then, the next section reviews important electrical properties of conducting polymers. This section will describe mechanisms that govern charge carrier transport at the interface and within conducting polymers. The last section reviews the existing and potential applications that are based on CPNWs.

1.2 Conducting Polymers

1.2.1 Conjugated or Semiconducting Polymers?

The reader may have noted that several appellations are used in the literature for speaking about conducting polymers. For clarity of the discussion, we give in this section, commonly accepted terminology and a few definitions that will be used in this manuscript.

First, a *polymer* is defined as a large molecule with a relatively high molecular mass that is composed of repeating units called monomers. Homopolymers contain only one type of monomer while copolymers (or heteropolymers) are constituted by mixture of several repeating units as shown in figures 1.2.(b) and 1.2.(d). Polymers can be organic or inorganic depending if their backbone is constituted or not of carbon atoms. Inorganic polymers such as polysulfur nitride $(SN)_x$ and silicone are very famous examples of inorganic polymers. Indeed, $(SN)_x$ is a unique polymer that exhibits superconducting behavior at low temperatures ($T < 1\text{ K}$) [45] while everyone knows silicone (see Fig. 1.2.(a)) as it is used in the caulking of everybody's bathroom. Others examples of polymers are given in figure 1.2. When speaking about conducting polymers,

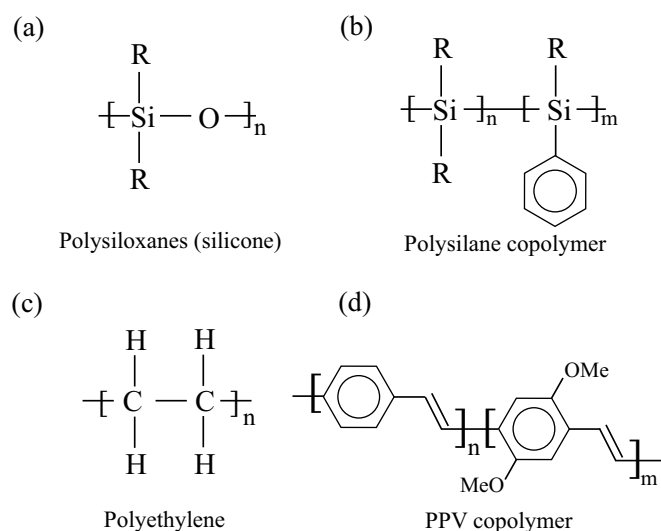


Figure 1.2: (a-d) Chemical structures of inorganic and organic polymers. (a) Silicone is a famous example of inorganic homopolymer. (b) Example of an inorganic copolymer (c) Polyethylene is one of the most popular and widely used *plastics*. (d) Example of PPV-based conjugated copolymer.

some authors distinguish extrinsic conduction polymers (ECP) and intrinsic conducting polymers (ICP). While ECPs are composite polymers made of a mixture of a non conductive polymer with an incorporated conducting material such as metal or carbon powder, ICPs are organic polymers that present, in their doped form, the electrical, magnetic, and optical properties of a metal with the mechanical properties and the processability commonly associated with polymers [46]. Nowadays, the term *conducting polymers* are mostly used to designate only ICP and therefore will be used in this manuscript. Among the very large family of conducting polymers, the *conjugated polymers* represent a very interesting group. Chemical structures of commonly used conjugated polymers are given in the figure 1.3. They are polymers that have a backbone with alternating single and double bonds.

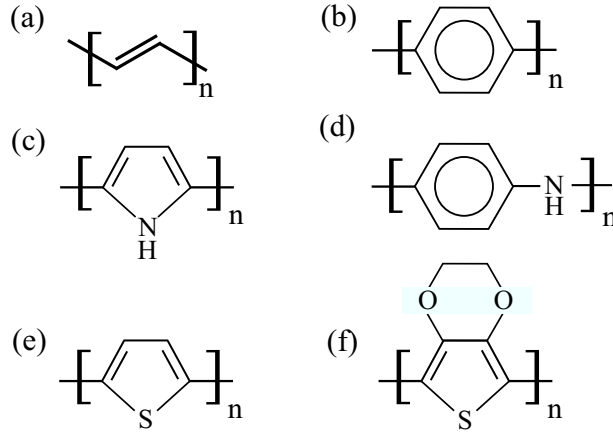


Figure 1.3: (a) Chemical structure of common conjugated polymers: (a) Polyacetylene (PA), (b) Poly (p-phenylene) (PP), (c) Polypyrrole (PPy), (d) Polyaniline (PANi), (e) Polythiophene (PT) and (f) Poly (3,4-ethylenedioxythiophene) (PEDOT).

A particularly simple conjugated polymer is given by PA. It will be taken as an example. The chemical structure of PA is depicted in figure 1.4.(a) and consists of a long chain of carbon (C) atoms, each with one hydrogen atom and connected together with alternating single and double bonds. Carbon atoms have four valence electrons, which in the ground state are found in the $1s^2 2s^2 2p^2$ configuration. C atoms are bound together in a planar configuration through σ and π bonds resulting from the overlapping of the hybrid sp^2 orbitals and p_z orbitals respectively. While σ -bonding electrons are concentrated in the plane of the molecule, π -bonding electrons are localized in a plane perpendicular

to the σ bond.

As depicted in the fig.1.4.(b), the π -orbitals of successive carbon atoms overlap along the PA backbone, leading to the existence of a pathway for delocalized π electrons along the backbone of the polymer. In a simple model of PA, the metallic binding stemming from the π electron should make PA a one-dimensional metal [47]. Nevertheless, due to the so-called Peierls distortion of the PA chain, a gap opens between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO). This phenomena is described in more details in the section 1.3 of chapter 2. Due to the analogy with crystalline inorganic semiconductors, the HOMO and LUMO are identified as the valence and conduction bands respectively, and the energy difference is also called the bandgap of the conjugated polymer. In conjugated polymers, this bandgap is within the range of 1 to 4 eV. For those similitudes with inorganic semiconducting materials, conjugated polymers are also called *semiconducting polymers*.

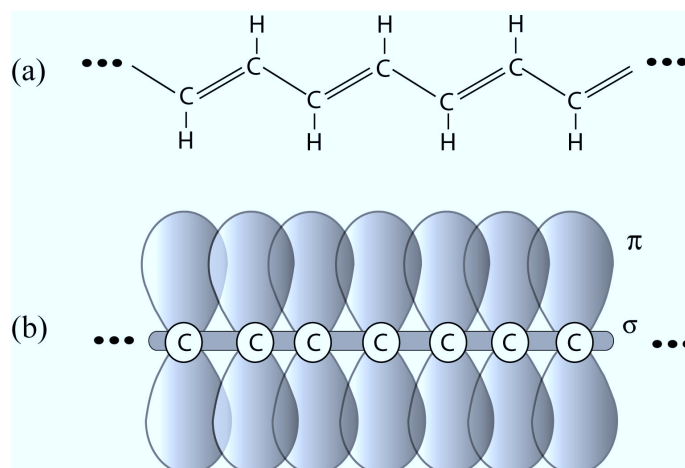


Figure 1.4: (a) Chemical structure of trans-PA (b) Corresponding electronic orbitals. The overlapping of p_z orbitals results in π -bond between carbon atoms in PA chain.

While in their undoped state, conjugated polymers are insulators, they exhibit large conductivities and interesting electrical properties, when electrons are removed from double bonds of the backbone. P-type and n-type CP are possible through oxidative and reductive reactions respectively. The doping procedure can be performed using either chemical or electrochemical techniques [3]. Nevertheless, the number of available n-type CPs is smaller and they are much less stable than p-type CPs. The principles and methods of conjugated polymer doping are detailed

in section 1.3.

The two following sections, will describes the main techniques used for the synthesis of CP: chemical polymerization and electrochemical polymerization. Although as the chemistry involved in the synthesis of the different CP is complex and still a matter of debate, the following sections will only present the basic principles of both polymerizations focusing on a few simple monomers. For more detail, we refer the reader to advanced textbooks, like Ref. [47]. While chemical polymerization is often preferred for producing a large quantities of CP, the electrochemical polymerization is more adapted to produced thin films of CP.

1.2.2 Chemical Polymerization

Many different chemical methods have been successfully developed to chemically synthesize CP and therefore, establishing a general pathway is quite a difficult task. Nevertheless, a good example of chemical polymerization is given by the oxidative polymerization of Pyrrole with $FeCl_3$ as oxidizing agent. Generally speaking, all polymerization processes can be divided in at least three steps: an initiation step, a chain propagation step and a termination step. The chemical polymerization of PPy begins with the initiation step, in which a pyrrole monomer is oxidized by $FeCl_3$, leading to a radical cation ($C_4NH_5^+$) (see figure 1.5.(a)) and the corresponding anion $FeCl_4^-$ that will be incorporated in the polymer chains as dopant ions (see figure 1.7.(a)).

Then a coupling between two radical cations can occur to form a bipyrrole dimer with deprotonation. Since the unpaired electron is now delocalized over the two rings in the dimer, its oxidation potential is lower than the oxidation potential of the monomer. The dimer is therefore more easily oxidized at the applied potential which is the oxidation potential of the monomer. Therefore, the chain propagation step consists in this oxidation of the bipyrrole dimer and its coupling with another radical cation, and so on. This process is repeated consecutively for the propagation of the chain and terminates due to the nucleophilic attack of water molecules or impurities in the polymer chains [3]. The resulting chemical structure of the PPy depends on the orientation of the radical cations coupling, but generally, breaking of the linearity and planarity of the PPy chains occurs by crosslinking of PPy chains [48]. Among the numerous conducting polymers prepared to date, polypyrrole is by far the most extensively studied. This stems from the fact that pyrrole is easily oxidized, water soluble and commercially available. Furthermore, polypyrrole presents several advantages including environmental stability, good redox properties and the ability to give high electrical

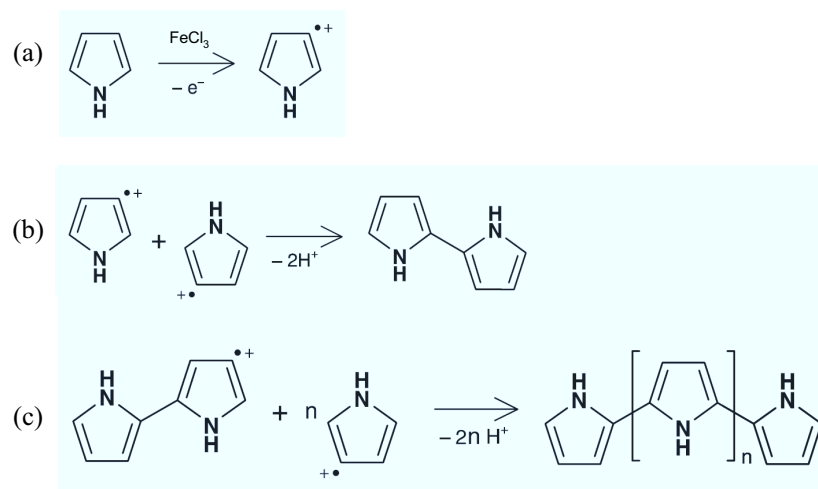


Figure 1.5: Chemical oxidative polymerization process of pyrrole can be divided in three steps: (a) the initiation step, the chain propagation and the termination step (c). Adapted from [3].

conductivities [48]. The PPy produced by chemical polymerization can be collected as a powder whereas electrochemical polymerization leads to the growth of PPy on an electrode, as we will see in the next section.

1.2.3 Electrochemical Polymerization

Electrochemical polymerization is classically carried out using a three-electrode cell equipped with a working electrode, a counter electrode and a reference electrode, typically (Ag/AgCl), as exemplified in the figure 1.6. The vessel contains a bath consisting of the monomer and an electrolyte/dopant dissolved in an appropriate solvent (generally water). The electrodes are connected to a potentiostat that is used for controlling the applied voltage difference between a working electrode and the reference electrode [49]. Different electrochemical techniques can be used such as potentiostatic (constant-potential), galvanostatic, (constant current) and potentiodynamic (cyclic voltammetry) methods [48].

The mechanism for electrochemical oxidation polymerization of pyrrole is usually described by Diaz's mechanism [50], which is constituted in a sequence of three steps: oxidation, coupling and deprotonation. Nevertheless, the exact mechanism is still a matter of debate [48] and other models have been proposed, like the model of Pletcher [51]. The CP polymerized by an electrochemical process is grown on top of an electrode (the working electrode) and its properties depends strongly on

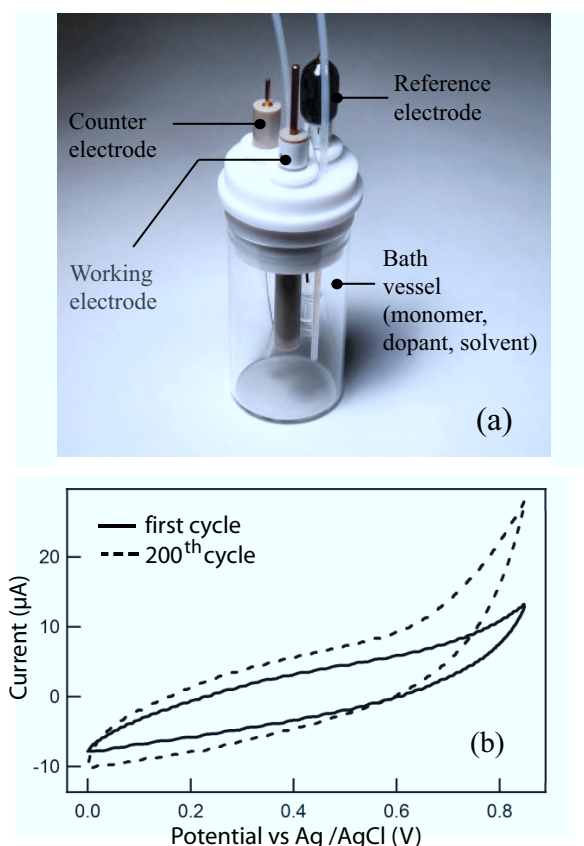


Figure 1.6: (a) Example of a typical three-electrodes electrochemical cell. Picture taken from [4]. (b) Cyclic voltamograms recorded during the deposition of PPy at the first and 200th cycles.

the synthesis conditions and parameters that have to be controlled during the deposition. The most important parameters are type of solvent (polar, aprotic,...), the choice made for the electrolyte, the synthesis temperature and pressure, the deposition technique (potentiostatic or galvanostatic). For example, it has been demonstrated that CP exhibit higher conductivity when synthesized at lower temperature [52] or when changing the dopant [16]. Electrochemical polymerization offers a better control of film thickness and morphology than chemical oxidation. Nevertheless, the main drawbacks arise from the low amounts of materials produced and the fact that the polymerization occurs only on top of the anode resulting in a thin film shaped materials. Another point is that the electropolymerization mechanism is still not well understood as a consequence of the difficulty to follow the fast growth of the species

in situ at the electrode/solution interface [48].

1.3 The Concept of Doping

Similarly to their inorganic counterparts, the conductivity of CP can be tuned in a wide range of values from their pristine (insulating) state to a highly doped (metallic) state. The main effect of doping is to increase the concentration of available charge carriers, however, the doping levels and the doping mechanisms differ from the conventional doping of inorganic semiconductors. Both p-type and n-type CPs can be produced by removing or adding an electron from the π -electron system. This charge transfer requires the insertion of a counter ion into the polymer chains for the overall charge neutrality of the CP and is generally called the dopant. An example is the oxidation of PPy (p-type) by injection of holes on the PPy backbone from a solution containing tetraethylammonium perchlorate. This charge is compensated for by the presence of the perchlorate anions [53]. The doping level is generally defined as the number of unit charges per thiophene or pyrrole ring [47]. The doping procedure is often carried out during the chemical or electrochemical polymerization of the CP but can also be carried out after the CP synthesis, electrochemically or by exposing the CP to vapors or solutions of dopants. This is generally referred to as secondary doping. These reactions are most of the time reversible and often accompanied by color changes (electrochromism) [54]. Besides, redox doping, it is also possible to create or remove charge carriers through an acid-base reaction. A well-known example of acid-base doped conjugated polymer is poly(aniline) which can exhibit an insulating-to-conducting transition through a simple protonation process (without any external redox process) [54].

Due to the strong electron-phonon coupling, each charge injection is accompanied by a deformation of the polymer chains geometry which relaxes over a few monomer units. This reduces the overall energy of the system and introduces new energy levels between the HOMO and the LUMO of the CP. This association of an electrical charge to a local chain distortion leads to the definition of polarons [55]. These quasi-particles are considered to be at the origin of charge mobility along and between the chains and determine the transport properties of CP [56]. A polaron carries spin half, whereas two nearby polarons in a single unit referred to as a bipolaron, is spinless (see Fig. 1.7).

Generally, the increase of the doping level of a CP results in an increase of its electrical conductivity. As explained before, the doping level

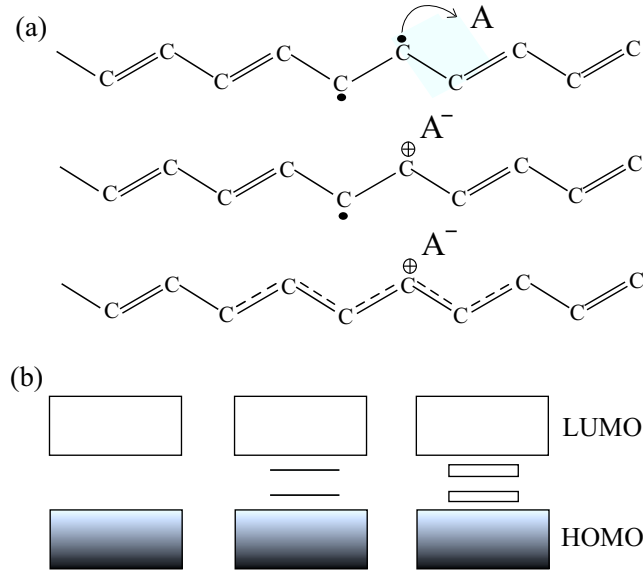


Figure 1.7: (a) Scheme of p-doping of PA which leads to the creation of a polaron. (b) Energy levels of a CP. From left to right: In neutral form. Lightly doped, with additional bipolaron levels. Heavily doped CP with bipolaron bands.

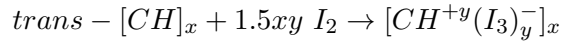
of CP synthesized electrochemically is mainly determined by the amount of counterion introduced within the CP chains during its synthesis. In the case of our HNWs, ClO_4^- is the counter-ion used for the PEDOT and PPy synthesis. Thus the doping level can be adjusted during the synthesis by modifying the initial ClO_4^- concentration and by properly adjusting the synthesis parameters (e.g. temperature, potential range, scan rate). Nevertheless, it is commonly accepted that the doping level has a maximum about 33 % which corresponds to the creation of bipolarons bands within the CP bandgap.

The next section presents the main strategies available for achieving anisotropic growth of CPs nanostructures. The aim of this section is not to provide a comprehensive and detailed review of all the synthesis schemes, but to give the reader the basics and present some state-of-the-art techniques allowing the synthesis of 1D conjugated polymer nanostructures.

1.3.1 P-Doping

The p-doping of CP is an oxidative process that removes electrons from the π bonds of the backbone. In the case of PA, the reaction in presence

of an oxidizing agent such as iodine can be written [46]:



To maintain the charge neutrality of the doped polymer, a counter anion is inserted near of the positively charged conjugated backbone, as depicted in figure 1.7. Also, this counter ion helps screen the charge on the polymer chain [57]. The induced positive charge of the backbone does not stay localized on a single C atom; as depicted in figure 1.7.(a) it spreads over many C atoms.

1.3.2 N-Doping

The n-doping of CP is a reaction in which electrons are added to the π electron system of the backbone. For example, a reduction can be performed, in the case of PA in presence of a reducing agent such as sodium naphthalide [46]. Practically, n-type CP are far less developed than p-type CP and they are not stable in the air because of the oxidation reaction that occurs in presence of oxygen. Furthermore, the fundamental structure-charge transport property relationships of n-type CP are still not well understood. However, n-type semiconductors are essential for the fabrication of organic complementary circuits [58].

1.4 Conjugated Polymer Nanowire Synthesis

As mentioned in the section 1.1, nanostructured materials have attracted a great deal of attention, particularly nanowires and nanotubes, as they represent the smallest dimensional structures that can be used for efficient charge transport [59] and thus represent a major orientation regarding the development of nanoscale electronic applications. However, CP NW and NT offer many more possibilities than the mere miniaturisation of electronic devices. They combine low dimensionality with the numerous advantages associated with polymers. Their properties can be tuned at will, they are easily processed, offer high mechanical flexibility, they can be functionalized, and present higher biocompatibility than inorganic semiconductors.

The synthesis of CP NWs can be achieved by several techniques that can be regrouped into two main families, depending if there are based or not on the use of a template. The template-free method is relatively simple and inexpensive but control over the morphology and diameter of the NWs is poor compared to the template method [60, 5].

The most commonly used templates are membranes made of ion track-etched polycarbonate (PC) and porous anodic aluminum oxide (AAO). Typical PC templates have a mean pore diameter ranging from 30 to 200 nm, pore densities ranging from 10^8 to 10^9 pores.cm⁻² and thicknesses around 20 μ m. Figure 1.8.(a). gives schematic views of a typical PC template used for synthesizing CP and hybrid metal-CP NWs.

Besides usual PC and AAO templates, other materials such as Si or polymethylmethacrylate (PMMA) can be used as templates [61, 62]. Examples of NW synthesis within PMMA templates are presented in section B.3.

1.4.1 Template Method

The template method is probably the simplest method for achieving the anisotropic growth of nanostructures. It is based on the use of a nanoscale mold serving as a host structure containing nanoscale void spaces. These void spaces act as the template, giving the shape, size and orientation of the produced structure [3]. The template method is very efficient for achieving a controlled growth of NWs: the shape, size and orientation of the produced structures are precisely defined by the template [63]. Moreover, it allows the synthesis of complex multi-segmented NWs, core-multishell, and coaxial NW structures [64, 65, 66].

Generally, a distinction is made between the so-called hard-template and soft-template methods. While ion track-etched membranes made of polycarbonate (PC) and anodic aluminum oxide (AAO) membranes are well-known examples of hard-templates [67, 64], soft-templates are host materials such as micelles or microemulsions that can guide the growth of the polymer during polymerization [6, 68, 59].

1.4.1.1 Hard-Template Method

The hard template method, presented for the first time by Martin and coworkers [69, 67], offers the ability to generate complex 1D conjugated polymer nanostructures with a very good control over the composition and spatial distribution [70].

The most used templates are membranes made of ion track-etched polycarbonate (PC) and porous anodic aluminum oxide (AAO); however, other materials such as Si, SiN_x , PMMA, etc [71, 61, 62] have been used for defining hard-templates. Typical PC templates² have a mean pore diameter ranging from 30 to 200 nm, pore densities ranging from 10^8 to 10^9 pores.cm⁻² and thicknesses around 20 μ m. Figure 1.8.(a)

²available, for example, at www.it4ip.be

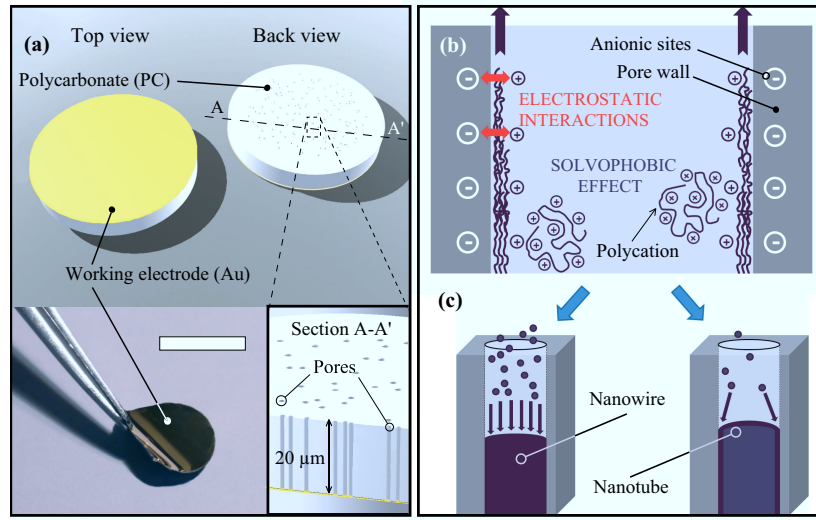


Figure 1.8: (a) Top and back views of a flexible PC template used for synthesizing nanowires. In the left inset, the scale bar represents 5 mm. (b) Scheme of the growth mechanism for polymer NTs and NWs within a single pore. (c) Usual relations between synthesis conditions and morphology: Fast reaction rate and insufficient monomer supply lead to NTs. Slow reaction rate and sufficient monomer supply direct NWs.

gives schematic views of a typical PC template used for synthesizing CP and hybrid metal-CP NWs. Both chemical and electrochemical methods can be used with hard-templates, nevertheless electrochemical methods are often preferred due to the better control of the polymerization process and others advantages compared to chemical polymerization (see section 1.2.3).

Other materials such as Si or polymethylmethacrylate (PMMA) can be used as templates [61, 62]. PMMA template were fabricated by EBL in a work conducted in a collaboration with the Bertrand group (UCL/PCPM). In this work, PANI NWs have been synthesized by electroless polymerization of aniline within PMMA templates defined by EBL on top of Pt microelectrodes. Various samples have been characterized by T -dependent electrical measurements. For consistency of the manuscript, these results are presented in a separate section B.3.

1.4.1.2 Soft-Template Method

The soft-template method is quite simple, cheap, and in contrast to the hard-template method, it is not based on the use of an insoluble membrane. Soft-templates can be formed by host materials such as micelles, ionic solvents, liquid crystals or microemulsions [6, 3, 68]. Typical soft-templates are made of surfactants that are known to self-assemble into micellar structures that exhibit cylindrical shape within specific conditions [59]. Schematic of such cylindrical micelle are given in the Fig. 1.9. These structures can be used as templates for a polymerization process of a conjugated polymer.

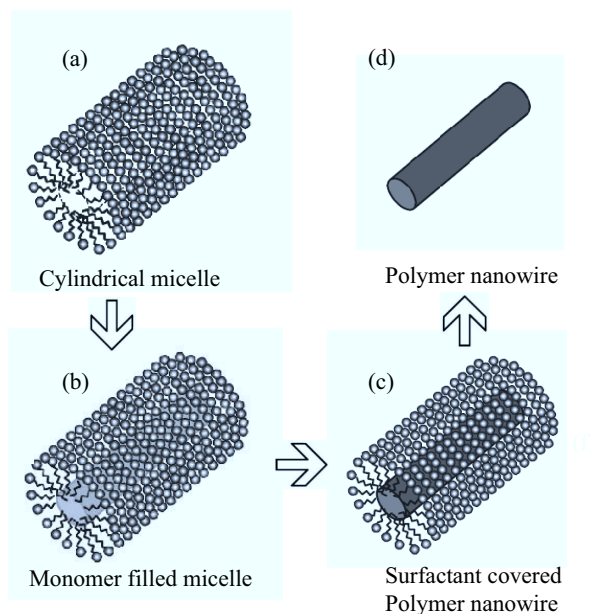


Figure 1.9: (a) Empty cylindrical micelle used as soft-template. (b) micelles filled with monomer. (c) Surfactant covered conjugated polymer obtained after chemical polymerisation within the micelle template. Conjugated polymer nanowire obtained after removal of the template. Adapted from [3].

1.4.2 Template-Free Method

It is possible to anisotropically grow CP nanostructures like nanowires or nanotubes without using any kind of hard or soft template. This process exploits the fact that conjugated polymers appear to have a predisposition to grow preferentially in one direction. Conjugated polymers are

semi rigid-rod polymers that grow linearly. It stands to reason that this anisotropy can be translated into a nanometer sized bundle by carefully controlling reaction parameters.

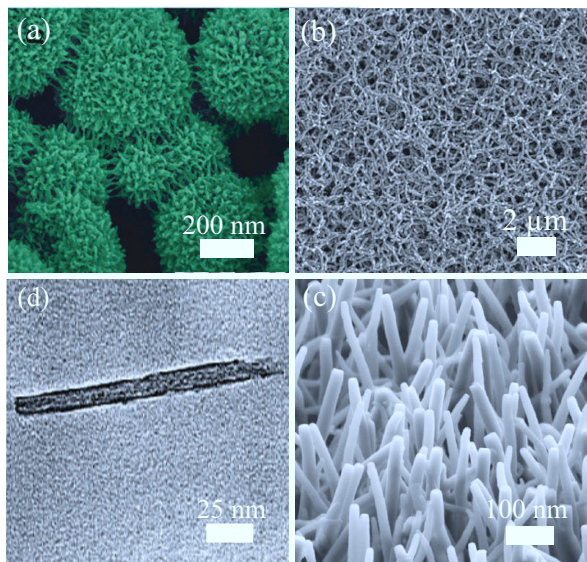


Figure 1.10: Examples of nanowire-like conjugated polymer structures synthesized by the template-free method: (a) 3D microstructures assembled from PANi NWs [5] (b) PANI-H₃PO₄ NT [6] (c) PPy NWs obtained by the template-free method using electrochemical polymerization [7], (d) PPy nanotubes [3].

Aligned and oriented CPNWs are generally produced by chemical or electrochemical polymerization using a hard-template, as it fixes the diameter and length of the produced NW. However, removal of the templates can lead to collapse or destruction of the aligned nanofibres [72]. Interestingly, it was discovered accidentally that PANi nanotubes could be synthesized by conventional in-situ doping polymerization in the presence of an acid (as the dopant) without using a membrane as a hard template. The template-free method is simple and inexpensive [5, 73]. The main drawback is that the controllability of the morphology and diameter for the self-assembled nanostructures is poor compared with that of the hard-template method [5].

1.4.2.1 Electrospinning

For the sake of convenience, the electrospinning method has been defined here as a template-free method while in the literature, it is usually clas-

sified as a physical method [43, 59]. Electrospinning is an efficient technique used for the fabrication of polymer nanofibers [74, 75, 76, 8, 77, 78]. Many polymers have been successfully electrospun to form fibers with diameter ranging from tens of microns down to tens of nanometers.

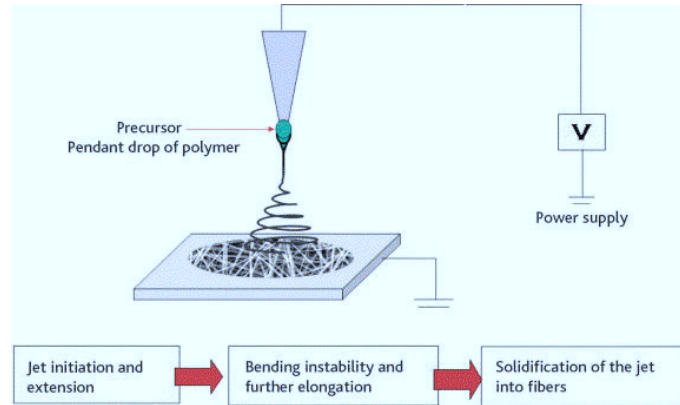


Figure 1.11: schematic diagram of the electrospinning setup composed by a high voltage supply, a small diameter needle, and a collecting screen. Taken from reference [8].

This technique allows to produce very long and continuous NWs. Its principle is based on a high voltage applied between a the needle of a syringe containing a polymer solution, and a collecting screen [76] (see figure 1.11). The polymer solution is charged by a high electric field (about 10 kV). When the repulsive electrostatic forces within the solution caused by the electric field overcome the surface tension which holds the fluid, the solution ejected from the needle stretches to form a very thin fiber landing on the metal collector. The figure 1.11 gives a schematic diagram of a typical electrospinning setup.

Many parameters can influence the transformation of polymer solutions into nanofibers through electrospinning: solvent properties such as viscosity, elasticity, conductivity, surface tension, ambient parameters such as solution temperature, and humidity. In the following section, we provide a brief review of potential applications of CP NWs and NTs to highlight the properties required.

1.5 Applications

In recent years, investigators in industry and academia have increasingly tamed the structural and electronic properties of NWs and NTs

which offer an impressive potential in applications ranging from bio-environmental sensing and energy harvesting to ultra-low power electronic devices and high density memories [79, 80, 81]. The Fig. 1.12

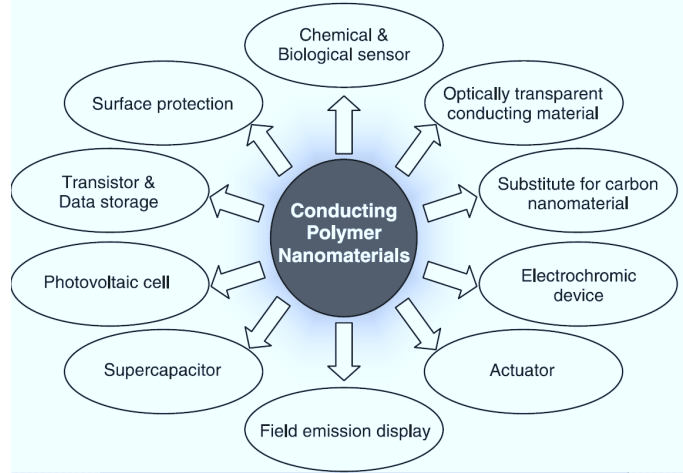


Figure 1.12: Application fields of CP nanomaterials. Taken from [3].

The Fig 1.12 gives the multiple application fields where CP could be advantageously used. In the following sections, we present a brief non-exhaustive list of important potential applications of NWs and especially CPNWs.

1.5.1 Resistors, Diodes and Transistors

The use of conducting polymers as electrical elements (resistors, diodes or transistors) is of key importance for the development of the new field of plastic electronics [36, 37]. Based on their high aspect ratio, NWs offer excellent building blocks for designing high-density nanoscale devices as they are the smallest dimension structures that can be used for efficient electrical charge transport [81]. the ability to prepare NWs of different aspect ratios allows fine tuning of their intrinsic electronic properties [82] which could be useful for the development of NW-based devices. In order to achieve highly integrated device architectures, NWs can be used primarily as interconnects, thanks to their high aspect ratio. Interestingly, systems exhibiting novel functions could be based on the versatility associated with the ability to generate multi-segmented NWs consisting of different materials and hence different spatially resolved functions [82]. Indeed, several studies have shown that the unique properties of CP NWs enable them to function as active device elements such

as rectifying diodes [74, 83, 77], field-effect transistors (FET) [84, 85] or variable resistor integrated in sensor devices.

1.5.2 Chemical and Bio-sensors

Because of their high surface-to-volume ratio, chemically tunable transport properties, binding affinities for various biomolecules, and biocompatibility, and because biomolecules can be incorporated into the CP in a single step during synthesis, CP NWs have emerged as attractive candidates for fabricating (bio-)sensor devices [49]. Several CP NW-based sensors have been demonstrated to be very sensitive (to NH_3 concentrations as low as 0.5 ppm) for a wide range of analytes from NH_3 [86, 21], HCl [3], H_2S [87], CH_3OH , C_2H_5OH [88] to more complex biomolecules such as biotin-DNA [89]. Basically, an effective sensor should exhibit a significant and measurable variation of one of its physical properties upon the interactions with the target material. Most of the existing CP NWs-based sensors use the variation of electrical properties of PANi, PPy or PEDOT NWs for developing new sensor technologies. Generally, the CP NWs are deposited on interdigitated electrodes, and their resistance changes is monitored in real-time. An example of HCl and NH_3 vapor detection is given in Fig. 1.13.(a-b) The sensors are based on PEDOT NWs which exhibit reversible and reproducible responses for HCl and NH_3 analytes [9]. Strikingly, as shown in the panels (c-d) of the Fig. 1.13, NWs-based sensors showed enhanced sensitivity (at least six times more sensitive) compared to equivalent bulk film sensor. This could be explained by a high surface-to-volume ratio and a rapid diffusion of analytes into and out of the material [3].

1.5.3 Photonic Devices

Over the past two decades, organic materials have shown great potential for use in high-performance optoelectronic devices and in the development of light-emitting [90] and photovoltaic devices [10], as well as lasers and optical amplifiers [10, 78]. A recent example of single NW photodiodes was demonstrated for an organic/inorganic P-N junction NW consisting of PPy and CdS fabricated using an AAO template [10]. Fig. 1.13.(e-f) compares the current dependence under light illumination for a single PPy NW and a hybrid PPy/CdS NW. The strong photodependent rectifying effect is only observed in the hybrid NWs. While such single CP NW configurations are very useful to understand the mechanism of large-area nanowire-array based photonic devices such as solar cells or light-emitting devices, at least CP NW arrays are needed to meet

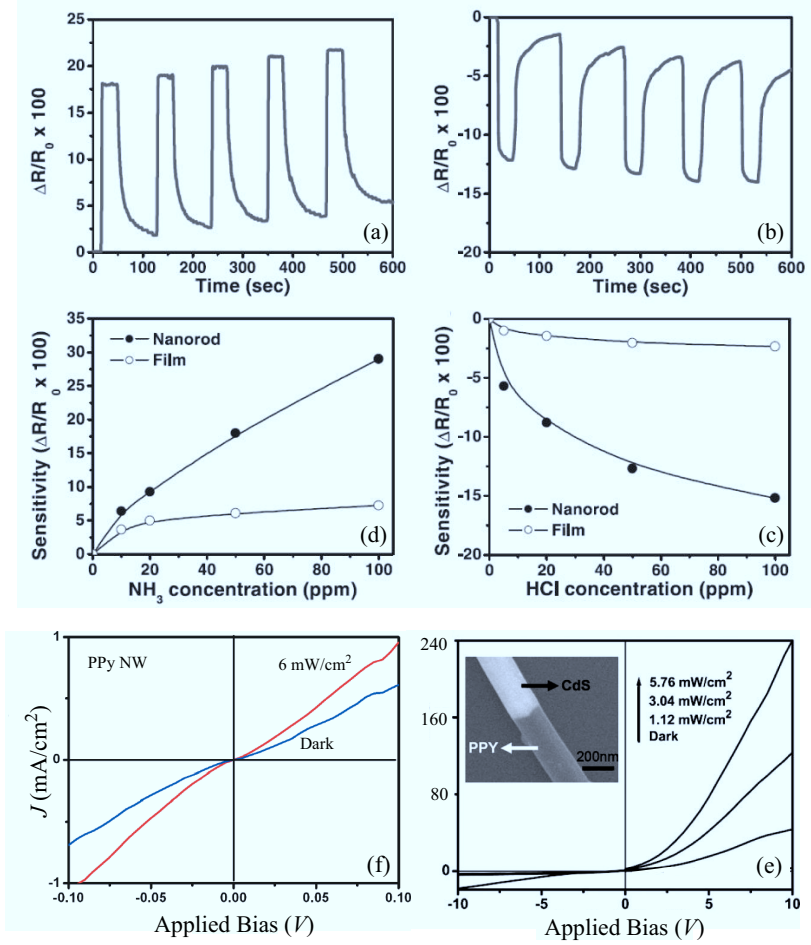


Figure 1.13: Comparison of the sensitivity of PEDOT NWs and films as a function of (a) NH_3 and (b) HCl vapor concentration. Reversible and reproducible response of PEDOT nanorods upon periodic exposure to (c) NH_3 and (d) HCl vapor. Taken from reference [9]. (c-d) Typical ($I-V$) curves for single PPy and CdS-PPy heterojunction NWs under light illumination. A strong photodependent rectifying effect is observed. The inset gives a SEM image of CdS-PPy heterojunction. Adapted from [10].

the minimum requirements of commercial photonic applications.

1.6 Summary

Nowadays, the fabrication of CP NWs is considered as an important topic in polymer material science. In this chapter, we introduced the

reader to the fascinating materials that are conducting polymers. We reviewed the synthesis of conducting polymers and briefly presented the concept of doping of conjugated polymers. Then the main fabrication paths for CP NWs have been reviewed, namely, the template methods (soft and hard template methods) and template free method. Finally, a variety of applications have also been highlighted. It has been shown that conducting polymer nanomaterials exhibit excellent performance and are characterized by an enhancement of their physical and chemical properties compared to that in the bulk state. In the next chapter, we focus on the electrical charges transport of conjugated polymers.

Chapter 2

Charge Transport in Conducting Polymers

Ce sont rarement les réponses qui apportent la vérité,
mais l'enchaînement des questions.

La fée Carabine, Daniel Pennac

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2.1 Overview

Since the discovery of CP, a very large amount of experimental work was dedicated to study the properties of bulk CP and has brought to light several electrical charge transport mechanisms. Systematic studies have shown how the transport properties of CP are influenced by the synthesis conditions [14], the type of dopant [52, 91], the presence of a magnetic field [92, 93, 94], the type of electrodes [95, 53, 96], the pressure, the temperature and electrical field ranges [96]. Astonishingly, the models usually used for describing the electrical properties of CP semiconductors are essentially the same as for inorganic semiconductors.

Despite the fact that the application of such models allows an explanation of the observed electrical properties of many CPs, some disagreements exist, for instance in the low- T limit, and require the use of specific models. In this chapter, we recall classical models and related concepts of charge transport which are relevant to derive quantitative information on our samples and finally, we briefly review the literature dealing with charge transport in CPs and more specifically CP NWs. The analysis of the electrical measurements presented in the next chapters will often refer to models, concepts and equations described in this chapter.

This chapter will be divided as follows: firstly, general transport theories of the interface injection and bulk transport mechanisms will be presented with a special emphasis on the variable range hopping (VRH) model. Then a brief review of the literature dealing with charge transport in CPs and more specifically CP NWs will be given to close this chapter.

2.2 Charge Injection Mechanisms

The charge carrier injection from a metal electrode into semiconductors is a key issue for the characterization of all electronic devices such as transistors, solar cells, or sensors [53]. Compared to inorganic semiconductors, for which the physics of charge transport is pretty well understood and for which an abundant literature is available, charge injection

into organic materials and particularly into CPs is still not fully understood [97, 98, 35].

Generally, Inorganic semiconductor are highly ordered materials, with delocalized states which allow definition of valence and conduction bands whereas organic materials are often amorphous or poorly ordered with highly localized states and as such a definition is not obvious. Although the use of traditional models for explaining the charge injection at metal/organic semiconductor interfaces could be in some cases questioned, they have been successfully applied for many organic semiconductors and in particular CPs such as PPy, PEDOT, PA or PANI [99, 100, 101]. It is still an efficient and tool to obtain important information about the charge transport at the metal/organic semiconductor interfaces. Nevertheless, specific mechanisms of charge injection at metal/organic interfaces were proposed recently. For instance, the Gaussian distribution model (GDM), describes a two-step hopping process, in which charge carriers hop from delocalized states in the metal to localized states in the first interfacial layer of the organic semiconductor, followed by a subsequent hop to spatially deeper states in the organic semiconductor [102, 96].

Here, we focus on a few charge carrier transport mechanisms across a metal-semiconductor junction described within the framework of the band theory, focusing especially on the Schottky model as it will be successfully applied in chapter 5, to explain the tunable electrical properties of tetra-segmented HNWs.

2.2.1 The Ohmic Contact

The achievement of Ohmic contacts on a sample is essential for its electrical characterization as it is a necessary condition for probing the bulk-limited mechanisms of charge transport [53]. An Ohmic contact is formed between a metal and a CP when the current density J is proportional to the applied voltage V . This means that the contact can supply any charge flow which is only limited by the bulk CP.

The figure 2.1 depicts the band diagram of the junction between a metal and an p-type semiconductor and the formation of a barrier. The situation before contact is depicted in the panel (a) of the figure 2.1. When the metal and the semiconductor are brought into contact, a flow of charges pass through the junction until an equilibrium is reached and the two Fermi energy levels equalize. charges will be accumulated on both sides of the interface creating an electric field and therefore a potential gradient according to Poisson's equation $\nabla^2 V(x, y, z) = -\rho(x, y, z)/\epsilon$ which translates in a band bending [103]. The induced

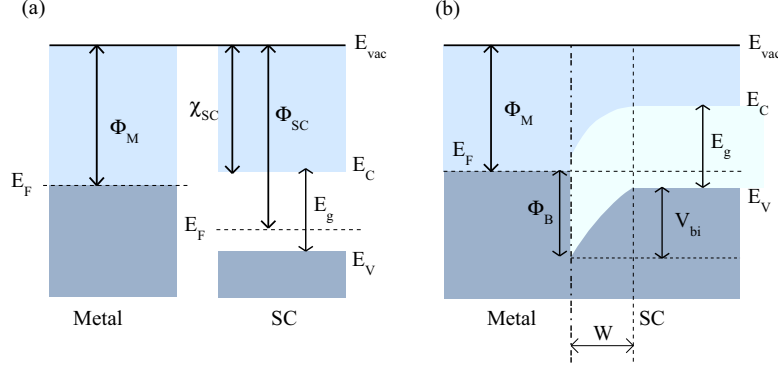


Figure 2.1: Formation of a barrier between a metal and an semiconductor. (a) The metal and the semiconductor are isolated and supposed to be electrically neutral. (b) Once contacted, when the thermal equilibrium is reached, the Fermi levels equalize and a depletion area is created.

electric field causes the majority carriers (holes, in a p-type semiconductor) to move away from the interface.

Consequently, a region of width W filled with uncompensated (negative) charges will be created and is usually called the depletion region. This depletion region width W depends on the doping concentration, and ranges from 10 nm for doped CP ($N(E_F) = 10^{19} \text{ cm}^{-3}$), to much higher values $W \gg 100 \text{ nm}$ for lightly doped CP ($N(E_F) < 10^{17} \text{ cm}^{-3}$). As shown in the figure 2.1.(b), carriers coming from the metal into the p-type semiconductor, see a potential barrier given by

$$\Phi_B = E_g - (\Phi_M - \chi_{SC}), \quad (2.1)$$

where E_g is bandgap, χ_{SC} is the electron affinity and Φ_M is the metal work function.

Theoretically, an Ohmic contact presents no Schottky barrier ($\phi_B \leq 0$). Practically, an Ohmic contact to a given CP is performed by tuning the work function of the metallic electrode. Usual CPs such as PPy, PEDOT or PANI present high work functions which allows Ohmic contact for holes by using noble metals such as gold or platinum [104]. Nevertheless, despite the optimization of the contacts based on the work function, a barrier may still exist resulting for instance from the Fermi level pinning at the midgap or interface dipoles [105].

Generally, the injection of charge carriers across a potential barrier is described by the T -dependent Schottky emission model (also called the field enhanced thermionic emission model) and by T -independent tunneling processes [103]. Lets first, consider the Schottky emission

mechanism.

2.2.2 Schottky Emission Mechanism

The Schottky emission theory states that only the thermally activated carriers with an energy larger than the top of the Schottky barrier height (SBH) ϕ_B will participate to the current [103, 102, 100, 96]. The band diagram of the Schottky emission is depicted in the Fig. 2.2. When a forward bias, V , is applied to the metal-CP junction, the SBH is reduced resulting in a current density, which can be written as

$$J_S = A^* T^2 \exp \frac{-e\phi_B}{k_B T} \left[\exp \frac{e(V + \Delta\phi_B)}{k_B T} - 1 \right], \quad (2.2)$$

where $A^* = 4\pi q m^* k_B^2 / h^3$ is the effective Richardson constant with m^* the carriers effective mass. T is the absolute temperature, k_B is the Boltzmann constant, V is the applied voltage. $\Delta\phi_B$ is the barrier lowering term which takes into account the charge image force induced by the electric field F present at the metal-CP interface¹. As a result, the barrier seen by the carriers is lowered by $\Delta\phi_B = \sqrt{\frac{eF}{4\pi\epsilon_0\epsilon_{CP}}}$. In the reverse direction the dominant effect is due to the Schottky barrier lowering and the current is given by the following equation

$$J_S = A^* T^2 \exp \left[\frac{e\sqrt{eF/4\pi\epsilon_0\epsilon_{CP}}}{k_B T} \right], \quad (2.3)$$

where ϵ_{CP} is the permittivity of the CP [103, 100]. It is important to notice that the Richardson free electron constant ($A^* = 120 \text{ A/cm}^2 \text{K}^2$) is often taken as in most of the cases, the exact value is unknown. Nevertheless, this could lead to large error in the case of disordered CP where A^* is orders of magnitude lower [95]. Several methods can be used to measure the SBH ϕ_B of a metal-semiconductor contact: capacitance-voltage measurements, $(I - V)$ measurements and photoelectric methods [103]. From the $(I - V)$ characteristics taken at different temperatures, ϕ_B can be determined. Generally, Schottky plots consisting of $\ln[I/T^2]$ versus $1/T$ at various fixed V s and $\ln I$ versus $V^{1/2}$ at different temperatures are used. ϕ_B is deduced from the slope of the linear fit of the Schottky plots.

The Schottky emission process is generally observed at low or moderate electric field while at high electrical field, tunneling process occur. Moreover, an interesting phenomenon occurs when the dimensions of

¹ F combines the field resulting from the space charge effects and from the applied bias V .

a Schottky diode decrease as it was demonstrated recently by Smit *et al.*. They showed that in case of the size of the metal-semiconductor interface is smaller than a characteristic length l_c , the thickness of the barrier is no longer determined by the doping level or the free carrier concentration, but instead by the size and shape of the diode [106]. This results in enhanced tunneling process, which could explain large increase of the reversed current in small Schottky diode without the necessity of assuming a reduced barrier Φ_B . Interestingly, this effect could have an impact on the observed nonlinear behavior of multi-segmented HNWs.

Another important tunneling mechanism often encountered in semiconductor, is Fowler-Nordheim tunneling [100].

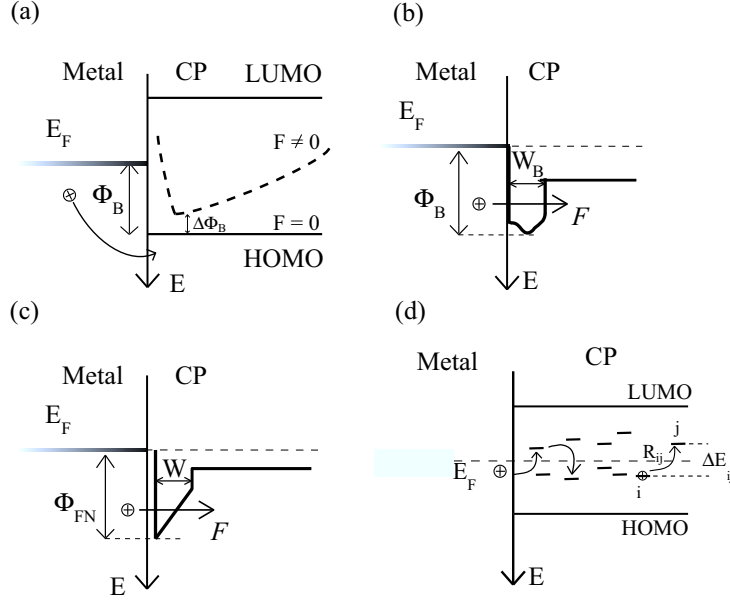


Figure 2.2: Bands diagrams of a metal/CP for different injection mechanisms. a) Schottky emission mechanism. b) Direct-tunneling through a barrier of width W . c) Fowler-Nordheim tunneling. d) Hopping mechanisms.

2.2.3 Fowler-Nordheim Tunneling

In the case of large applied electric field F , the charge injection at the metal-polymer junction is generally described by Fowler-Nordheim (FN) tunneling process. FN tunneling injects through a triangular shaped energy barrier (see Fig. 2.2.(c)) in the available electronic states of the CP [103, 100]. For large electric field F , the current density through a

barrier of height ϕ_{FN} is given by

$$J_{FN} = \frac{e^3}{8\pi h \Phi_{FN}} F^2 \exp \left[-\frac{4\sqrt{2m^*}(\Phi_{FN})^{3/2}}{3\hbar e F} \right] \quad (2.4)$$

where m^* is the effective mass of the carriers. The resulting current is strongly correlated to F .

2.3 Bulk Charge Transport Mechanisms

Depending on the SBH Φ_B present at the metal-CP interface, a measured current can be electrode or bulk limited. It is usually assumed that the Schottky barrier can be neglected when $\Phi_B < 3k_B T$, that is for $\Phi_B < 75 \text{ meV}$ at RT. In such a case, the metal-CP contacts are considered as Ohmic and the measured current is bulk-limited. In this regime, the charge transport depends only on the intrinsic properties of the semiconductor considered such as the structural ordering.

2.3.1 Disorder and Localization

Traditional inorganic semiconductors are single crystal solids, with delocalized states² whereas, usual CPs such as are primarily disordered van der Waals solids, containing defects and impurities. The amount of disorder together with the defects and impurities introduce backward scattering which greatly influence the electronic structure of disordered systems. In these systems, charges may become localized and the corresponding wave function (see Fig. 2.3) decays exponentially $|\phi(r)| \propto \exp[-r/r_0]/\xi$ where ξ is defined as the localization length [107]. In these materials, the concept of band conduction by free charges does not apply and the conduction is mainly based on a hopping mechanism in which the carriers *jump* between localized states. Anderson studied the influence of disorder in terms of localization effects and disorder induced metal-insulator transition (MIT) [108]. An important consequence of the disorder, is the appearance in the density of state of *band tails* of localized states (see Fig. 2.3.(d)). The resulting electronic properties of materials depends on the location of the Fermi level E_F . The material exhibits a metallic behavior if E_F lies in the range of extended states, while the material is an insulator even though there is a finite density of states at the Fermi level when E_F lies in the range of localized states [109]. It is possible to vary E_F by changing applying a magnetic field or a gate voltage, and to make the system shift from a metallic to a non-metallic state.

²Bloch waves

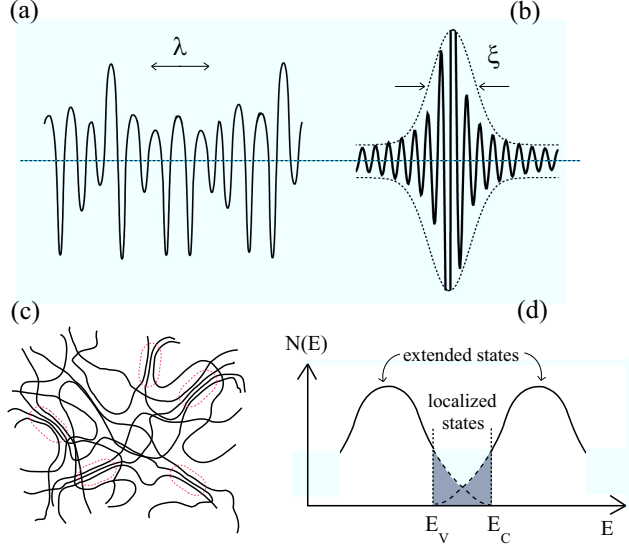


Figure 2.3: Typical wave functions of (a) an extended state characterized with mean free path λ and (b) of a localized state defined with its localization length ξ . (c) Schematic view on a typical structure of a CP where lines represent the CP chains and the dashed lines mark the region where the CP chains are ordered. d) Formation of a pseudogap with localized states in the regime of overlapping bands.

2.3.2 The Ohmic Regime

The Ohmic regime of transport holds as long as the density of injected carriers $N_{CP} - N_0$ is lower than the density of thermally generated charges $N_0(T)$ within the CP [53]. Assuming the conduction is via holes which have a constant mobility μ_h , the current density is given by

$$J_{Ohm} = eN_{CP}\mu_h \frac{V}{d} \quad (2.5)$$

where d is the thickness of the sample and N_{CP} is the total concentration of holes in the valence band. Generally, in CP systems, this Ohmic regime is associated to a thermally activated conductivity σ which follows the relation

$$\sigma_{Ohm} = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (2.6)$$

The Ohmic regime is often encountered in CP for small applied bias V . For intermediate applied bias, the injected charge density could exceeds

the free charge density under thermal equilibrium. As a result, the system could transit to space-charge-limited current (SCLC).

2.3.3 Space Charge Limited Current

Bulk limited or space charge limited current (SCLC) occurs generally in low mobility and low doped SCs in which a space charge region is formed inside the SC which limits the current flow [110, 102]. Within the SCLC [111] theory, assuming an exponential distribution of traps $g(E) \propto \exp\left[-\frac{E}{l k_B T}\right]$, the field dependence of the current density J is given by

$$J_{SCLC} \propto \epsilon \mu_{CP} \frac{F^{l+1}}{L} \Theta \quad (2.7)$$

where ϵ is the permittivity of the CP, μ_{CP} is the field-independent mobility of the carriers, L is the thickness of the sample. l is a measure of the width of the trap distribution. The SCLC theory predicts the crossover from the Ohmic regime ($m = 0$) at low applied voltage to the SCLC regime governed by a shallow-trap ($l = 1$) and to a trap-filled regime ($l \gg 1$) [112, 113]. and Θ is the fraction of free charge [103, 100]. In the presence of traps with an energy distribution, Θ and μ_{CP} are temperature and field dependent [99].

2.3.4 The Poole-Frenkel Mechanism

While the Schottky emission mechanism is associated with the existence of a barrier between the electrode and the CP, the Poole-Frenkel mechanism is linked to barriers existing in the bulk of the materials [114, 103]. When the Poole-Frenkel mechanism occurs, the current density is written as

$$J_{PF} = \sigma_0 F \left[\exp\left(\frac{\Phi_B V}{k_B T}\right) - 1 \right] \quad (2.8)$$

2.3.5 Fluctuation Induced Tunneling

The fluctuation-induced tunneling (FIT) model proposed by Sheng [115] describes the electrical conduction in disordered materials made of metallic islands separated by small insulating barriers. It was used to explain the temperature and field dependences of $(I - V)$ characteristics for different systems (PPy, PA, V_2O_5 NWs and SWCNT mats), for temperatures ranging from RT down to $T \approx 100$ K [116, 117, 118, 17].

Following the FIT model, the non-Ohmic regime is described by

$$J_{FIT} \propto J_0 \exp \left[-\frac{T_1}{T + T_0} \left(1 - \frac{F}{F_c} \right)^2 \right] \quad (2.9)$$

where T_0 is the temperature at which fluctuations in the voltage across a barrier become sufficiently large to make the electron energy higher than the barrier height, T_1 is the temperature above which thermally activated over-barrier conductivity becomes possible [119], and F_0 is the field required to lower the top of the potential barrier to the cathode [100].

2.3.6 Zener Tunneling

The Zener-type tunnelling conduction was observed in PA nanofibres [117, 120, 121] where in the absence of an ohmic part of the low- T ($I-V$) characteristics, the non-linear and weakly temperature dependent ($I-V$) behavior is not consistent with pure hopping models. The Zener interband tunneling occurs in a presence of a large electrical field $F \geq 10^5$ V/cm and is characterized by a non saturating exponential field dependence of the current [103, 119]. The high electric field allows a direct transfer of charge carriers between the band of the CP, and the resulting current density is given by [19]

$$J_Z \propto F \exp \left[-\frac{F_0}{F} \right] \quad (2.10)$$

where $F_0 = \frac{4\sqrt{2m^*}E_g^{3/2}}{3e\hbar}$ is the characteristic field. In the presence of a field F , the carriers energy is increased by $-eFx$. So electrons are able to tunnel between valence and conduction band states at the same energy if these states are separated by a distance $l = E_g/eE$ or more (where E_g is the SC bandgap).

2.4 The Variable Range Hopping Model

In the following we will present a very simple model proposed by Sir Nevill Mott, but which is very efficient to calculate the conductivity in a disordered system. The model is called *Mott's Variable Range Hopping* (VRH) model [122]. The VRH is one of the most important mechanisms of charge transport in disordered materials and differs depending on the inclusion or exclusion of electron-electron interactions. Primarily, the VRH model were used to explain the unusual low- T resistivity $\rho(T)$

in various amorphous inorganic SCs. The VRH model is still considered today as the most reliable theory for the evaluation of the electric conductivity and thermoelectric power of non-crystalline SCs [47].

In highly disordered materials, charges may become localized and are characterized by the localization length. We have seen that in such disordered materials, the concept of band conduction by free charges does not apply and the conduction is based on a hopping mechanism in which the carriers *jump* between states localized in space and energy. The hop from a site i with an energy E_i and a site j with an energy E_j was first described by Miller and Abrahams [107] and can be characterized by the range

$$\mathbf{R}_{ij} \approx \begin{cases} 2\frac{R_{ij}}{\xi} + \frac{\Delta E_{ij} + q\vec{R}_{ij} \cdot \vec{F}}{k_B T} & \text{if } \Delta E_{ij} > -q\vec{R}_{ij} \cdot \vec{F} \\ 2\frac{R_{ij}}{\xi} & \text{if } \Delta E_{ij} \leq -q\vec{R}_{ij} \cdot \vec{F} \end{cases} \quad (2.11)$$

where $\Delta E_{ij} = E_j - E_i$ is the energy difference between the two sites in the absence of the electric field.

The basic assumptions of the Mott VRH model are firstly, to state that the hopping transport takes place only from localized states distributed around the Fermi level E_F with $N(E_F)$ the density of states (DOS) around this energy level. Secondly, at sufficiently low temperature, most of the hopping processes are not *nearest neighbor hopping* processes as the range of each hop is determined by a compromise between the overlap factor and the energy factor of the equation (2.11). Neglecting the effect of the electric field, a carrier has a better chance to reduce the energy term when making a longer hop. Within the framework of the VRH [122, 123], as expressed by Sir Nevil Mott, the net current induced by an electric field F at the temperature T can then be written as the product of

- $2eN(E_F)k_B T$, the number of charges involved,
- ν_{ph} , an attempt-frequency which characterizes the electron-phonon interaction,
- $\bar{R}_{hop}$, is the average hopping distance traveled per hop,
- $\langle \exp(-\mathbf{R}_{ij}) \rangle$, is the average hopping probability optimized in the sense of Mott.

As a result, the total current density induced by the presence of an electric field F is given by

$$J_{VRH} \propto e\bar{R}_{hop}N(E_F)k_BT\nu_{ph} \langle \exp(-\mathbf{R}_{ij}) \rangle \quad (2.12)$$

ν_{ph} is of the order of the characteristic phonon frequency $f_{ph} \approx 10^{12} \text{ s}^{-1}$ [124]. The critical factor in the equation (2.12) is the exponential factor $\exp(-\mathbf{R}_{ij})$. We describe the effect of this term by examining the low high electric field regimes to derive the evolution of the current as a function of the temperature and the electric field magnitude.

2.4.1 The Low Electrical Field Regime

In presence of a low electric field such as $|e\bar{R}_{hop}F| \ll k_BT$ the equation 2.12 can be rewritten

$$J_{VRH} \approx 2e\bar{R}'_{hop}N(E_F)k_BT\nu_{ph}\exp(-\bar{R}')\sinh\left(\frac{e\bar{R}'_{hop}F}{k_BT}\right) \quad (2.13)$$

where $\bar{R}'$ and $\bar{R}'_{hop}$ are the average nearest hopping range and the hopping distance, respectively, without the presence of an electric field. The temperature dependence of the hopping distance $\bar{R}'_{hop}$ is found following the reasoning of Mott which consists to optimize the hopping range (2.11) with the condition that there is at least one state j , within a radius $\bar{R}'_{hop}$ from a given site i , which presents the lowest energy separation ΔE_{ij} . Mott expressed this condition as follows

$$\int_0^{\bar{R}'_{hop}} dr \int_0^{\Delta E_{ij}} N(\epsilon) d\epsilon \approx 1 \quad (2.14)$$

Considering the general case of the volume V_d ³ defined in an isotropic system of dimensionality $d > 1$ which possesses a constant density $N(E_F)$ of localized states around the Fermi energy, equation 2.14 gives $\Delta E_{ij} = 1/V_d N(E_F)$. If substituted into the expression 2.11, the optimization of the hopping range $\mathbf{R}_{ij}$ yields

$$\bar{R}'_{hop} \left(\frac{\xi d}{V_d k_B T N(E_F)} \right)^{1/(d+1)} \equiv \xi \left(\frac{T_0}{T} \right)^{1/(d+1)} \quad (2.15)$$

where T_0 is the Mott temperature and given by the following equation

$$T_0 \equiv \frac{C_d}{k_B N(E_F) \xi^d} \quad (2.16)$$

where C_d is a numerical coefficient that depends on the dimension d and differ slightly depending on the assumptions made, the authors, and the

³ $V_d(r) = r^d \pi^{d/2} / \Gamma(d/2 + 1)$, where $\Gamma(x)$ is the gamma function.

parameters of the percolation model used [125]. For example, $C_3 = 21.2$, $C_2 = 13.8$ [126]. All through this manuscript, the generally accepted and more frequently encountered value of $C_3 \approx 16$ will be taken for the 3D-VRH ($d = 3$). From equation 2.13, the conductivity σ can be expressed by $\sigma = \frac{J}{F} = \sigma_0 \exp(-\frac{T_0}{T})^{1/d+1}$, which results in the well-known $T^{-1/4}$ dependence of the resistance in the tri-dimensional case of the Mott VRH:

$$\ln[R(T)] \propto (\frac{T_0}{T})^{1/(d+1)} \equiv (\frac{T_0}{T})^{1/4} \quad \text{for } d = 3, \quad (2.17)$$

In the strongly localized regime, the long-range electron-electron interactions (EEI) open up a soft gap in DOS at the Fermi level, which governs the VRH mechanism as described by Efros and Shklovskii [127]. In this case, the observed resistance follows the relation

$$\ln[R(T)] \propto (\frac{T_{ES}}{T})^{1/2} \quad (2.18)$$

where $T_{ES} = 2.8e^2/\epsilon\xi k_B$ is the characteristic ES temperature.

2.4.2 The High Electrical Field Regime

When the electric field strength is increased such that the energy gained by a carrier during a hop is higher than the energy spacing of the two states $|e\bar{R}_{hop}F| \geq \Delta E_{ij}$, the equation (2.11) shows that carriers hop to the closest hopping range satisfying the condition $\Delta E_{ij} = |e\bar{R}_{hop}F|$. As a result, no temperature dependence of the conductivity is expected and applying the Mott conditions (2.14), the hopping distance can be expressed as

$$\bar{R}_{hop} = \xi (\frac{F_0}{F})^{1/(d+1)} \quad (2.19)$$

Then, from the equation 2.12, in the electric field induced hopping, the current can be written

$$J_F = \exp(-\frac{F_0}{F})^{1/(d+1)} \quad (2.20)$$

where F_0 is a constant called the critical electric field and is linked to ξ and $N(E_F)$, i.e.

$$F_0 = C_F k_B T_0 \xi / e N(E_F) \quad (2.21)$$

where C_F is a numerical constant [128, 129, 130]. The transition to the field-induced-hopping regime occurs for $F > k_B T / 2e\xi$. The parameter $\beta \equiv eF\xi/k_B T$ is useful to determine the regime of hopping. For $\beta \ll 1$,

transport is dominated by thermally-assisted hopping, while for $\beta \gg 1$, electric field-induced hopping mainly contributes to the transport [129].

The next section briefly presents the influence of a magnetic field B on the VRH mechanism.

2.4.3 Magnetoresistance in the VRH Regime

Recently, there was growing interest in magnetoresistance (MR) effects due to its potential interest in a wide range of magnetic applications [131, 132, 133]. Interestingly, large MR effects (up to 10% for low magnetic field $B \approx 10$ mT) were recently observed without ferromagnetic electrodes (no spin coherent charge injection spin valve effect) at RT in nonmagnetic CP [134, 135, 136]. Three models were proposed for the explanation of the OMAR effect but it is still under debate [137, 138, 139].

Here we present the MR effects induced by the presence of a magnetic field B when the VRH is the dominating charge transport mechanism. The MR is defined as $MR \equiv R(B) - R(0)/R(0) \times 100$ (%) and is positive (negative) when the resistance of the sample increases (decreases) with the magnetic field B . In the VRH model, both signs were predicted.

In recent years, the negative MR effects were usually interpreted in terms of the forward interference (FI) model developed by Nguyen, Spivak, and Shklovskii [140, 141]. The FI model takes into account quantum interference effects in the hopping process which increases the localization length, and hence produces a negative magnetoresistance. The negative MR dependence can be linear or quadratic in B and can be written

$$R(B)/R(0) \propto -B^a T^{-b} \quad (2.22)$$

where $a = 1$ or $a = 2$ depending on the model, and $b = 3/(1 + d)$ where d is the dimension of the system [142].

On the other hand, when the VRH is the dominant mechanism, a large positive $MR(B)$ is expected for sufficiently low temperatures and was predicted by the model of the wave-function shrinkage model developed by Shklovskii and Efros [127]. The effect of the magnetic field on the carrier transport in the VRH regime where the charges are strongly localized is to cause the impurity orbitals to shrink, reducing the overlap of the localized state wavefunctions. Consequently, a decrease in the tunneling probability between states occurs which translates in a large positive magnetoresistance. This was observed in many inorganic [143] and organic [92, 142, 144, 145, 146] materials. For the low- B range, the wavefunction shrinkage model predicts a typical quadratic dependence

of the MR which can be written

$$\ln [R(B)/R(0)] = t(B/B_c)^2 (T_0/T)^{1/4} \quad (2.23)$$

where t is a numerical constant ($t \approx 0.1$) and B_c is the critical magnetic field and is given by

$$B_c = 6\hbar/[e\xi^2(T_0/T)^{1/4}] \quad (2.24)$$

In the high- B limit, that is when $B \gg B_c$, a $B^{1/3}$ dependence of the MR is expected

$$\ln [R(B)/R(0)] \propto (e\xi^2/6\hbar)^{1/3} (T_0/T)^{1/3} B^{1/3} \quad \text{for } B \gg B_c \quad (2.25)$$

Finally, the total measured MR could exhibit both contributions, i.e. a negative contribution and a positive contribution as it was found for various materials and CP [144]. While at low temperature, the positive contribution is very large and dominant, when the temperature increases the wavefunction shrinkage model predicts a decreasing MR as it can be seen from the equations 2.23 and 2.25. The MR effect becomes negligible typically for $30 \text{ K} < T$ in our samples.

2.5 Charge Transport in Conducting Polymer Nanowires: Literature Review

In this section, we provide a brief review of recent advances in the study of electronic transport properties of CP NT/NWs. Charge transport in bulk CP was thoroughly studied over the last few decades, as a function of several parameters such as the T , the type of dopant [52, 16], the magnetic field [92] the pressure [52] or the electrical field intensity [96], to give only a few examples. Nonetheless, it still remains a topic of significant controversy because of the strong influence of the synthesis techniques and conditions on the transport properties of these materials [147], especially for the low-dimensional CP structures such as NWs and NTs. The electrical characterization of NWs can be performed in vertical configuration (for template-synthesized NWs) or in planar configuration, with NWs dispersed on a substrate. Both techniques are present in the literature and have also been used in this work. Remarkably, almost all the literature presented here concerns pure CP NWs or NTs and not hybrid metal-CP NWs, as only a few other groups have studied metal-CP HNWs.

2.5.1 Temperature Dependent Electrical Conductivity

The experimental results of transport properties of CP samples have indicated that most of the CP contain both crystalline and noncrystalline regions. Depending on the extent of disorder (see section 2.3.1), three different transport regimes were observed in CP NWs/NTs: metallic, critical, and insulating [147]. Usually, the empirical parameter $R_r \equiv R(1.4\text{ K})/R(300\text{ K})$ is used⁴ to quantify the extent of disorder and for sorting out the various regime [148]. Generally, one assumes that the insulating regime, critical and metallic regimes of the M-I transition correspond⁵ respectively to $R_r > 100$, $10 < R_r < 100$ and $R_r < 10$. To explicitly describe the behavior of $\rho(T)$ one can define a reduced activation energy $W(T) \equiv -d(\ln\rho(T))/d(\ln T)$ [148]. In the insulating regime, $W(T) > 1$ and presents a negative temperature coefficient; in the critical regime, $0.3 < W(T) < 1$ and is nearly temperature independent while in the metallic regime, $W(T) < 0.3$ and has a positive temperature coefficient. The Fig. 2.4.(b) shows the $W(T)$ for PEDOT NWs exhibiting the three regimes depending on diameters [12].

In the insulating regime, the conductivity exhibits an exponential temperature dependence with an exponent $p = 1/(1+d)$ which depends on the dimension d of the system (see equation 2.17). Thus one obtains respectively $p = 0.5$, 0.33 and 0.25 for one-, two-, and three-dimensional Mott-VRH. As shown in Fig. 2.4, the exponent $p = 0.25$ was observed in many samples such as PANi-CSA, PPy-ClO₄ and PEDOT NT/NWs [73, 144, 149, 13], for temperatures between RT and $T_C \approx 60\text{ K}$. All the measurements presented in the Fig. 2.4 are single NW data excepted the panels (d-e) which are measurements of CP NW arrays. Astonishingly $p = 0.33$ was also observed in PEDOT NWs [14] down to $T_C = 1.5\text{ K}$ and $p = 0.5$ was found for 200 nm PPy NWs and 35 nm diameter PEDOT NWs [11, 16]. Remarkably, one can notice that $p = 0.5$ does not correspond only to the 1D-VRH as the same T dependence is associated to the Efros-Shklovskii-VRH.

Several authors also reported on a smooth crossover from the 3D-Mott-VRH to the Efros-Shklovskii-VRH (ES)-VRH, when the temperature decreases below $T_C \approx 60 - 100\text{ K}$ [73, 144, 150, 149]. As shown by the equation 2.18, this change is observed generally at low temperature by a change in the exponent n in the plots of $\ln R(T)$ vs $T^{1/n}$.

⁴The definition of R_r is not absolute and sometimes, other definitions of R_r are used with a smaller temperature difference such as $R_r \equiv R(10\text{ K})/R(300\text{ K})$ [12] or $R_r \equiv R(77\text{ K})/R(300\text{ K})$ [11].

⁵The values delimiting the three regimes of transport are empirical values and could be a little bit different depending on the authors.

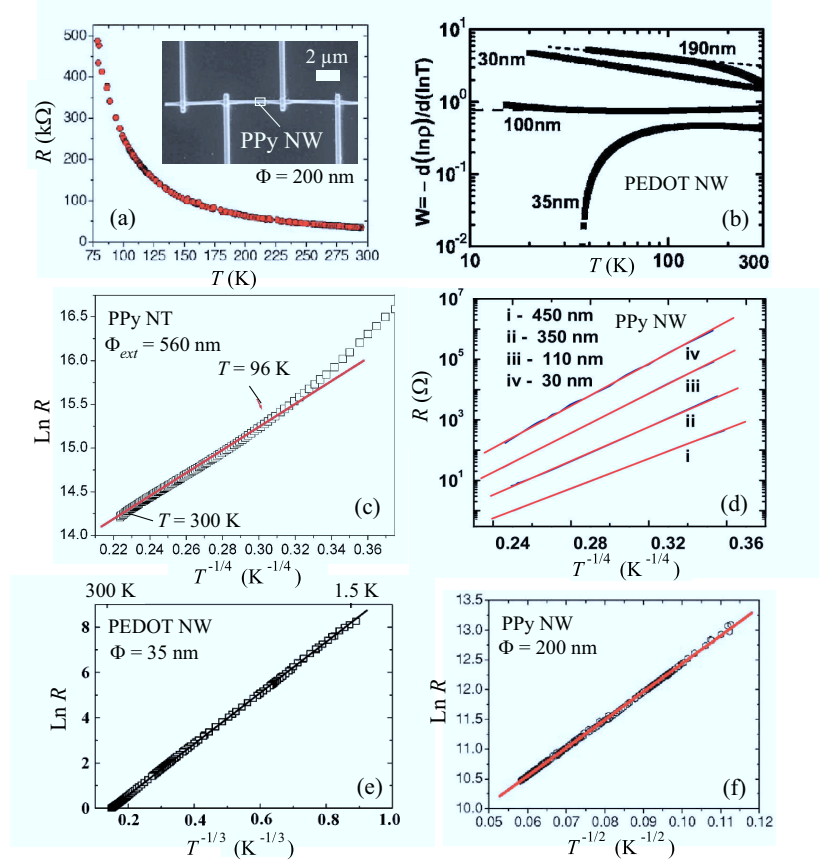


Figure 2.4: (a) Typical T -dependence of the resistance of a template-synthesized single PPy NW measured in a four-probe configuration. The inset gives a SEM micrograph of the NW. Adapted from Ref. [11]. (b) Log-log plot of the reduced activation energy $W(T)$ as observed for PEDOT NWs for various diameters [12]. (c-f) T -dependence of the resistance of PPy [13, 11] and PEDOT [14] NWs plotted as $\ln R \propto T^{-1/1+d}$. The solid lines are linear fits to the VRH model.

Such a crossover from Mott to ES-VRH conduction was also observed in PANi and PPy-PF₆ bulk films at lower crossover temperature $T_C = 2-10$ K [52].

Samples characterized by a higher conductivity, a smaller resistivity ratio $10 < R_r < 100$ and a constant $W(T)$ are in the critical regime of the M-I transition. Their resistivity temperature dependence is described by the following power law

$$\rho(T) = (e^2 p_F / \hbar^2) (k_B T / E_F)^{-1/\eta} \propto T^{-\gamma} \quad (2.26)$$

where p_F is the Fermi momentum and the exponent γ is expected to vary from 0.3 to 1 as the sample goes through the transition from the metallic to the insulating side.

The figure 2.5 gives two examples of CP NW/NT samples in the critical regime of the M-I transition. The panel (a) gives the log-log plot of the temperature dependence of resistance of a PPy NT ($\sigma_{RT}=73$ S/cm) [73]. It is found that its resistance follows a power-law dependence with $\gamma = 0.488$. The panel (b) gives the T -dependence of a 500 nm diameter PEDOT/CIO₄ NW exhibiting a high conductivity at room temperature ($\sigma_{RT}=200$ S/cm) and lying in the metallic side of the M-I transition. $W(T)$ is constant with a positive value of 0.2 [16]. As shown in the Fig. 2.5.(d), metallic behaviour was also observed in 35 nm diameter PEDOT NWs [12]. Above the crossover temperature ($T_C = 32K$), the sample lies in the critical regime and the resistivity follows the equation 2.26 with $\gamma = 0.44$ whereas below T_C , the samples becomes metallic presenting linear ($I - V$) characteristics and having a positive temperature coefficient of resistivity (TCR).

Generally single CP NWs/NT in the insulating side of the M-I transition present low RT conductivities ($\sigma_{RT} < 1$ S/cm) whereas samples in the metallic regime exhibit much higher RT conductivities (100 S/cm $< \sigma_{RT}$) that can reach very high values such as $\sigma_{RT} \approx 500$ S/cm [15]. Nonetheless, it is not systematic relation as Duvail *et al.* recently showed that 20-25 nm diameter PEDOT NWs presenting a relatively high RT conductivities ($\sigma_{RT} \approx 390$ -450 S/cm), could exhibit a very strong temperature dependence ($R_R \approx 10^5$) and an insulating behavior at low temperature [12]. Moreover, dimensions greatly influence the conductivity (σ_{RT}) and the regime of charge transport. As shown in the inset of the panel (a) and the panel (c) of the Fig. 2.5, σ_{RT} increases greatly with decreasing diameter for PPy NTs and PEDOT NWs. Interestingly, it was shown that a transition from an insulating to a metallic regime occurs for PEDOT NWs with diameter decreasing from 190 to 35 nm while a transition from a metallic to an insulating regime takes place for the smaller diameters [12]. Others experiments put into light comparable dimension effects on the electrical properties of CP NWs/NTs [151, 152]. Most probably, the enhancement of the electrical properties with decreasing diameter is due to an improvement of the molecular and supermolecular structures associated with an increase in the conjugation length [14].

2.5.2 Non-Linear ($I - V$) Characteristics

The T -dependent ($I - V$) characteristics of individual NWs/NTs made of CP such as PANi, PPy, PA or PEDOT were explored extensively in

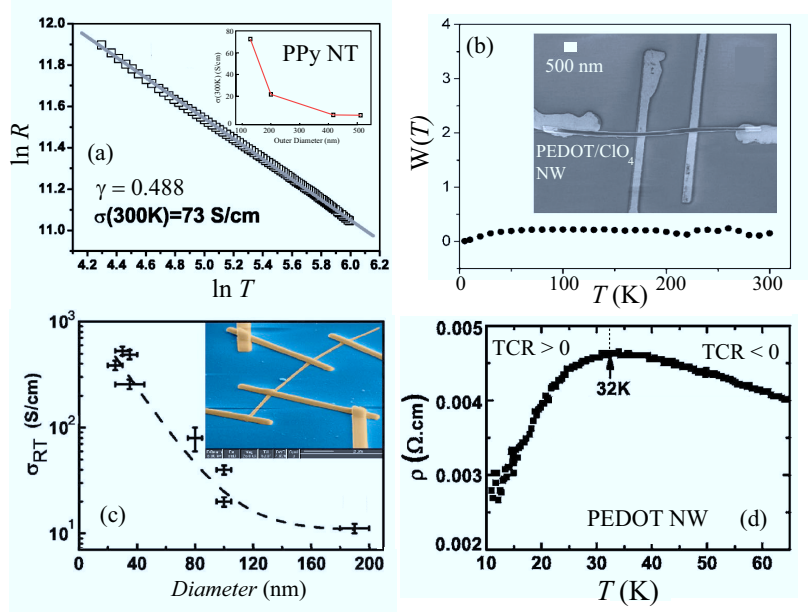


Figure 2.5: (a) Temperature dependence of resistance of a single PPy-PTSA NT plotted as $\ln R$ vs $\ln T$, which indicates that the sample is close to the critical regime of the M-I transition. The inset gives σ_{RT} as a function of the diameter for PPy NT. Adapted from ref. [15]. (b) Reduced activation energy $W(T)$ for a 500 nm diameter PEDOT NW are slightly ($W \approx 0.2$) on the metallic side of the M-I transition. The inset gives a SEM micrograph of a contacted NW. From ref. [16]. (c) Diameter dependence of σ_{RT} for pure PEDOT NWs. (d) Metallic transition shown in the resistivity vs T for 35 nm diameter PEDOT NW. (c-d) Taken from ref. [12].

the past ten years by several authors [153, 117, 83, 73, 149, 116, 17, 120, 154, 147, 119]. A common feature arises from the comparison of all these works as described recently by Long et al. [15]: With decreasing temperature, a transition from linear to non-linear ($I-V$) characteristics is usually observed, and a clear zero bias anomaly (ZBA) (i.e., Coulomb gap-like structure) gradually appears on the differential conductance (dI/dV) curves. A typical example of ($I-V$) characteristics and the corresponding dI/dV for a single PPy NT are given in the Fig. 2.6.(a-b). The panel (d) of the Fig. 2.6 gives the plot of dI/dV vs. the applied voltage V for PPy NWs measured in vertical configuration [18]. Similar non-linear ($I-V$) characteristics and ZBA were observed in many other systems such as CNT and inorganic NWs [155, 156, 121, 157, 73].

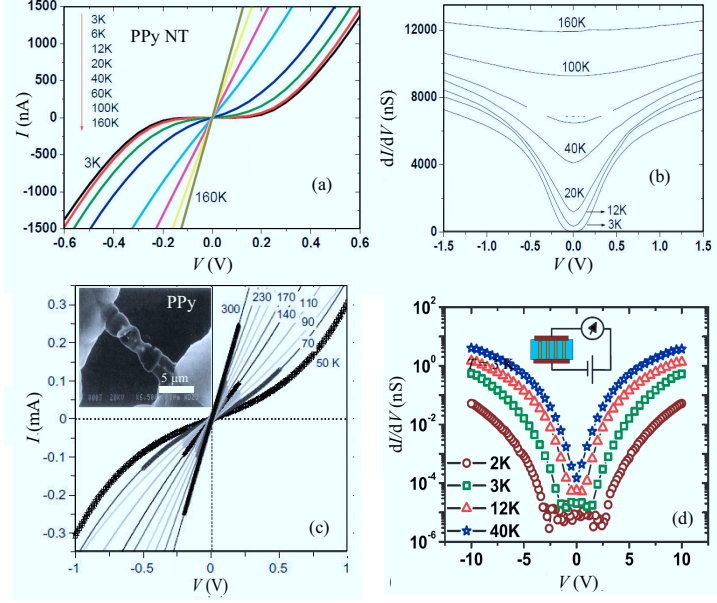


Figure 2.6: (a) ($I - V$) characteristics and (b) corresponding differential conductance (dI/dV) curves for a single PPy NT at low- T . Adapted from Ref. [15]. (c) ($I - V$) characteristics of a single PPy micro-line synthesized using a scanning probe microscope. From ref. [17]. (d) Differential conductance dI/dV plotted as a function of bias voltage V for a 30 nm diameter PPy NW array at various temperatures. Adapted from Ref. [18].

CP NW/NT are often considered as disordered hopping systems in the framework of the MIT (see section 2.5.1). In most cases, the high- T range charge transport is thermally activated and results in ohmic ($I - V$) relation. The T -dependence of the conductivity of CP NW/NT is generally described by the VRH or the fluctuation-induced tunneling FIT (see section 2.3.5) models [19]. Generally, with decreasing temperatures, as the applied electric field increases, the deviation from the Ohmic behavior becomes apparent. At $T \approx 60 - 100$ K a zero-bias anomaly (ZBA) (i.e., the suppression in differential conductance around the zero bias point) is usually observed and ascribed to the depletion of the density of states.

In the low- T regime ($T < 60$ K), several models such as the field activated FIT (see section 2.3.5), the activation-free phonon-emission-assisted model [158], the Zener tunneling [121, 159] have been proposed to explain the observed ($I - V$) characteristics in CP NW systems. Nevertheless, the data obtained for various CP NWs are not uniform and

there is no generally accepted model of the dominant transport mechanism in CP NWs/NTs till now. Recently, it was suggested that the inherent 1D nature of CP might be responsible of these specific low- T transport properties [19, 35].

2.5.3 1-D Charge Transport in CP NWs

In this last section, we focus on recent experimental results indicating that transport in CPs could be dominated in specific conditions (high bias and low- T) by EEI due to their inherent 1D nature.

Most of the CP NWs can be seen as quasi-1D conductors because they are composed of a high number of parallel carbon atom chains for which transport is essentially one-dimensional. The hopping probability is dependent on both electric field and temperature as they energetically help localized electrons to hop across the barrier. Nevertheless, the electric field increases the probability of hopping along the field (chain) direction whereas the thermal energy is direction independent and is in favour of interchain hopping. Thus 1D nature of CP is expected to be enhanced in high electric field and in the low- T regimes [13]. In 3D systems, when EEI are important enough to be taken into account, a crossover occurs between the Mott-VRH and the ES-VRH and can be identified by a change in the exponent of the temperature dependence of the conductivity. On the other hand, the EEI have a dramatic impact on the electrical properties of quasi-1D systems. The presence of EEI could have a significant effect on the charge transport in quasi-1D CP as it can lead to the formation of phases different from the ordinary Fermi liquid even in case of arbitrarily weak interaction [120]. In particular, the short-range repulsion between electrons leads to the formation of a Luttinger liquid (LL) [160] while the long-range Coulomb interaction induces the formation of a Wigner crystal [161, 18].

One manifestation of LL behavior is in tunneling experiments, in which charge carriers are injected from leads into the one-dimensional conductor through tunneling barriers [162]. Tunneling near the Fermi level is strongly suppressed and this results in a characteristic power law dependence of the conductance G on T and on the applied voltage V

$$\begin{cases} G \propto T^\alpha & (eV \ll k_B T) \\ I \propto V^\beta & (eV \gg k_B T) \end{cases} \quad (2.27)$$

Such power-law variations of $G(T)$ and $I(V)$ were attributed to tunneling in a LL in different 1D systems such as SWNT (single-walled

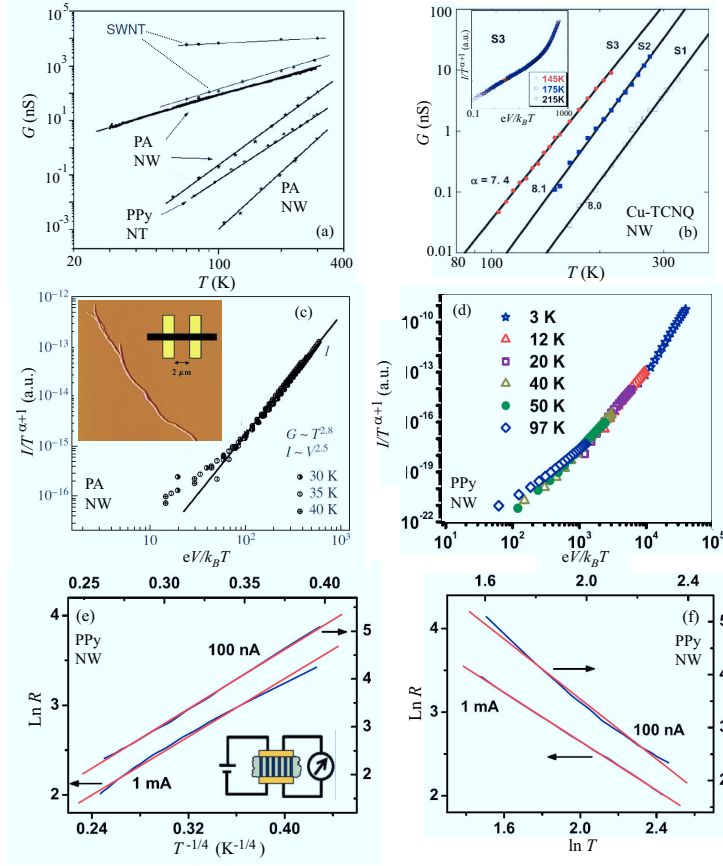


Figure 2.7: Power-law dependences of the conductance $G(T)$ vs. T for (a) different CP NWs/NTs in comparison with $G(T)$ for SWNT (b) $G(T)$ vs. T for Cu-TCNQ organic NWs. (c-d) $I/T^{\alpha+1}$ vs. $eV/k_B T$ for PA NWs and PPy NWs. (e) $\ln R$ versus $T^{-1/4}$ data of 70 nm diameter PPy NW arrays plotted for low and high bias. The inset is a schematic of the measurement setup. The red lines are linear fit to the data. The low bias data give a better fit to 3D VRH behavior. (f) The power-law gives better fit with $\alpha = 1.5$ for high bias data. Adapted from Refs. [19, 20, 13].

nanotube) and MWNT (multi-walled nanotube) [163, 164, 165] molybdenum selenide NWs [166] or organic NWs [167, 20]. $G(T)$ vs. T are given in the Fig. 2.7.(a-b) for various NWs/NTs.

More precisely, the LL theory predicts the following universal equation for the measured current I at different temperatures

$$I = T^{1+\alpha} \sinh(eV/k_B T) |\Gamma(1 + \beta + ieV/\pi k_B T)|^2 \quad (2.28)$$

where Γ is the Gamma function, I_0 is a constant [164, 166]. If the above scaling relation is valid, it should be possible to collapse various curves taken at different temperatures onto a single universal curve like what was performed for SWNT and MWNT. Examples of such scaled ($I - V$) curves are given in the Fig. 2.7.(c) for a PA fiber and (d) PPy NW arrays at low temperatures. By plotting $I/T^{\alpha+1}$ vs. $eV/k_B T$, the curves collapse into a single curve where α is the power-law exponent estimated from the $G(T) \propto T^\alpha$ curve for the same sample.

Strikingly, the LL model was applied to CP thin-film FET [35] and several classes of CP NWs and NTs in planar [120, 20] and in vertical configurations [168]. Moreover, Rahman *et al.* described recently, a bias-dependent crossover from VRH to power-law characteristics in PPy NW arrays [13].

The Fig. 2.7.(a) gives the plot of $\ln R$ versus $T^{-1/4}$ data of 70 nm diameter PPy NW arrays measured at low applied bias (100 nA) and at high bias (1 mA) [13]. The red lines are linear fit to the data. Clearly, the low bias data fit to 3D VRH behavior over a wide range of temperature. The same data are plotted on a log-log scale to show that a power law gives a better fit (with $\alpha = 1.5$) for high bias data and in the low- T range. To check the validity of the LL model, the dependence of $I/T^{\alpha+1}$ versus $eV/k_B T$ were plotted. As shown in the panel (d) of the Fig. 2.7 for 30 nm diameter PPy NW array, the curves collapse (for $T < 100$ K) onto a single universal curve suggesting that the data are consistent with the LL model.

Chapter 3

Characterization of Hybrid Nanowire Arrays

Celui qui déplace la montagne, c'est celui qui commence à enlever les petites pierres.

Confucius

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3.1 Overview

We saw in chapter 1 that among the different strategies for synthesizing conjugated polymer (CP) nanowire (NW)-like structure, the template method is an efficient technique for producing well rod-shaped NWs. One interesting aspect of this method is that it permits the growth of multi-segmented or multi-layered NWs simply by sequential deposition of each layer [169, 64, 170]. Interestingly, this method can be applied to produce hybrid nanowires (HNW) where CP segments are combined with metallic segments [83, 84, 171, 172, 145, 16]. These HNWs permit the study of the electrical properties of CP NW as metallic nanoprobe are directly synthesized on every side of the CP NW. Also, this gives the opportunity to study the electrical charge transport through metal/CP interfaces at the nanoscale. Remarkably, HNWs could benefit from the functionalities associated to each of its segment. For instance, the magnetic assembly of Au-PPy-Ni-Au HNW onto ferromagnetic electrodes was recently demonstrated by using the magnetic field imposed by the ferromagnetic electrodes to align the Ni segments and thus the entire HNWs, parallel to the electrodes (see Fig. 3.1) [21]. The high conductivity of the gold segments provided a good electrical contact while the PPy segment was used as a sensing element in a gas (NH_3) sensor and photodetector devices. This example demonstrated that HNWs offer an appropriate way to characterize the electronic properties of conjugated polymer NWs and are also promising functional materials for achieving CPNW-based applications.

In this chapter are presented most of the results of the publications [145, 173, 174] which deal with the structural and electrical properties of metal(Au,Pt)-CP(PPy) HNW arrays. Unpublished and more recent data set of electrical characterization of several classes of HNW arrays have been added and will be discussed. For conciseness of the manuscript and as a thesis is not just a collection of ($I - V$) curves, a large number of data will not be shown. The first section of the chapter briefly presents the HNW arrays, describing the electrochemical synthesis, the morphology and the microstructure of various HNW classes, paying special attention to the metal-polymer interfaces. The third section reviews the electrical measurements performed on HNW arrays, including current-voltage characteristics and magnetotransport at low temperatures.

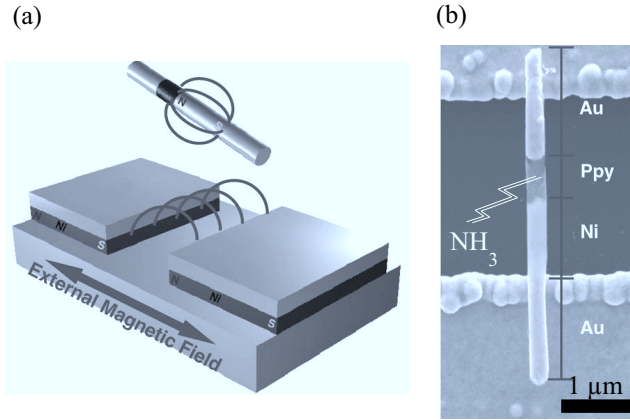


Figure 3.1: Example single NW application benefiting from the advantages of HNWs. (a) The assembly of HNWs is facilitated by aligning the Ni segment onto the electrodes. (b) SEM picture of an aligned HNWI. Adapted from ref.[21].

3.2 Hybrid Nanowire Arrays

Here, we present the metal-CP HNWI arrays that were studied and characterized in this work. All the metal-CP HNWI arrays were developed and synthesized by Dr. Vincent Callegari under the supervision of Pr. Sophie Demoustier (IMCN/BSMA).

Firstly, we present the electrochemical process for synthesizing such HNWI arrays without going into the details of the complex and interesting electrochemical synthesis. The scope of this section will be more to present the relevant parameters and synthesis conditions of the various characterized samples. For more details about the synthesis of HNWI arrays, the reader is referred to the following reference [49]. For the ease of the discussion, the synthesis process of a tri-segmented Metal-CP-Metal NW will be taken as an example all through this section. More complex HNWs were synthesized and characterized (see Fig. 3.3), but as their preparation mainly mainly from the number of steps, their synthesis will not be detailed here.

3.2.1 Synthesis of Tri-segmented NWs

A schematic view of a such tri-segmented Metal(Au)-CP(PPy)-Metal(Au) HNWI synthesized by an all-electrochemical method is given in the Fig. 3.2.(a). The synthesis is performed by three sequential electrodepositions performed within a PC template (see Fig. 1.8). The first step

consists in the electrodeposition of the first metal segment. In the case of a first Au segment, a cyanide free solution containing 0.1 M KCl, 0.1 M K_2HPO_4 and 0.03 M $HAuCl_4 \cdot 3H_2O$ (Acros) in deionized (DI) water could be used [172]. The electrodeposition is achieved by the cyclic voltammetry method (CV) which consists in cycling the potential from 0.7 to 0 V at a typical scan rate of 400 mV.s⁻¹. Figure 3.2.(b) gives a cyclic voltammogram recorded during the deposition of a first gold segment within a 100 nm pore diameter PC template. The typical growth rate is about 5 nm.s⁻¹. It is important to notice that the gold electrodeposition rate is highly dependent on the pore diameter and keeping the other synthesis parameters constant, logically, the growth rate decreases with increasing the pore diameter. Then the second segment, the CP

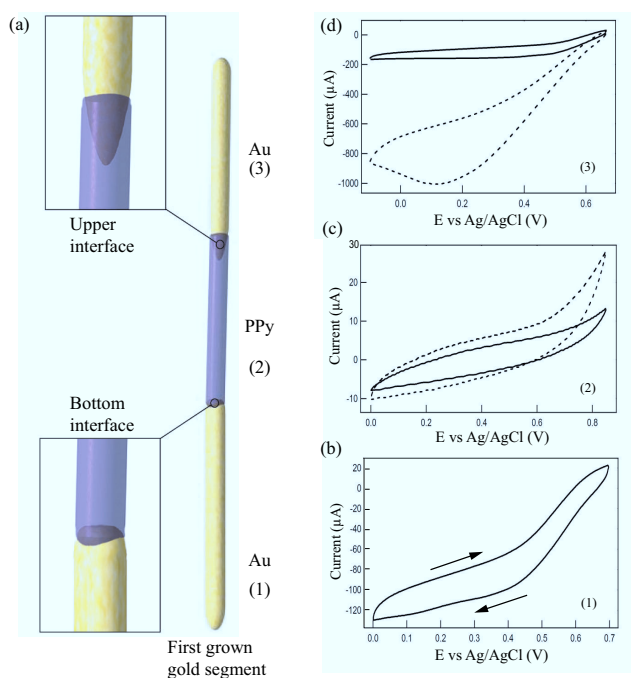


Figure 3.2: Electrochemical process consisting in the sequential deposition of metallic and conjugated polymer segments within the pores of polycarbonate membranes. (a) Schematic view of a tri-segmented Au-PPy-Au NW. The insets are magnified views of both polymer-metal interfaces. (b-d) Typical cyclic voltammograms obtained for the synthesis of each NW segment. (c) The 1st cycle (full curve) and 200th cycle (dashed curve) are given for the PPy segment. (d) Cyclic voltammograms acquired during the deposition of the upper gold segment before (full curve) and after overflowing (dashed curve).

block can be deposited into the pores by the electropolymerization of the corresponding monomer. For instance, the synthesis of PPy onto noble metal segments (Au, Pt) is realized via CV by sweeping the potential from 0 to 0.85 V at a typical scan rate of 400 mV.s^{-1} for 100 nm diameter HNWs.

The electrolyte is an aqueous solution containing 0.1 M LiClO_4 and the monomer (5 to 100 mM range). In some cases, 7×10^{-4} M sodium dodecyl sulfate were added and used as surfactant. Figure 3.2.(c) gives the cyclic voltammograms corresponding to the deposition of the PPy segment at the first (full curve) and 200th cycle (dashed curve). PEDOT segment were synthesized by the electropolymerization of EDOT monomer from an aqueous solution containing 0.1 M LiClO_4 and 14 mM EDOT, by sweeping (CV) the potential between 0.2 V and 1.1 V at a scan rate of 400 mV.s^{-1} [49]. In both PEDOT and PPy electrodeposition, the synthesis conditions were optimized for obtaining homogeneous polymer segments with strong mechanical interfaces with metals [70].

Finally, the upper metallic segment was electrodeposited under similar conditions to those used for the first metal segment. As shown in the Fig. 3.2.(d), a drastic change of the CV curve shape, accompanied by a strong increase of the current, indicates that deposition overflows the nanopores. This allows to detect easily the end of the synthesis. After the synthesis of each NW segment, the sample was rinsed in DI water for at least 30 minutes in order to remove the remaining plating solution left inside the pores of the membrane. As it has been said, earlier, more complex HNWs can be synthesized following the same fabrication route. Most of the HNWs that were characterized in this work are listed in the figure 3.3.

Because the low potential range used for the synthesis of the upper metallic segment, a possible de-doping (reduction) of the CP segment is expected to occur during the growth of the upper metallic segment. It is worthy of note that an important dedoping of the CP segment should be reflected in the electrical properties of the HNWs containing a metal-onto-polymer interface. Indeed, an important reduction of the CP segment results in a decrease of its work function which translates into asymmetric ($I - V$) curves due to well-known Schottky effects. Nevertheless, as it will be shown in the following sections, as-synthesized HNWs always present Ohmic behaviour.

3.2.2 Structural Properties of HNWs

The characterization of the morphology and the microstructure of HNWs is decisive for understanding their intrinsic electrical and mechanical

	Structures	Φ [nm]
	{ M-CP-M M-Thiol-CP-M M-CP-M M-CP-M' Ni-CP-M	{ 30, 40, 50, 70, 90, 110, 160 70, 90, 110 70, 90 90, 110
	M-CP-M'-CP-M	70, 90
	M-CP-M-CP-M	70, 90
	M-CP-CP'-M	70, 90
	M-CP-CP'-M'	100

Figure 3.3: Schematic view of the different structures of HNWs that were characterized in a single NW and/or NW array configuration.

properties. While optical and SE microscopes were used mainly for locating HNWs on a substrate, TEM microscopy is generally preferred for the description and characterization of their structural properties as it offers very high resolution and combines imagery capabilities with useful tools such as electron diffraction or elemental analysis based on EDX or EEL spectroscopies. The TEM observation of HNWs requires to free them by dissolving the PC template. This step is quite critical as the dissolution is quite violent and may weaken the HNW interfaces. A procedure was developed for the release of HNWs and their deposition on a substrate. It will be presented in the chapter 4, dealing with single NWs characterization. When tri-segmented HNWs are dispersed on a substrate and observed by optical or SE microscopes, it is readily noticeable that a large proportion (around 50 %) of HNWs was broken. Almost all breaks occur at one of the metal-polymer interfaces. This led us to investigate the strength and the morphology of both PPy-metal interfaces in our devices. When observing HNWs by TEM, the polymer block appears more transparent than the metallic segments, due to its

lower electronic density, thus, giving high contrast snapshots. Consequently the metal and CP segments are unambiguously distinguishable without any particular contrasting treatment which allows to observe precisely the M-CP interfaces. The Fig. 3.4 gives typical TEM pictures collected for various structures of HNWs represented in the Fig. 3.3. Several informations follow from the TEM analysis:

- Each interface of the M-CP-M structure presents a distinctive shape
- the electrochemical synthesis allows to produce HNWs with very short PPy segments as small as 20 nm
- The PEDOT segments present a distinctive curved shape compared to PPy segments
- The PPy/PEDOT heterojunction can be localized by the diameter decrease

The bottom interface is relatively flat, indicating that the first metal section growth is homogeneous under the given synthesis conditions. On the other hand, for the upper interface, a conical metal meniscus soars into the CP section, ensuring a strong mechanical link between the polymer and the upper metal section. This results in a larger adhesion surface compared to that of the bottom interface, explaining why the metal-onto-polymer interface is mechanically more robust than the polymer-onto-metal interface. The presence of this meniscus could be explained by pore wall effects¹, similar to those leading to the formation of PPy nanotubes [172, 175]. The natural tendency of CP to grow along the pore walls was thwarted by properly adjusting pyrrole electropolymerization rate [145]. The creation of the meniscus seems to occur as soon as the electropolymerization is initiated and it was observed in all investigated samples displaying various CP segment length. The gold meniscus length L_m was measured by TEM for several upper interfaces of 70 and 90 nm diameter tri-segmented HNWs (Au-PPy-Au) with different CP junction lengths. The results are reported in Table 3.1. The corresponding adhesion surfaces are also given in Table 3.1. For both NW sizes, L_m and the adhesion surface increase with the length of PPy junction. Nevertheless, L_m and the adhesion surface are smaller for all the 70 nm diameter NWs compared to the 90 nm diameter NWs.

¹The pore wall effects consist in the electrostatic interactions between the growing polycation chains and the anionic sites along the membrane pore walls (see Fig. 1.8.

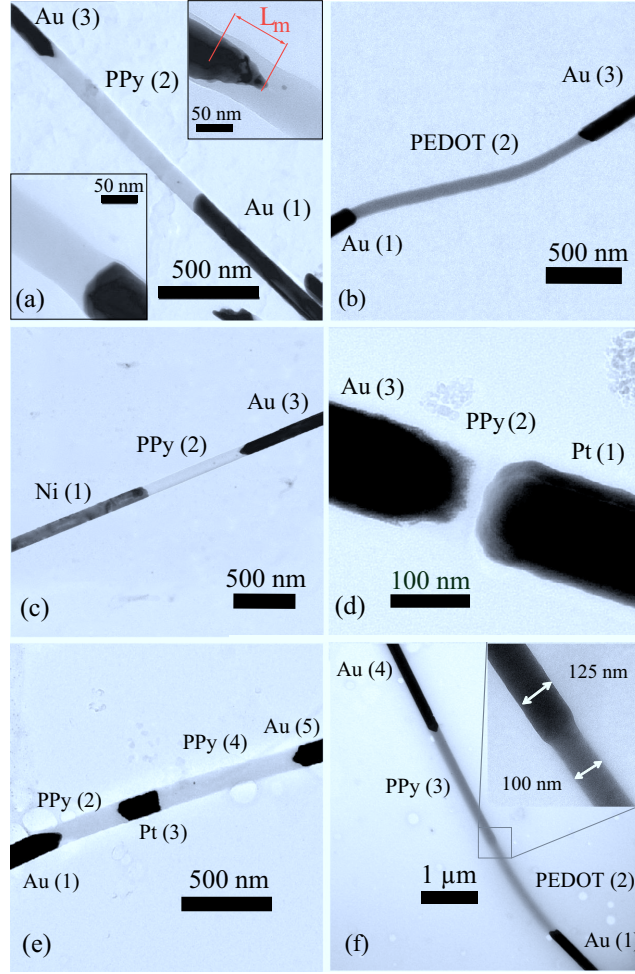


Figure 3.4: TEM characterization of various HNWs presenting various structures. The numbers indicate the synthesis order. (a,b) Typical M-P-M HNWs (a) Au-PPy-Au HNW with its bottom (first grown) and upper (second grown) interfaces. The size of the gold meniscus L_m is indicated. (b) Au-PEDOT-Au HNW. The PEDOT is clearly identified by its typical curvature. (c-d) M-P-M' structures (c) with a magnetic segment (Ni) and displaying very short PPy in-wire junctions (d). (e-f) TEM pictures of a multisegmented HNWs.

The adhesion surface roughly correlates with the percentage of unbroken NWs dispersed onto devices and it is thus an important parameter in assessing the mechanical robustness of the NWs.

ϕ (nm)	70			90		
PPy length (nm)	670	1680	3110	915	1440	3340
L_m (nm)	66	75	88	85	180	225
Ad. surface (nm ²)	9680	11000	12900	16400	33740	42600

Table 3.1: Length of the PPy segment for various tri-segmented Au-PPy-Au HNWs with the corresponding gold meniscus length (L_m) and the calculated adhesion surface of the upper interface.

3.2.3 Interface Modification

Several strategies were considered to improve the mechanical strength of the interfaces of HNWs. Here, we discuss possible improvements taking, again, the case of the simplest HNW structure as an example (structure Au-PPy-Au shown in the figure 3.2). First, it is possible to optimize the electrochemical parameters for the growth of the Au-onto-PPy interface by systematically investigating the effects of the potential sweep rate and the monomer concentration on its mechanical strength [145]. Concerning the bottom PPy-onto-Au interface, as its morphology cannot be modified just by playing on electrodeposition parameters, its mechanical strength could be enhanced by increasing the adhesion between the two different materials. Among the different possible strategies, we first investigated the use of self-assembled alkylthiol monolayers (SAMs) onto gold [176]. We used 11-mercaptoundecanoic and 3-mercaptopropionic acids. The SAM was inserted between the gold and the PPy segment to create an electrostatic bond between the negatively charged carboxylate groups of the chemisorbed monolayer and the positively charged growing polycation as shown in the Fig. 3.5.(a). The SAM was deposited by immersion of the template containing a first grown metal segment, in a solution containing the alkylthiol. Above the 11-mercaptoundecanoic acid SAM no CP growth was observed. This is probably due to the presence of long aliphatic chains that passivated the Au surface. The CP growth occurred on top of the thinner chemisorbed SAM (3-mercaptopropionic acid) for producing tri-segmented HNW arrays (Au-(SAM)-PPy-Au). Such arrays were characterized by T -dependent electrical measurements. While the electrical measurements (shown in the Fig. 3.10) exhibited clear evidence of the presence of the SAM, no qualitative improvement of the mechanical strength was confirmed upon this chemical modification of the interface. Even if the amount of broken HNWs has not been reduced by the assembly of SAM, this chemical modification of the first grown interface is essential for the synthesis of HNWs containing a transition

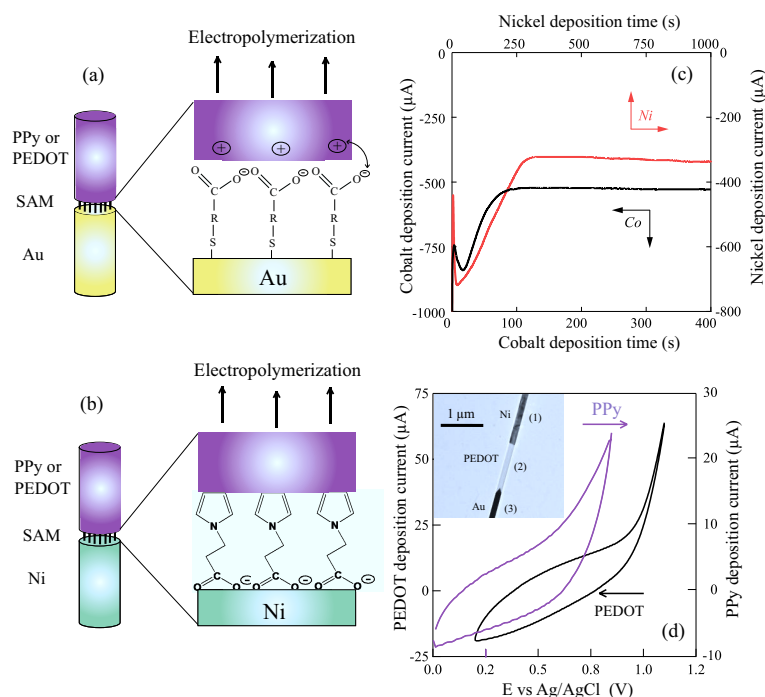


Figure 3.5: Schematic views of the modified metallic (Au, Ni) interfaces using SAMs. In the case of Ni (b), the presence of the SAM improves the electropolymerization process. (c) Typical chronoamperograms for the electrodeposition of Co (Ni) NW segments. (d) Cyclic voltammograms recorded during the deposition of PPy (PEDOT) segment on top of the first grown Ni segment modified by a SAM. The inset displays a typical 110 nm diameter Ni-PEDOT-Au NW as seen by TEM.

metal segment as it is explained in the following section.

3.2.4 Transition Metals

The synthesis of a first grown segment made of transition metals such as nickel (Ni) or cobalt (Co), can be carried out by changing the electrochemical bath and synthesis conditions. For instance, the electrodeposition is performed by chronoamperometry at -1.05 V from an electrochemical bath containing Ni sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) and boric acid (H_3BO_3) in the case of a first Ni segment. The length of the transition metal segments are easily controlled by the electrodeposition time. Typical growth rates for Ni and Co, within a 110 nm pore diameter PC template are about 0.5 and $0.7 \mu m \cdot min^{-1}$, respectively. A

difficulty arises during the synthesis of tri-segmented HNWs containing a transition metals segment. Indeed, the electropolymerization of the CP segment on top of a Ni or Co segment is not straightforward to achieve as the oxidation potentials of these metals are much lower than the one of conjugated monomers [49]. Consequently, the dissolution of the transition metal occurs before electropolymerization begins. Toward preparing hybrid transition metal-CP NWs, it is therefore necessary to find synthesis conditions that will strongly passivate the metal without impeding electropolymerization. The chosen approach consisted in the use of a SAM. The 3-(Pyrrol-1-yl) propanoic acid was chosen due to its facile synthesis and because it contains two end-functional groups, a carboxylate group at one extremity and a pyrrole group at the other end, that can specifically interact with the Ni substrate and the growing CP, respectively (see Fig. 3.5.(b)). Prior to the electrodeposition of the CP, the SAM was deposited by immersion of the PC template containing the Ni segment in a 3-(Pyrrol-1-yl) propanoic acid solution for more than 18 hours. The CP segment (PPy or PEDOT) could be then synthesized by CV using standard electrodeposition parameters. The electrical properties of thiol-modified HNW (Au-Thiol-PPy-Au) will be presented and discussed in the section 3.3.2.

3.3 Electrical Transport Measurements

In this section, we present the electrical characterization of different classes of HNWs. The electrical characterization was performed in vertical configuration, that is, with multiple NWs contained within the template. Measurements of single NWs freed from the template and dispersed on a substrate, were also performed for comparison but will be presented in the chapters 4 and 5 dealing with single nanowire integration. Let's first briefly present the vertical contacting techniques.

3.3.1 Vertical Contacting Techniques

The simplest way to perform electrical measurements of CP NWs consists in pressing into pellets (film) a bulk quantity of CP NWs. This technique was widely used for characterizing CPNWs produced by either template or template-free methods [177, 178, 43, 179, 144] and allowed to demonstrate for the first time dimensionality effects on the properties of CP NWs with a bulk characterization technique. More specifically, template synthesized NWs can be characterized electrically by another bulk characterization technique, which consist to let the NWs embedded

in the template and to perform the measurements with electrodes deposited on each side of the template. This vertical configuration is quite convenient and was frequently employed those last years for the electrical and thermal characterization of NWs [180, 181, 182, 183, 173, 66] as it is very fast and requires no complex processing of the sample to be measured. Figure 3.6.(a) gives an optical micrograph of a PC template mounted on a sample holder and electrically contacted to the sample holder's pins using silver paint and 25 μm diameter gold wires ² immediately after the electrochemical synthesis. The NWs enclosed within the template are mechanically supported by the PC membrane and are protected from the effect of both oxygen and ambient humidity [184].

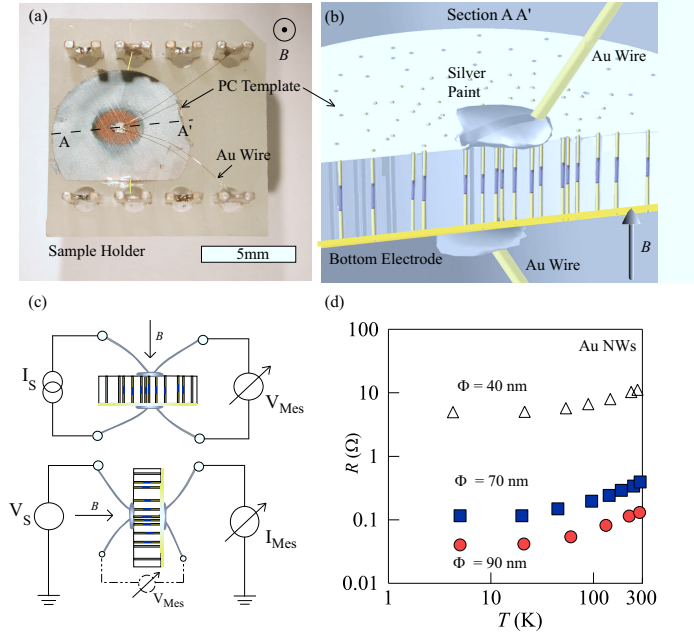


Figure 3.6: HNW arrays electrical characterization setup. (a) Optical micrograph of multiple NWs contacted in vertical configuration within the PC template. (b) Schematic view (for tri-segmented NWs) of the section AA' defined in the panel (a). (c) Electrical measurement configuration: constant-current method and constant-voltage method (d) Temperature dependence of the resistance $R(T)$ of Au NW arrays for various diameters.

²The sample holders are glass epoxy component mounting boards purchased from Wearnes Cambion Ltd, Castleton, Hope Valley, Derbyshire, S33 8 WE, England. The Ag paint and the gold wires were purchased from LABORIMPEX S.A., B-1190 Brussels.

A huge number of experiments can be used for the characterization of the electrical properties of organic materials [185]. The most important techniques are the $(I - V)$ spectroscopy, the $(C - V)$ measurement, the magnetoresistance measurement, the thermally stimulated current (TSC), the time of flight (ToF) [186], the deep-level transient spectroscopy (DLTS) [187, 188, 189]. While, most of the previous techniques have been successfully applied for characterizing bulk structure CP, only a few of these techniques can be directly applied to characterize nanoscale samples such as HNWs. In this work, mainly current-voltage $(I - V)$ spectroscopy as a function of the temperature T and the applied voltage V and magnetoresistance measurements have been used for the characterization. The low- T electrical measurements were performed using a *HP-Agilent 3245A* Universal Source and a *Keithley 6517* electrometer. The pseudo-four-probe configuration were carried out using also a *Keithley 2182* nanovoltmeter. The magnetotransport measurements were performed in an *Oxford Instrument Kelvinox 300* dilution refrigerator with a base temperature of $T_{MC} \approx 30 \text{ mK}$ and equipped with a superconducting coil generating a magnetic field up to 17 T. The data acquisition was performed using the Nanofreeze acquisition program developed with *Igor Pro* software by Dr. Cédric Gustin [190]. In the following sections are presented measurements performed on different type of samples presenting different structures (M-CP-M, M-CP-CP'-M, Ni-CP-M, ...) and geometries (segment lengths, diameter, pore density, ...) . Nevertheless, not all the data will be shown and we will present only most relevant samples. A list of the *good* HNW arrays with their characteristics can be found in the appendix A.

3.3.2 Current-Voltage Characteristics

The current-voltage $(I - V)$ spectroscopy is a powerful technique to gain insight into various transport phenomena such as tunneling and rectification. The obtained $(I - V)$ characteristics were performed as a function of the temperature varying from Room T ($T = 290 \text{ K}$) down to very low temperature ($T = 0,05 \text{ K}$). Both constant-current and constant-voltage methods can be used in a pseudo four-probe configuration for the electrical characterization of samples as shown in the Fig. 3.6.(c). While the four-probe technique was used for low resistivity samples³, the two-probe configuration was used for highly resistive samples. Furthermore, the constant-voltage method was used for samples exhibiting a resistance dependence on the applied voltage, which occurs at sufficient

³Such as the Au NWs shown in the panel (d) of the figure 3.6.

low temperature for most of the samples. The accuracy of the measurements was checked by measuring standard resistances of various values up to tens of $\text{G}\Omega$ and empty templates which present resistance higher than $10^{12} \Omega$.

Typical current-voltage ($I-V$) characteristics are given in Fig. 3.7 for different specimens⁴. The left column in the Fig. 3.7 regroups the Ohmic regime ($T > T_{NL}$) while non-Ohmic ($I-V$) curves are listed in the right column. In all samples, the ($I-V$) plots are symmetrical and are Ohmic above a certain temperature T_{NL} . Below T_{NL} , the ($I-V$) characteristics deviate from the linearity increasingly when the temperature is lowered. Approximatively, $T_{NL} \approx 100 \text{ K}$ for all the samples. At liquid ^4He temperature, the ($I-V$) curves of samples with diameter $\Phi \geq 50 \text{ nm}$, are always highly non-linear, presenting a typical sinh-shape with a zero-current plateau around the zero-bias point. Astonishingly, for smaller diameter samples ($\Phi < 50 \text{ nm}$), the Ohmic regime extends to lower temperature with only slightly non-linear ($I-V$) curves at liquid ^4He temperature as exemplified in the Fig. 3.15. This suggests that a change in the mechanism of charge transport may occur at small diameters. The influence of the diameter on the transport properties of HNW arrays and will be discussed in details in the section 3.4.

From the ($I-V$) characteristics, resistance values $R(T)$ are obtained from the $(dI/dV)^{-1}$ values at zero bias are shown in the Fig. 3.9 for various samples. Despite the non-linearity, for most of the samples, $R(T)$ can still be measured for $T_{NL} < T$ around the zero-bias point until the zero-current plateau appears. To check the consistency of the measurements, the obtained values were compared to resistance values calculated from the current-temperature ($I-T$) dependence recorded at fixed bias, with a typical cooling (heating rate) $|\Delta T| < 0.5 \text{ K/min}$. An example of a such dependence ($R-T$), taken with an applied bias of 10 mV is given in the Fig. 3.9.(d) for sample $M50-B$. Generally, there is a very good agreement between the two measurements for $T \gtrsim 50 \text{ K}$ as for lower temperature, a zero-current plateau develops in the ($I-V$) characteristics, precluding the determination of samples' resistance from the $(dI/dV)^{-1}$ values at zero bias. As shown in the Fig. 3.9, the resistance monotonically increases with decreasing T , indicating that the CP segments (PPy, PEDOT) has a non-metallic behavior.

At high temperature, the Ohmic regime of transport in CP is usually attributed to thermally excited carriers. This mechanism yields an exponential dependency on the temperature and is characterized by an activation energy E_a (see equation 2.6).

⁴The samples are listed with their characteristics in the table A.1 of the appendix.

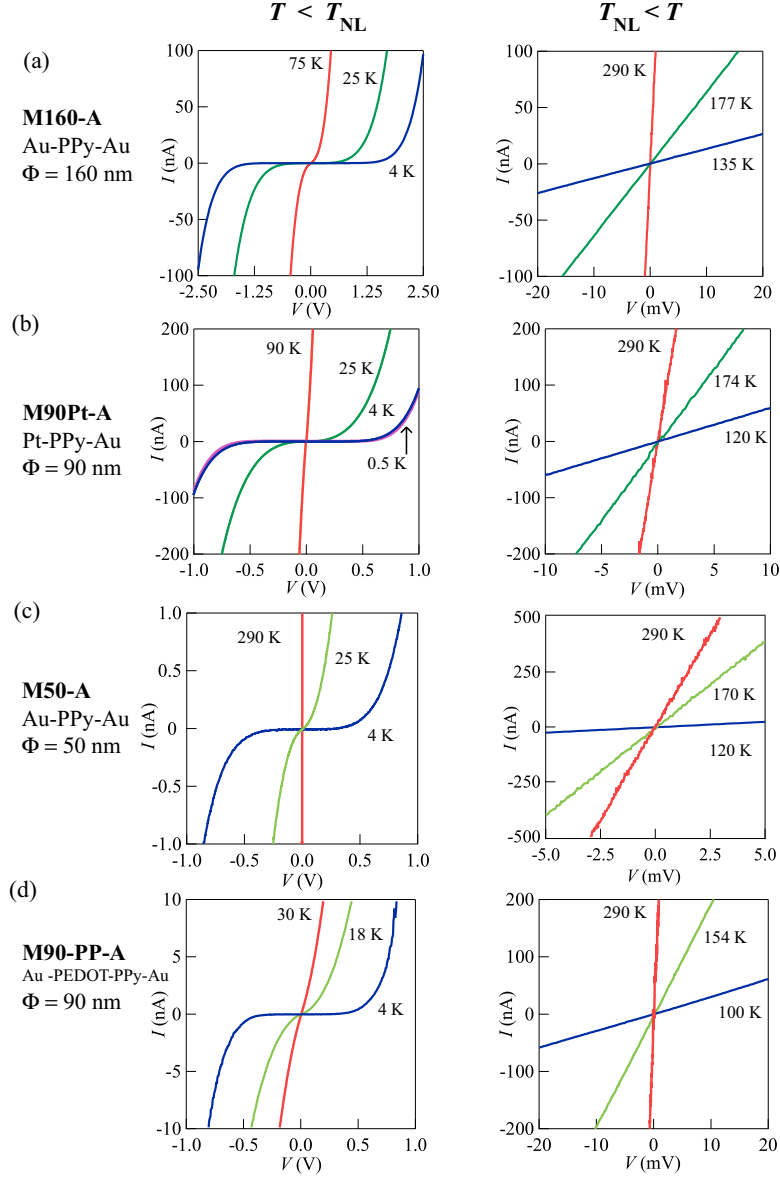


Figure 3.7: $(I - V)$ characteristics of various multisegmented samples with diameter ranging from 50 to 160 nm. Data in the Ohmic regime are given in the right column whereas the nonlinear characteristics appearing at low temperature are given in the left column.

Activation energies E_a can be deduced from the slope of a linear fit of $\ln(R)(T)$ vs. T^{-1} . From the data given in the Fig. 3.8, E_a values ranging

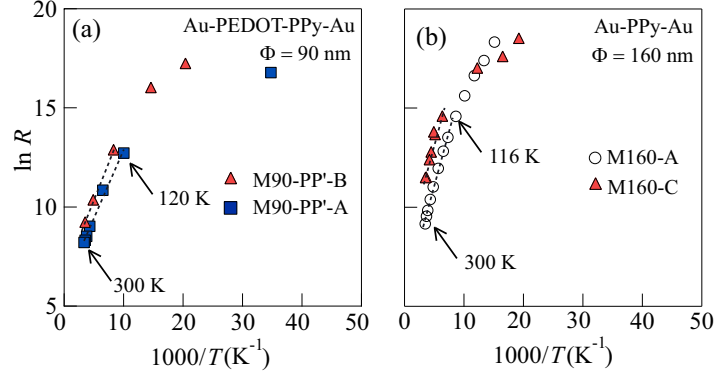


Figure 3.8: Typical Arrhenius plot obtained for tetra-segmented (a) and tri-segmented (b) HNW arrays. Plots of $\ln[R(T)]$ vs. T^{-1} . for $T_{NL} < T$, the slope of a linear fit (dashed lines) is proportional to the activation Energy (E_a).

from 50 to 100 meV were obtained for $T_{NL} < T$. The values are reported in the table A.2 for all the samples. These values compare well with the values previously reported for tri-segmented HNWs (Au-PPy-Au) [83]. On the other hand, the value ($E_a = 270$ meV) reported recently by Banger *et al.* [21] for tetra-segmented HNWs (Au-PPy-Ni-Au) is significantly higher than in our samples tetra- and penta-segmented HNWs, probably because of a consequent barrier at the Ni/PPy junction.

However, the activated transport fit only the high temperature data ($T > T_{NL}$) and cannot explain our low- T data as well as the non-linear characteristics appearing at higher excitation voltage and lower temperature as the curves presented in the left column of Fig. 3.7.

Non-linear ($I - V$) characteristics can be encountered when charge transport is dominated by carrier injection mechanisms through the interfaces [103]. The injection of carriers from a metal to a disordered hopping system is generally described by the T -dependent Schottky emission (or thermionic emission) mechanism described in section 2.2. Schottky plots consisting of $\ln[I/T^2]$ versus $1/T$ at various fixed V 's and $\ln I$ versus $V^{1/2}$ at different temperatures can be used to check if the conduction is electrode limited. For all HNW samples, when a Schottky barrier height (SBH) can be extracted from a linear fit to Schottky plots, it is always negligible compared to the energy brought by the electric field. An example is given in the Fig. 3.10.(e), where a SBH of $\Phi_B = 36$ meV was extracted for sample M50-A. Furthermore, for all the samples, $\ln I$ does not follow a linear relationship with $V^{1/2}$. These results are not surprising since it is expected that PPy forms Ohmic contacts with met-

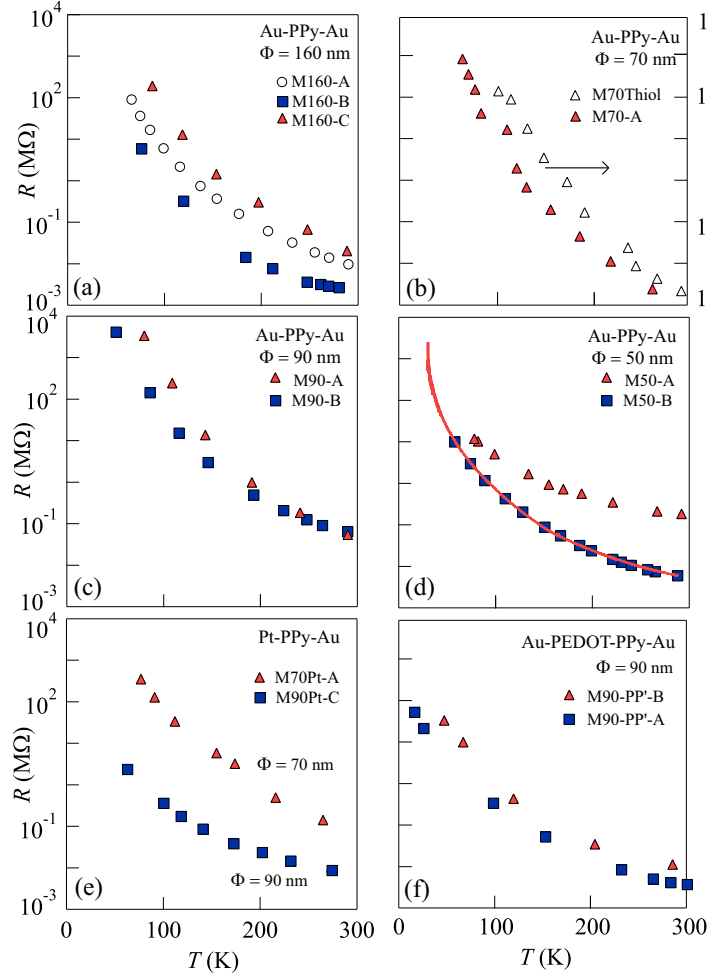


Figure 3.9: Temperature dependence of the resistance values $R(T)$ obtained from the $(dI/dV)^{-1}$ values at zero bias for different HNW arrays with diameter ranging from 50 to 160 nm. (d) The red curve represents $R(T)$ as obtained from the current-temperature ($I - T$) dependence recorded at fixed bias, with a typical cooling (heating rate) $|\Delta T| < 0.5$ K/min.

als with a high work function like Au and Pt [104]. Furthermore, for all HNWs, tri, tetra or penta-segmented, Ohmic ($I - V$) characteristics are observed at room temperature.

To assess the influence of the interfaces on the charge transport, we modified the carrier injection at the metal-polymer interfaces by assembling thiol monolayers on the metal electrodes as shown in the fig-

ure 3.5.(a). In the presence of thiol monolayers adsorbed onto the metallic segments, we expected the HNW arrays to have a different transport signature. This interface modification is quite important regarding the synthesis of HNWs containing transition metals such as Co or Ni (see section 3.2.1). As explained in the section 3.2.3, we have assembled a monolayer of $SH - (CH)_2 - COOH$ onto the first grown Au segments, of two samples (see appendix A).

The measured ($I - V$) characteristics for sample M70-Thiol are given for various T in the Fig. 3.10.(a-b). They are similar to those measured for tri-segmented NWs with a typical transition from the Ohmic regime to the non-linear regime but occurring at a slightly higher $T_{NL} \approx 150 K$. This variation of T_{NL} is accompanied by an important shift of the zero-bias resistance by ≈ 3 orders of magnitude. This resistance represents the sum of PPy NW resistance and that of the molecular junction at the bottom interface. The dominant transport mechanism in molecular junctions is the coherent non-resonant tunneling [191]. Applying the same analysis to the thiol modified sample M70-thiol, a SBH of $\Phi_B = 0.12 eV$ is extracted from the Schottky plot of the Fig. 3.10.(e). Furthermore, the field-dependent Schottky plot for sample M70-thiol exhibits a clear linearity when compared to a sample with the same characteristics but without SAM (M70-A), confirming the presence of a Schottky barrier. Both Schottky plots are given for comparison in the panels (c) and (d) of the Fig. 3.10.

When large bias is applied at a metal-CP junction presenting a high barrier height, the Fowler-Nordheim tunneling could be the dominating mechanism. Thanks to the large applied bias, a current of carrier tunneling through the barrier is possible and its field dependence is given by the equation 2.4, i.e. $\ln(I/F^2) \propto F^{-1}$. However, since our data do not follow a such dependence, this model is ruled out. Another important mechanism of charge transport often encountered in disordered materials is the VRH model of Mott. We show in the following section that the VRH of Mott [122] can be used for explaining the charge transport in our samples. The 3D-Mott VRH model provides a complete framework for the understanding of transport in Au-PPy-Au HNWs, including nonlinear current-voltage characteristics and magnetotransport at low temperatures.

3.3.3 Hopping Charge Transport in CPNW Arrays

The VRH mechanism is a general form of charge transport for insulators and usually dominates over the thermally-activated transport at sufficiently low T . The VRH model is presented in details in the chapter 2.

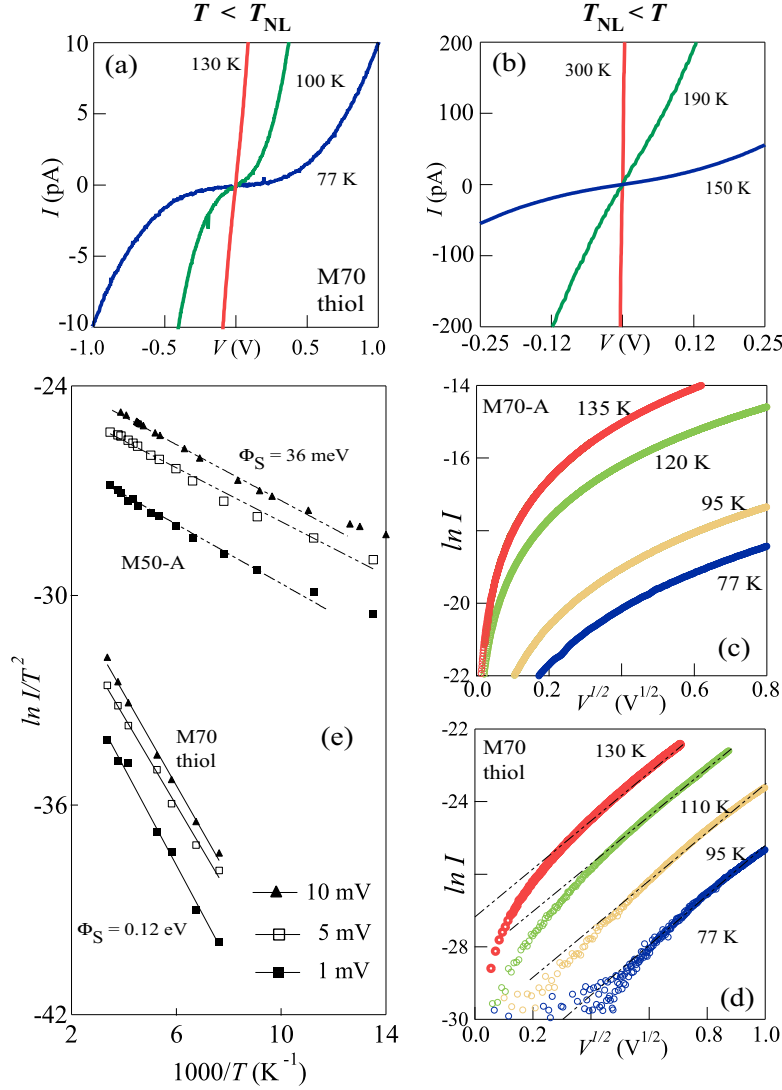


Figure 3.10: Charge transport properties of thiol-modified trisegmented HNW array (M70-thiol). (a-b) Low- T and High- T ($I-V$) characteristics of $\Phi = 70$ nm diameter sample *M70thiol* (Au-Thiol-PPy-Au). (c-d) field dependent Schottky plots consisting of $\ln I$ versus $V^{1/2}$ at various fixed temperatures for a $\Phi = 50$ nm diameter (Au-PPy-Au) M50-A and M70-thiol. (e) Schottky plots consisting of $\ln[I/T^2]$ versus $1/T$ at various fixed V 's for the same samples.

3.3.3.1 Current-Voltage Characteristics

The $(I - V)$ curves presented in the Fig. 3.7 and their evolution with the temperature, i.e. the Ohmic and the non-linear regime can be both explained by considering the Mott VRH mechanism for which the current density follows the equation 2.13. Generally, at room T , small voltage are applied to the sample⁵. As a result linear $(I - V)$ characteristics are obtained from equation 2.13 as the $\sinh$ term can be linearized when the following Ohmic condition is verified

$$F = \frac{V}{d} \ll \frac{k_B T}{e R_{hop}} \quad (3.1)$$

where d is the length of the CP NW and R_{hop} is the hopping distance. It is easy to see that for the measurements in the high- T range ($T_{NL} < T$), this condition is clearly fulfilled⁶. On the other hand, when temperature decreases, the inequation 3.1 is not verified anymore as to conserve a constant current range, higher voltages are needed. The result is a slight deviation from the linearity increasingly when the temperature is lowered below $T_{NL} \approx 100$ K. This effect is amplified as the hopping distance increases with decreasing temperature as shown in the equation 2.15 until a zero-current plateau appears in the $(I - V)$ characteristics. when T is further decreased, the electric field strength is high enough to allow the electric field induced hopping to occur. This regime of transport will be detailed in the section 3.3.3.4.

3.3.3.2 Resistance-Temperature Dependence

From the $(I - V)$ characteristics, resistance values $R(T)$ are obtained from the $(dI/dV)^{-1}$ values at zero bias for $T_{NL} < T$ around the zero-bias point until the zero-current plateau appears. The resistance (shown in the Fig. 3.9 for various samples) are divergent as the temperature is lowered demonstrating a clear insulating behavior. Within the framework of the VRH mechanism, the resistance is expected to follow the relation given in the equation 2.17. The best fits to our data were obtained with $d = 3$. This suggests that the three-dimensional (3D) VRH is the appropriate model of transport in our samples. The $\ln[R(T)]$ versus $T^{-1/4}$ plots are given in Fig. 3.11 for $T \gtrsim 50$ K. From these plots we extract the parameter T_0 . The values are listed in the Table A.2.

⁵Generally, only small voltages V are applied during measurements at high T for preventing high current to burn the samples and/or the contacts.

⁶For instance, one can assume typical RT values of CP segment length, hopping distance and applied voltage: $d = 1 \mu m$, $R_{hop} = 40 nm$ and $V = 10 mV$ respectively.

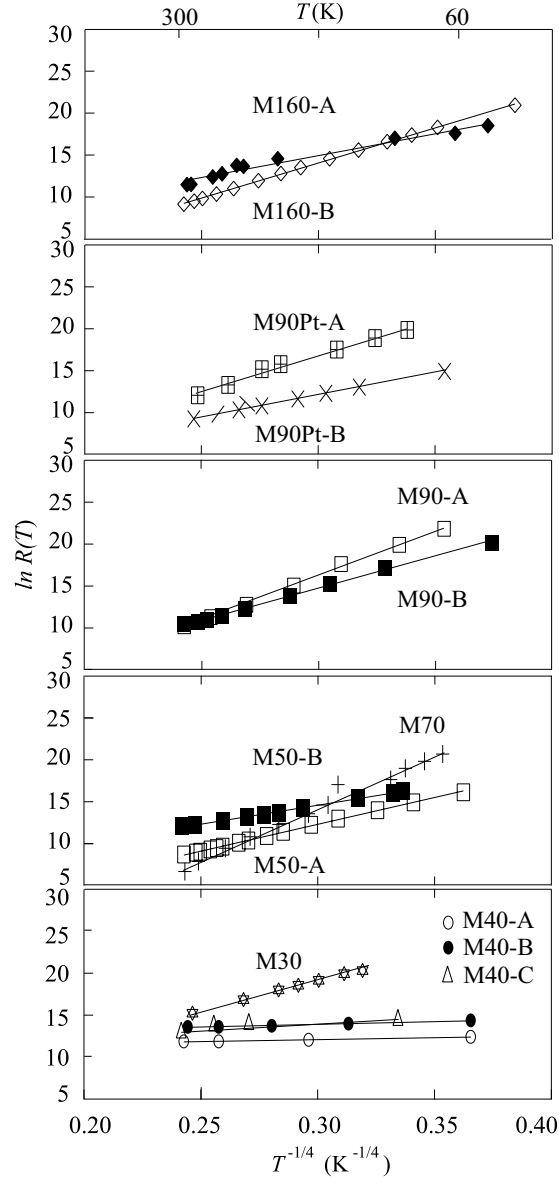


Figure 3.11: 3D-VRH plots for 160, 90, 70, 50, 40 and 30 nm tri-segmented (Au,Pt)-PPy-Au samples. The solid lines are the 3D-VRH fits to the data (see text).

The Mott temperature T_0 is linked by the relation 2.16, to important parameters characterizing the CP such as the localization length ξ , which is linked to the amount of disorder of the CP and the density of states at the Fermi energy $N(E_F)$. It is not possible to determine both parameters

only from the T_0 value. In the following section, we show that both ξ and $N(E_F)$ can be deduced from low- T magnetoresistance data (Fig. 3.12).

3.3.3.3 Magnetoresistance Measurements

In this section we present magnetoresistance (MR) measurements performed at low- T on several HNW arrays presenting several tri-segmented structures (M-CP-M, M-CP-M' and Ni-CP-M) or penta-segmented M-CP-M'-CP-M. (see Fig. 3.3). The MR measurements are performed with B aligned along the NWs axis as depicted in the Fig. 3.6. The measurement of multi-wire samples offer a higher level of current (less sensitive to noise) compared to single NWs measurements [144].

The plots of $\ln[R(B)/R(0)]$ with respect to B for sample M90-B and M90Pt-A are given in Fig. 3.12 at $T = 11, 5$, and 0.5 K. Generally, the MR signal was measured close to the $I = 0$ plateau of the $I - V$ curves (see arrow in inset to Fig. 3.12.(a)). But as it will be shown in the following section, the MR is bias dependent.

Several features are noteworthy in our data:

1. (i) the observed magnetoresistance is always positive,
2. (ii) it is symmetric in magnetic field: $R(B, T) = R(-B, T)$,
3. (iii) it increases as T is lowered,
4. (iv) and it displays a parabolic-like behavior at low B for all investigated temperatures.

These observations suggest that our MR data could be cast within the wavefunction shrinkage model presented in the section 2.4.3. While both positive and negative MR were observed in PANi NWs [144], here due to the narrow T range such negative MR has not been observed. The left inset to Fig. 3.12.(b) shows that, at high B , the magnetoresistance follows the expected $B^{1/3}$ dependence. The low- B data are displayed in Fig. 3.12.(b) as $\ln[R(B)/R(0)]$ versus B^2 at indicated temperatures. The B^2 dependence is observed up to few Teslas. From the linear fits to these data, we extract $B_c(T)$, which is plotted as a function of $T^{1/4}$ in the right inset to Fig. 3.12.(b). The T dependence of B_c given in the Eq. 2.24 is particularly useful, as it allows us to determine the localization length: $\xi = 1.4$ and 2.1 nm at $T = 5$ K for samples M90-B and M90Pt-A, respectively. Using the above-mentioned values for ξ , we are able to deduce for the density of states $N(E_F) \approx 10^{18} \text{ eV}^{-1} \cdot \text{cm}^{-3}$ for samples M90-B and M90-Pt. The calculated values of $N(E_F)$, listed in Table A.2, are two orders of magnitude lower than typical values found in highly

doped PPy films [52, 192, 193, 194]. Nevertheless, this low density of states corroborates with the low doping level ($< 13\%$) of tri-segmented HNWs. As detailed in the section C.1, the low doping level of HNWs originates by the unavoidable reduction of the CP segment during the electroplating of the upper metal segment [145]. Recently, Hulea *et al.* [195] reported on the correlation between the doping ratio and $N(E_F)$ in PPy films. They showed that a decrease of the doping level from 16% to 6% corresponds to an increase of T_0 of about four orders of magnitude. Thus, the wide range of T_0 observed for identical samples (e.g. 160 nm diameter Au-PPy-Au samples) could be partly explain by a slight variations of the doping level.

Interestingly, the magnitude of positive MR in HNW arrays depends on the applied electric field. Indeed, as shown in the Fig. 3.13, we observed a decrease of MR for increasing applied voltage. Such effect was observed recently in PANi NWs networks by the Epstein's group [196]. At Low- T , PANi NWs networks exhibit strong non-linearity which could originates, as proposed by the authors, from a reduction of the hopping activation energy and the hopping length induced by the increasing applied electric field, as given by the equation 2.19. As a result, when high electric field is applied to the sample, the hopping length is reduced and the shrinkage of electron wavefunction by magnetic field becomes less effective and MR decreases [196]. Nevertheless, the authors do not discuss about the possibility that this effect could stem also from self-heating effects of the samples. Indeed, even if the temperature as given by the thermometer of the measurement system is constant (as observed during the measurements), the sample temperature could be significantly higher since the thermal conductance between the sample and the sensor is extremely low (mainly because of the high separation between the sample and mixing chamber thermometer).

Here, in the MR measurements the total dissipated power was kept below 500 nW corresponding to an average power of 5 pW per NW. Taking a typical value of the low- T thermal conductivity for amorphous polymers [197], this corresponds to the limit of the applied power for which the sample heating estimated is still lower than 0.5 K. For comparison, in their work, power as high as 10 mW were applied to the sample at $T = 50$ K.

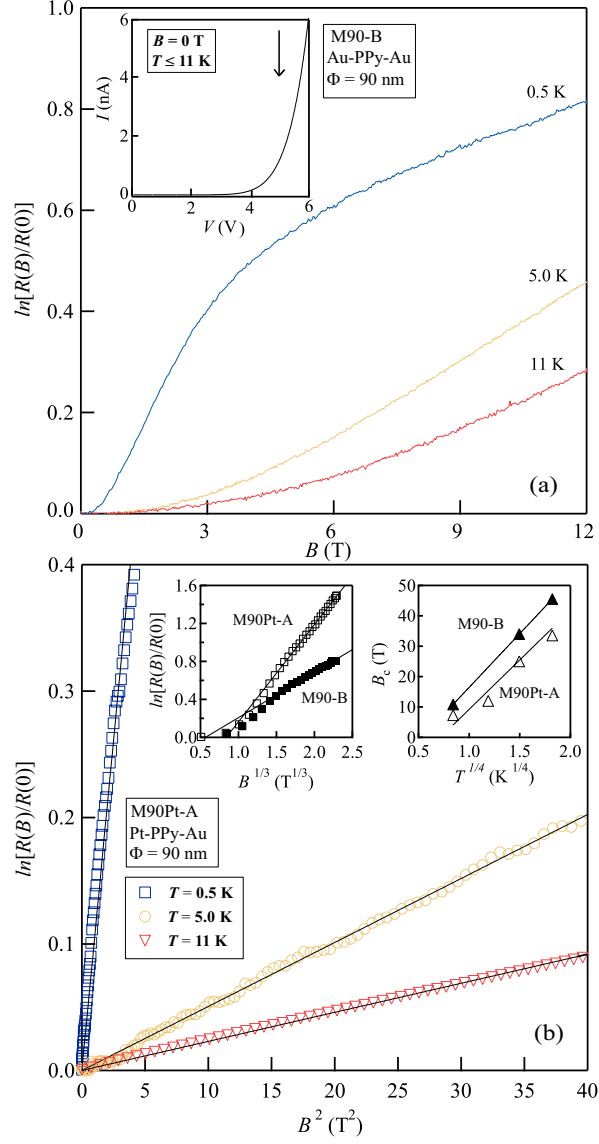


Figure 3.12: (a) Variation of $\ln[R(B)/R(0)]$ with B at indicated T 's for a tri-segmented HNW array. Inset: Below $T = 11$ K the $(I - V)$ curves are indistinguishable. The arrow indicates the point of the $(I - V)$ curves where the MR measurements were recorded. (b) Variation of $\ln[R(B)/R(0)]$ as a function of B^2 in the low magnetic field range at $T = 11$, 5 , and 0.5 K for the sample M90Pt-A. The solid lines are fits to the data. The left inset shows $\ln[R(B)/R(0)]$ as a function of $B^{1/3}$ for samples M90-B and M90Pt-A at $T = 0.5$ K. The lines are guides to the eye. The right inset displays $B_c(T)$ as a function of $T^{1/4}$ for both samples (see text). The solid lines are fits to the data.

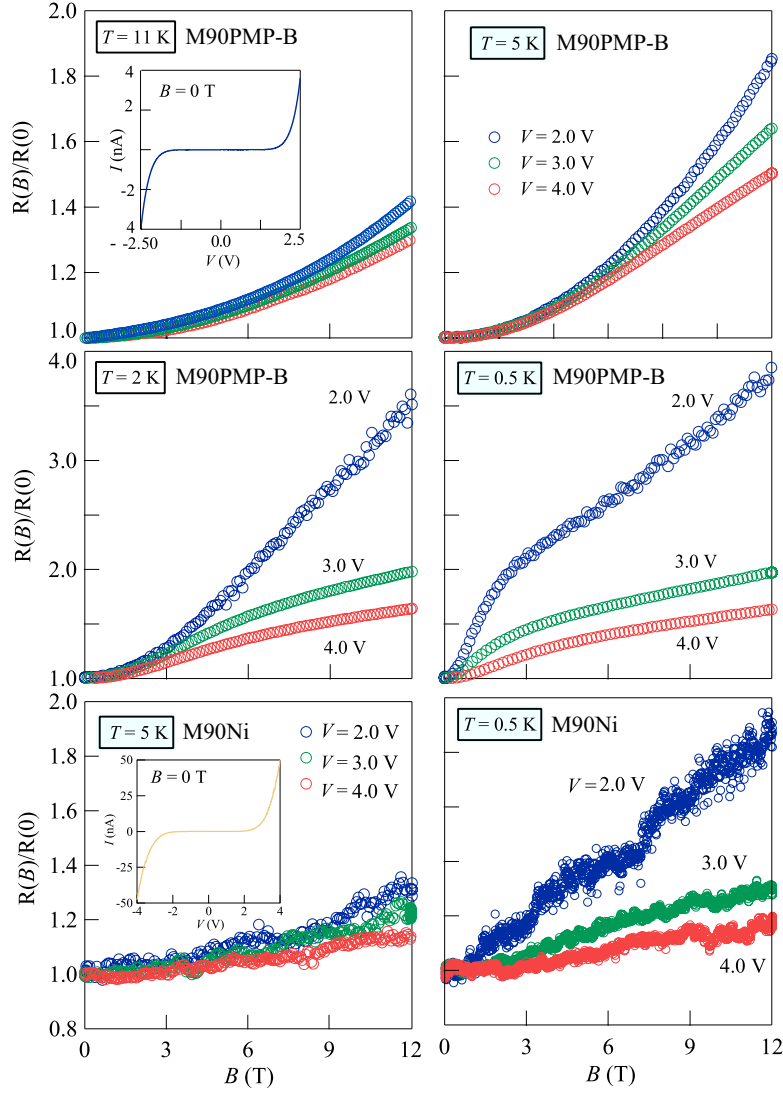


Figure 3.13: Variation of the MR as a function of the applied voltage for the 90 nm diameter samples M90Ni (Ni- $C_7H_9NO_2$ -PPy-Au) and M90PMP-B (Au-PPy-Pt-PPy-Au) at indicated T 's. The insets give the ($I - V$) characteristics of the sample taken at $B = 0$ T.

3.3.3.4 Electric-Field-Induced Hopping

To understand the non-Ohmic conduction at low T , we have analyzed the electric field F dependence of the current defining a parameter $\beta = eF\xi/k_B T$ which defines two different hopping transport regimes. For $\beta \ll 1$, transport is dominated by thermally assisted hopping, while for $\beta \gg 1$, the electric field-induced hopping mainly contributes to the transport. Within the electric field-induced hopping regime, the current follows the equation 2.20, with F_0 standing for the critical electric field [128, 129, 130].

Assuming that the electric field-induced hopping regime is a 3D mechanism, we plotted $\ln I$ versus $F^{-1/4}$ for different HNW samples in the Fig. 3.14. To reach the $\beta \gg 1$ regime, data were taken down to liquid helium temperatures and below. Clearly, a linear behavior is observed at the lowest temperatures, which remains almost unchanged upon further decrease of T . At the first glance, this effect seems to stem only from electron heating due to the high imposed electric field. Indeed, the applied electric voltage V could increase the electronic temperature T_{el} above the measured temperature T (i.e. the mixing chamber temperature). Practically, the temperature T_{el} acquired by the electron due to the applied external voltage V is determined by the balance between the Joule heating and the cooling by the phonon bath [198]. For temperatures below 4 K, the total dissipated power was kept below 100 nW corresponding to an average power of 1 pW per NW. Taking a typical value of the low- T thermal conductivity for amorphous polymers [197], it can be shown that the sample heating is negligible (less than 10 % of the base temperature) down to $T = 0.5$ K. The critical electric field F_0 could be extracted from a linear fit to the lowest T data. The deduced values for samples are included in Table A.2.

Remarkably, F_0 is linked to the localization length ξ as shown in the equation 2.21. from F_0 values we can estimate the localization length $\xi(F_0, T_0)$ using the Mott temperature T_0 . The deduced values are presented in Table A.2. These values can be compared to those obtained from the magnetoresistance analysis for samples M90B and M90-Pt. A reasonable agreement is found, which further substantiates our conclusion that the transport mechanism in our samples is the 3D-VRH.

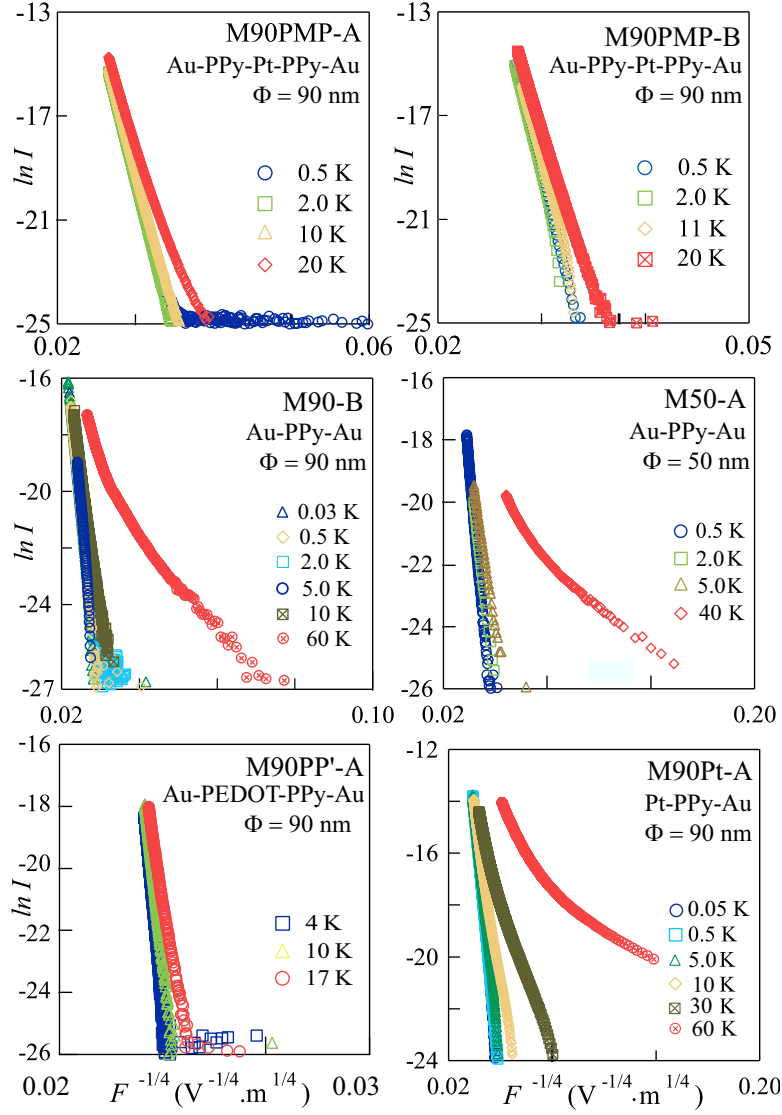


Figure 3.14: Electric-field-induced hopping regime observed at low- T . Data plotted as $\ln I$ versus $F^{-1/4}$ for various samples in the electric field-induced hopping regime. For $T < 30$ K, the current is almost T -independent and the critical field F_0 is obtained from the slope of a linear fit to the data.

3.4 Size-Dependent Transport Mechanisms

In the last twenty years, many studies were devoted to the charge transport properties of CP films. It was shown that conjugated polymer films can be tuned from metallic to insulator by adjusting doping level of the CP or by the application of a magnetic field as well as applying high pressure [52]. Since the seminal work of Martin *et al.* [199, 200, 67], several authors observed an improvement of the molecular and supramolecular structures of template synthesized CP films made of compacted CP NWs compared to films prepared by conventional methods [201].

More recently, studies suggested that intrinsic properties of CP can also be affected by electron-electron interactions [18, 35, 202] and quantum effects such as a M-I transition [12]. Obviously, this kind of physics is rather expected for systems such as 2D-electron gas, CNT or graphene sheet made of defect free materials with highly controllable composition and structure. Nonetheless, in the following, we present strong evidences that suggest that tri-segmented (Au-PPy-Au) HNWs exhibit a disorder-induced metal-insulator transition. Finally, we analyze and discuss the low- T data obtained for several class of HNWs, comparing with several recent experimental works which taking into account the EEI and suggest the possible formation of Luttinger liquids in CP systems.

3.4.1 Electrical Transport Near the Metal-Insulator Transition

In this section, we analyze the electrical transport data for tri-segmented Au(Pt)-PPy-Au NWs of diameter down to 30 nm. We showed in the previous sections that the three-dimensional Mott VRH model provides a complete framework for the understanding of transport in Au-PPy-Au HNWs, including nonlinear current-voltage characteristics and magnetotransport at low temperatures. We saw that samples with diameters ranging from 160 to 50 nm have resistances that follow the relation $\ln[R(T)] \propto (T_0/T)^{1/4}$. Strikingly, the $(I - V)$ characteristics of the $\phi = 40$ nm samples (given for two samples in the Fig. 3.15), are quite different from those measured for other samples as they exhibit Ohmic behavior until $T \approx 30$ K while all samples with diameters above 40 nm present strong nonlinear $(I - V)$ characteristics and a zero-current plateau for $T < 50$ K. Furthermore, as shown in the Fig. 3.11, the $\phi = 40$ nm samples exhibit very low T_0 values⁷ listed in the table 3.2. The Mott temperatures found for specimens M40-A, M40-B and M40-C are at least three orders of magnitude smaller than for sample M50-A.

⁷obtained from the slope of the linear fit of $\ln[R(T)]$ versus $T^{-1/4}$.

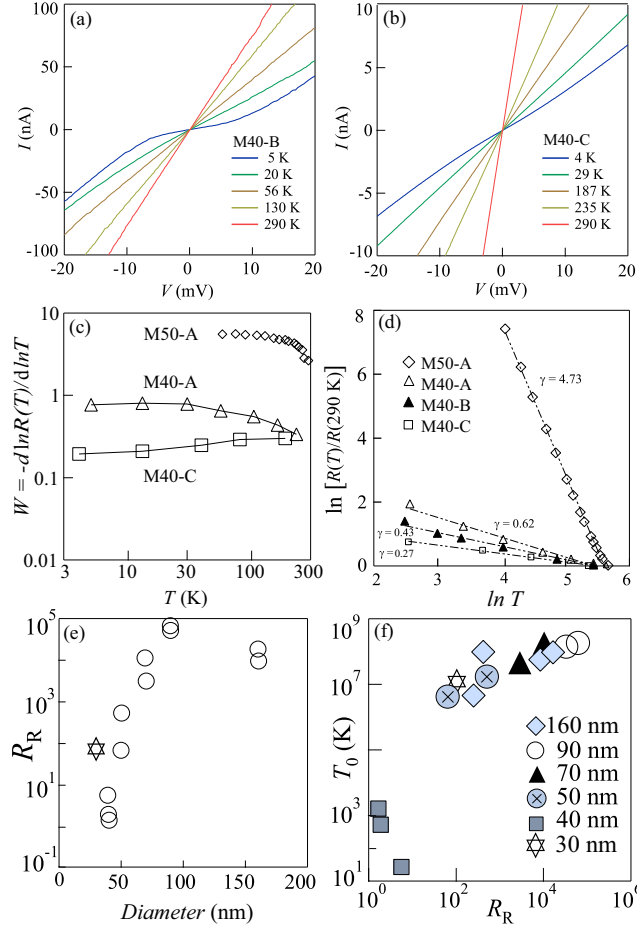


Figure 3.15: Electrical data analysis for low diameter tri-segmented (Au-PPy-Au) samples. (a-b) ($I - V$) characteristics for two $\phi = 40 \text{ nm}$ samples (M40-b and M40-C). c) Reduced activation energy $W(T)$ for samples M50-A, M40-A and M40-C. d) Log-log plot of the resistance with temperature for samples M50-A, M40-A and M40-B. The resistance follows a power-law temperature dependence for the 40 nm samples. Solid curves are fit to the data. e) Evolution of the parameter R_R versus the diameter (see text). f) The Mott temperature T_0 plotted as a function of the parameter R_R for samples presenting diameters ranging from 30 to 160 nm.

The peculiarity of the $\phi = 40 \text{ nm}$ specimens can be highlighted using the empirical parameter $R_R = R(77 \text{ K})/R(290 \text{ K})$ given as a function of the diameter in the Fig. 3.15.(e). This parameter was frequently used to characterize the extent of disorder in conjugated polymers such as

PPy or PEDOT [52, 12]. The R_R parameters of M50-A and the 40 nm diameter samples are listed⁸ with other parameters in the table 3.2. The parameter R_R is found to be four orders of magnitude smaller for the M40-A, M40-B and M40-C specimens than for the $\phi \geq 70$ nm samples, while it is still two orders of magnitude smaller than for 50 nm diameter samples. This suggests that the $\phi = 40$ nm specimens exhibit a dramatically lower disorder strength compared to $\phi \geq 50$ nm samples. In the panel (f) of the Fig. 3.15, we plotted the Mott temperature as a function of the parameter R_R for all investigated samples. One can easily notice that M40-A, M40-B and M40-C specimens are disparate from the group of other samples.

By assuming typical values of DOS for lightly doped PPy [$10^{18} - 10^{20} \text{eV}^{-1} \text{cm}^{-3}$], and by taking into account the unavoidable variation of the doping level from sample-to-sample, these data suggest a dramatic change of the disorder strength in the 40 nm specimens. Similarly to a recent study performed on PEDOT NWs [12] and studies focusing on PANi [203], PPV [91] or PPy [52] films, the behavior of our 40 nm samples can be understood in the framework of a disorder-induced metal-insulator transition.

Indeed, in the critical regime of the disorder-induced metal-insulator transition, the resistance follows a power-law temperature dependence $R(T) \propto T^{-\gamma}$ with $0.3 < \gamma < 1$ [52]. The log-log plot of $R(T)$ versus T is given in Fig. 3.15.(d) for samples M50-A, M40-A, M40-B and M40-C. Remarkably, in the low- T regime, the power-law fit is found to be much better than the 3D Mott VRH fit for the 40 nm samples. It should be noticed that the quality of the fits were estimated by comparing the Chi-Square values. From these fits, the extracted parameters γ are 4.73, 0.62, 0.43 and 0.27 for M50-A, M40-A, M40-B and M40-C, respectively. The exponent γ is expected to vary from 0.3 to 1 as the sample goes through the transition from the metallic to the insulating side [52].

The existence of a finite conductivity extrapolated at $T = 0$ K, is considered as defining the boundary of the M-I transition [52]. Strikingly, from the extrapolation of the data given in the Fig. 3.15.(d), it seems that the $\phi = 40$ nm samples - especially M40-C, could exhibit such finite conductivity at $T = 0$ K. However, such a low-temperature extrapolation is risky and can lead to erroneous identification of the various regimes near the M-I transition [91].

To obtain quantitative insight into $\rho(T)$, it is preferable to use the reduced activation energy $W(T) \equiv -d(\ln \rho(T))/d(\ln T)$ [148] (see section 2.5.1). The low- T behavior of $W(T)$ is useful to discriminate be-

⁸The R_R parameters are collected for all measured samples in the table A.2

tween several regimes of the metal-insulator transition [52] as demonstrated recently for single PEDOT NWs [12].

Despite the low number of points, the log-log plot of $W(T)$ given in the Fig. 3.15.(c) allows to identify clearly distinctive behavior for $\phi \geq 50$ nm samples and $\phi = 40$ nm diameter samples. While $\phi \geq 50$ nm samples exhibit $W(T) > 2.5$ with a negative temperature coefficient ($dW(T)/dT < 0$) characteristic of the insulating regime, M40-A and M40-B demonstrate roughly constant values of $0.5W(T) < 0.9$ at low temperatures $T < 50$ K which is characteristic of the critical regime of the MIT. On the other hand, M40-C sample exhibits much lower value of $\gamma < 0.3$ with a small but positive temperature coefficient ($dW(T)/dT > 0$). This indicates that M40-C is just entering into the metallic side of the MIT from the critical regime.

Recently, *Cao et al.* observed identical T -dependence $W(T)$ and enhanced electrical conductivity, for single Au-PEDOT(ClO₄)-Au HNWs [16]. These samples were located slightly on the metallic side of the M-I transition while Au-PEDOT(poly(4-styrenesulfonic acid))-Au exhibited insulating behavior. Despite the differences existing between our samples and the specimens characterized by *Cao et al.*⁹, in either case, the mechanisms that determine the electrical conductivity are related to the microscopic structure of the CP segments. *Cao et al.* proposed that the enhanced microstructure of PEDOT(ClO₄) compared to PEDOT/PSS, originates from the synthetic conditions. Indeed, they noticed that the perchlorate ion is much smaller (monomeric) and thus should introduce less disorder in PEDOT than PSS, which is also believed to induce a much more important conformational disorder [16]. Also, they suggest that the use of two different solvents used for the synthesis of the CP segments - that is acetonitrile for PEDOT/ClO₄ whereas a mixture of (1:1 v:v) acetonitrile/water was used for PEDOT/PSS, could further strengthen the microstructural dissimilarities between the PEDOT/ClO₄ and PEDOT/PSS segments as acetonitrile is known to minimize side reactions that terminate the CP chain propagation [48, 16].

Unfortunately, for our samples, these explanations do not apply because the same counter ion (ClO₄) as well as the same solvent (water) were used for the synthesis of all the samples, even for the $\phi < 50$ nm samples. We propose that the molecular and supermolecular structures of our samples could be enhanced by specific growth mechanisms associated to the electrochemical synthesis within small diameters PC tem-

⁹*Cao et al.* characterized HNWs Au-PEDOT-Au with $\phi = 500$ nm PEDOT CP segments with /ClO₄ and poly(4-styrenesulfonic acid)(PSS) counter ions.

Samples	$W(4\text{ K})$	$T_0\text{ (K)}$	R_R
M50-A	4.94 ¹	7.6×10^6	498
M40-A	0.86	580	1.8
M40-B	0.77	1608	1.5
M40-C	0.19	19	5.6

Table 3.2: Small diameter samples measured in this study, listed with decreasing values of the reduced activation energy $W(T)$ at liquid helium temperature. The Mott temperature T_0 and the empirical parameter $R_R = R(77\text{ K})/R(290\text{ K})$ are also given. ¹ $W(T=58\text{ K})$ as $R(T)$ is not accessible at lower T .

plate as reported for films made of compacted CP NT with diameter smaller than 60 nm [204, 199, 178, 152] and more recently for PEDOT NWs [12]. The basic idea is that the relative proportion of ordered and amorphous polymer chain materials produced by the template method, varies as a function of the pore's diameter. Consequently, small diameter CPNWs contain more ordered chains which translates into higher localization length and RT conductivity.

Based on the experimental facts, we argue that our 40 nm diameter Au-PPy-Au NWs are in the critical regime of a disorder-induced metal-insulator transition. While M40-A and M40-B specimens lie at the limit of this transition, on the insulating side, sample M40-C is in the metallic side. Samples with higher diameters are clearly in the insulating side ($\gamma > 1$). The transition can be explained by a consequent decrease of the disorder strength of the CP segment, in the 40 nm specimens due to the specific growth mechanism involved in the template method, similarly to the suggestion made for pure PEDOT NWs [12].

In a naive view of this mechanism, a metallic behavior is expected for smaller diameter HNWs ($\phi < 40\text{ nm}$). Strikingly, the $\phi = 30\text{ nm}$ sample (M30-A) presents the typical characteristics of samples located far in the insulating regime ($\phi > 50\text{ nm}$). The T -dependence of $R(T)$ of sample M30-A follows the 3D-Mott VRH (see Fig. 3.11). The parameters $R_R = 193$ and $T_0 = 2.98 \times 10^7\text{ K}$ are orders of magnitude higher than for 40 nm sample. This result is quite intriguing as intuitively, the growth mechanism and the doping level of 30 nm diameter CP NWs should be very close to what is found within 40 nm diameter samples, not to say the same.

Unfortunately, because the electrochemical synthesis of HNWs within PC templates with diameter below 40 nm is not straightforward, only a

unique sample with $\phi = 30 \text{ nm}$ was characterized.

The first reason that comes to mind to explain this behavior is related to the main disadvantage of the vertical contacting technique, namely the averaging of the diameter of the measured HNWs which could be combined to the possible error on the nominal diameter of the PC membrane. However, the total uncertainty on the diameter required¹⁰ would be abnormally high (higher than 67 % of the nominal diameter) to account alone for such behavior.

As it will be shown in the two next chapters, this lack of precise structural information about the measured HNWs disappears by performing single NW measurements.

In the following section, we present measurements of the conductance of various HNW samples as a function of temperature and voltage that could suggest a tunneling mechanism into a Luttinger liquid.

3.4.2 Electron-Electron Interactions in CPNWs

Low dimensional and 1-D structures are of great interest for investigating transport mechanisms on the nanoscale, where the quantum confinement effect, Coulomb charging energy, electron-electron interactions (EEI), and disorder all play important roles [20]. Especially, EEI are strongly affecting the transport in 1D systems by leading to phases different from conventional Fermi liquid [120]. While the effects of dimensionality on interacting electrons were predicted a long time ago [205, 206] it is only recently that they were shown experimentally (see section 2.5.3).

Recently, it was shown by Long *et al.* that EEI could become significant enough at low T to have an impact on the transport properties of single CP NWs [73]. EEI induce a depletion of the density of states at the Fermi energy resulting in the creation of a Coulomb gap at low temperature visible in zero-bias anomaly of dI/dV plots. In this case, the Efros-Shklovskii model replaces the Mott VRH and the observed resistance follows the relation 2.18. However, such T dependence has not been observed in our samples, most probably because the resistance in our samples cannot be measured at low temperatures $T < 50 \text{ K}$. The figure 3.16 gives typical dI/dV plots for a 160 nm diameter and a 40 nm diameter samples. Generally, such zero-bias anomaly in the dI/dV and the associated non-linear ($I - V$) characteristics can be explained by various models.

Indeed, up to now, several groups have studied the low T transport in various CP NWs such as PPy, PANi or PA and have analyzed

¹⁰To measure HNWs with a real diameter $\phi \geq 50 \text{ nm}$ whereas the nominal is $\phi 30 \text{ nm}$.

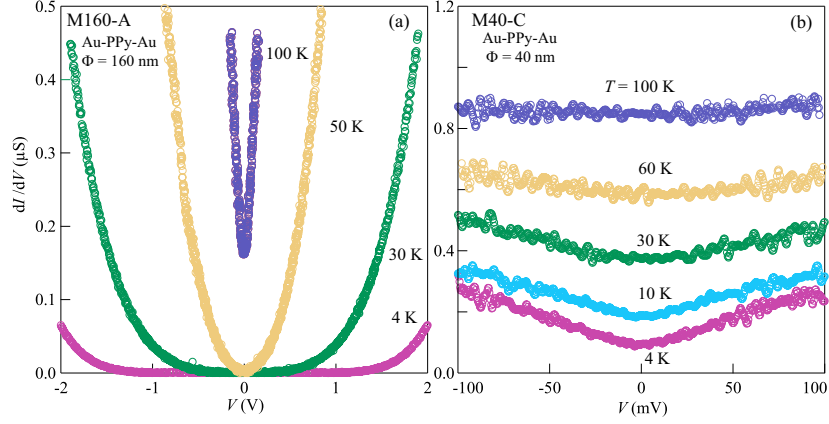


Figure 3.16: dI/dV vs V for two HNWA arrays at $T = 100, 50, 30$ and 4 K.

the obtained transport data in terms of specific models such as space charge limited current (SCLC) [112, 207, 113], quasi-1D variable range hopping [208, 124], fluctuation-induced tunneling [117, 17] or other based on electron-electron interaction (EEI) such as Luttinger liquids (LL) [18, 120], Wigner crystals (WC) [18, 168] or Coulomb blockade [209, 154].

The SCLC model (see section 2.3.3) is characterized by a current density J following a power-law of the applied voltage $J \propto V^\beta$, (see equation 2.7). Generally, in the case of a shallow-trap SCLC regime β equals 2 [112]. In the inset of the Fig. 3.17.(a), is given the exponent β as a function of temperature, for various samples. Obviously, at room T , $\beta = 1$ stems from the Ohmic regime of transport while for decreasing T , β increases exceeding the SCLC values for temperatures $T < 100$ K and reaches at liquid ^4He temperature values about 6. The SCLC is thus ruled out. Our samples are quite far from an ideal 1-D wire even though CP can be seen as 1-D conductors because they are composed of a high number of intertwined 1-D carbon atoms chains. Despite the unavoidable disorder, the optical and electronic properties of CP are intrinsically anisotropic due to their electronic structure (delocalization of π -electrons along their backbones) [71]. As a result, if the interchain hopping can be neglected, one expects, for highly ordered CP, the charge transport to be influenced by 1-D effects. In the following, we discuss our low- T data for HNWA arrays ($\Phi \geq 50$ nm) in terms of 1-D effects and EEI, in light of the recent work of Rodin and Fogler [210].

As we have seen in the section 2.5.3, the main feature suggesting a LL is a power-law dependency of the tunneling density of states near

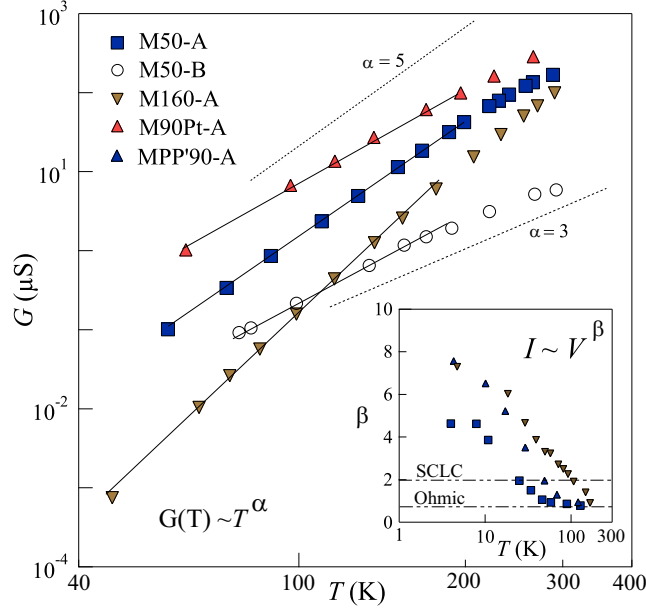


Figure 3.17: Conductance vs T for various samples. The dashed lines are guides for the eye. The inset gives the exponent β as a function of the temperature for samples M50-A, MPP'90-A and M160-A.

E_F , which translates in the power-law dependencies for the conductance and the current given in the equation 2.27. In our samples, power-law dependencies of the conductance -calculated around the zero bias point, were observed with $3 < \alpha < 5$ while power-law dependencies of the current are found at sufficiently low temperatures $T < 200$ K with $2 < \beta < 6$ as shown in the Fig. 3.17.(a). Power-law fit are always better at lower T . Remarkably, the power-law of $G(T)$ and $I(V)$ was found in many HNWs measured in the vertical configuration presenting diameter ranging from 50 to 160 nm, but also in planar configuration with single HNWs measured with the bottom-contact method (samples S70-A S70-B and S90) (see chapter 5).

To further investigate the presence of a LL in our samples, we plotted $I/T^{1+\alpha}$ against $eV/k_B T$, for samples M70-A, M160-A, M90Pt-A and M160-C. Indeed, if the tunneling in a LL is the dominant charge transport mechanism, the $(I - V)$ characteristics should be given by the general equation 2.28. The parameter α were found for each sample from the fit of $G(T)$. As shown in the Fig. 3.18, for many samples, the curves collapse pretty well in a single one, independently from the diameter and also for a wide range of temperatures 30 K $< T < 200$ K.

Strikingly, the sample M160-C with the same parameters than M160-A do not verify the scaling relation.

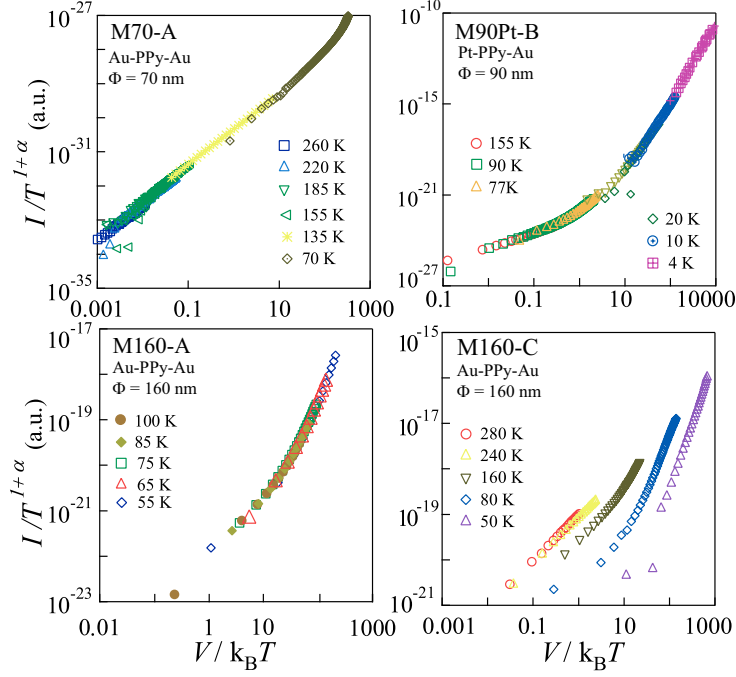


Figure 3.18: Collapse onto the universal curve $I/T^{1+\alpha}$ vs $eV/k_B T$ for samples M70-A, M90Pt-B, M160-A and M160-C. α is the exponent from $G(T)$ dependence. The sample M160-C exhibits clearly a deviation from the LL theory.

These results might suggest that the LL state could describe the electronic transport properties of HNW samples. Indeed, the power-law variations $G(T)$ and $I(V)$ observed in our samples follow the equation 2.27 and the scaling relation described by the equation 2.28. Interestingly, a recent work of Rahman *et al.*, dealing with PPy NWs embedded in PC template measure in the same vertical configuration than our samples, showed the existence of a crossover from the 3D VRH to a power law behavior for PPy NW arrays as a function of the applied bias [13]. Nevertheless, such crossover was not observed in our samples.

The values of the exponents α and β found for our samples are similar to values reported for PPy NW arrays by Rahman *et al.*. A strong T -dependence of β was also observed. Apart from a few exceptions, the values of β and α obtained for HNWs always exhibit $\beta \neq \alpha + 1$ ¹¹, while

¹¹The parameters α and β are listed in the table A.3.

$\beta = \alpha + 1$ is expected in the case of a single chain of LLs. Moreover, β is less than α in many cases, which contradicts the previous relation for a single chain of LLs. These discrepancies were found in other 1D-systems (CNT, CP and inorganic NWs) [166] and may depend on the number of channels, the impurity distribution or the presence of disorder and the interactions between the CP chains which have an impact on the properties of LL [163, 119]. In fact, if one considers only the values of β obtained at $T = 4\text{ K}$, then in many cases $\beta > \alpha$. While several authors noticed a diameter dependence of β [166, 13], no convincing diameter dependence was found for the exponents in our samples¹².

However, as mentioned recently [211], the LL theory requires clean and pure one-dimensional systems to be applicable [164]. Thus, the observation of such transport mechanism seems very surprising as each CP segment is composed of many chains which are not all perfectly parallel due to branching and high disorder which make our samples neither ideal 1D conductors nor perfectly clean. The behaviour of our samples should be explained by other means.

In a very recent paper [210], Rodin and Fogler emphasized that the observation of apparent power-law behavior is not sufficient to conclude about the presence of LL in disordered quasi-1D systems such as our HNWs. Moreover, they demonstrated, based on a numerical study, that the VRH conductance could deviate, in specific hopping configuration, from the usual exponential formula (equ. 2.17), to exhibit the collapse onto the universal curve of Eq. 2.28 and an apparent power-law behavior (equ. 2.27) within narrow T and V intervals.

Indeed, for our samples, the collapse onto the universal curve was obtained only for rather narrow T range (excepted for sample M90Pt-B for which the collapse occurs until liquid helium T) and exceptionally until RT (sample M70-A). Similarly, in the work of Rahman *et al.*, the scaling to the master curve is observed mainly at low- T ($T < 100\text{ K}$). The explanations brought by Rodin and Fogler allow to understand why a few samples (like sample M160-C) do not verify the scaling relation given by the equation 2.28, but also why the relation between the exponents $\beta = \alpha$ expected for the LL model is not verified in our samples.

¹²Here, we do not consider the $\Phi < 50\text{ nm}$ samples.

3.5 Summary

In this chapter, we presented briefly the synthesis of well-shaped multi-segmented hybrid nanowires by an all-electrochemical process. We described the structural properties focusing especially on the interfaces of the obtained metal-CP junctions. TEM Characterization of the polymer junctions unambiguously demonstrates the absence of short-circuits and reveals a strong structural difference between the bottom polymer-onto-metal interface and the upper metal-onto-polymer interface. Then, the electrical properties of several classes of hybrid nanowires were investigated as a function of the temperature, and in presence of a magnetic field. All samples present symmetrical and linear current-voltage characteristics at room temperature. The T -dependence of the resistance exhibited a typical insulating behavior for $\phi \geq 50$ nm samples. We analyzed the low- T data in terms of three-dimensional field-activated hopping mechanism. Our understanding of the non-Ohmic three-dimensional hopping transport is consolidated by the low T magnetoresistance data. Consequently, the three-dimensional Mott variable range hopping model provides a complete framework for the understanding the transport in hybrid nanowires with diameter down to 50 nm. Remarkably, 40 nm diameter samples exhibit a dramatically lower disorder strength together with a power-law temperature dependence of the resistance, characteristic of the critical regime of disorder-induced metal-insulator transitions.

Finally, we present low- T data for several classes of HNWs and discussed them in terms of electron-electron interactions and the one-dimensional model of Luttinger liquids comparing our data with recent works.

Chapter 4

Single Nanowire Integration

Vince, tes fils, ils cassent,...

Anonyme

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4.1 Introduction

In the previous chapter, the electrical measurements were performed on multiple nanowires-contained within the polycarbonate template. This method for measuring nanowires (NWs) is quite convenient as it is very fast and requires no complex processing of the sample to be measured. Furthermore, the NWs enclosed within the template are mechanically supported by the template and are protected from the effect of the oxygen and the humidity present in the air. However, two main drawbacks arise from this method. Firstly, the exact number of connected NWs is not known even if a rough estimated can be deduced from the porosity of the template and the surface of the electrical contact as follows: a typical value of porosity and contact surface are respectively 10^9 pores/cm^2 and 10^{-3} cm^2 . The contact surface depends on the technique used. Here, the electrical contacts were made by hand by depositing a silver paint drop on top of the sample and because of that the contact dimensions are always bigger than $100 \times 100 \mu\text{m}^2$. Assuming that all pores are filled, the number of connected NWs is about $N_{NW} \approx 1 \times 10^6 \#$. Among those NWs and even when a calibration of the synthesis parameters is carefully performed, one expects a wide distribution of the polymer segment length and of the quality of the interfaces.

Secondly, because we are dealing with multi-segmented NWs, the length of each segment can differ quite significantly between different NWs prepared with the same deposition parameters and within the same PC membrane. Also, because the diameter can differ slightly (10 - 20%) from one NW to the other, the intrinsic conductivity (calculated by using the geometrical parameters) can vary greatly. These distributions result in an averaging effect on the electrical measurements and contributes in masking the intrinsic properties of single NWs. More complex techniques were developed for the template electrochemical synthesis of NW, which allows the synthesis and the measurement of a single NW (more exactly, one to a few NWs are connected in parallel, depending on the control of the electrochemical synthesis) [212]. As a result, the averaging effect on the measured properties, is avoided. Nevertheless, for non-homogeneous NWs such as HNWs, the geometrical and structural characteristics (diameter and lengths of each layer/segment) cannot be precisely measured.

Thirdly, the available measurement techniques, which are the two-contact geometry and the pseudo-four-probe configuration, cannot avoid the contact resistance to be included in the measurements, in contrast to the four-probe geometry available in the planar measurement of a single NW.

Finally, as we have seen in the chapter 1, CP NWs exhibit a high application potential. Generally, these applications require that the NWs interact in some way with the environment or with any chemical, electrical or physical agent, which is not straightforward for NWs contained within a template. For all the above reasons, the use of NWs freed from the template is the best choice for the characterization of their intrinsic properties but also for applications oriented purposes.

Nonetheless, it is worthy of noting that the single NW configuration does not take advantage of all the benefits and properties of NWs arrays as it presumes to free the nanostructures from the template, destroying the structural ordering of the NWs array and the possible magnetic or optoelectronic properties that could be associated to it [213, 214, 215, 216]. Nevertheless, in this chapter, we will focus on the properties of single NW and we will not discuss the properties originating from arrayed HNWs.

Once the NWs are freed from the template, they must be connected to the outside world to eventually become part of an electronic circuit [217]. This integration requires NWs to be precisely aligned and positioned onto microfabricated contacts which is a quite challenging task. Hopefully, various techniques were specifically developed for the assembly of NWs onto electrodes and are based on the use of electric [218, 16, 219] or fluidic fields [22, 220]. The deposition and contacting techniques of single NWs are crucial issues for the characterization of the intrinsic properties of NWs as well as for the performance of NWs-based devices. Therefore we devoted the first part of this chapter to the contacting methods and the measurement techniques used for the characterization of single template-synthesized NWs in planar configuration. We review the the fabrication of single NW devices focusing on several technological aspects of contacting techniques used in this work.

In the last section, we present the fabrication of a multipurpose platforms, fabricated via Si micromachining techniques and state-of-the-art nanoscale processing which offer a unique tool for studying single nanostructures. These platforms are based on a thin (< 100 nm) Si_3N_4 membrane, on top of which nanomaterials such as nanoparticles or nanowires can be deposited, contacted and measured. Thanks to the excellent electrical and mechanical properties of the membrane, these platforms enable the correlation between structural properties (elemental compo-

sition, crystalline orientation, surface geometry, ...) - as contemplated, for instance, by transmission and scanning electron microscopies - and electrical properties of nanoscale materials. Consequently, the electrical measurements really gain in value and allow to get a better insight of nanoscale materials. The characterization of HNWs performed with these platforms are given in the section 5.4. These platforms can be used with a multitude of contacting techniques such as the standard e-beam lithography (EBL), dielectrophoretic trapping and electron-beam induced deposition (EBID) (see section 4.2). Strikingly, despite the useful information that could bring such tool, only a few publications proposed membrane-based devices for studying properties of nanomaterials such as CdS nanorods or CNT [221, 222, 223, 224, 225].

4.2 Deposition and Contacting Techniques

In the recent years, many studies were devoted to the structural and electronic characterization of low dimensional materials. Among them, nanowires (NWs) and nanotubes were intensely scrutinized because of their potential use in various applications requiring miniaturization. Besides the well-known CNT, many species of NWs-like nanomaterials can be synthesized from inorganic and/or organic materials and offer an impressive applicative potential from bio-environmental sensing and energy harvesting to ultra-low power electronic devices and high density memories. Nevertheless, the use of single NW in real applications asks for identifying their intrinsic behavior and requires to manipulate and contact them properly. At the nanoscale, a simple resistance measurement can revealed itself quite challenging.

Although it is possible to integrate NWs directly into some specific device platforms during synthesis (see appendix B.3), it is more common to make NW devices starting from a NW suspension [22]. Various methods were developed for positioning and aligning NWs on a substrate, using microfluidic [226], electrostatic interactions [214] or dielectrophoretic methods [227, 16] or again methods based on optical trapping [228, 229].

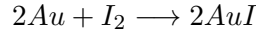
The techniques used for contacting a single template-synthesized NW in planar configuration can be divided in two approaches:

- **the bottom-contact method.** The NW is deposited on top of the electrodes.
- **the top-contact method.** The electrodes are deposited on top of the NW.

In the present work, the main results were obtained using two different techniques for contacting NWs. The first one, the dropcast deposition is a bottom-contact approach and consists in depositing NWs in solution onto metallic electrodes predefined by lithography. The other technique uses a standard electron-beam lithography for defining the electrodes on top of the NWs similarly to what was performed in the work of Vila, L. [230].

4.2.1 From Template to Solution

To obtain a planar single NW device, independently to the technique used for contacting the NWs, it is needed to free the NWs from the polycarbonate template. This step is performed by dissolving the polycarbonate template in dichloromethane (CH_2Cl_2). Doing this, without any special care leads to a very few NWs in solution as often most of the synthesized NWs stay stucked to the gold bottom electrodes. Therefore, the removal of the gold back electrode is mandatory for freeing a maximum of NWs. Often *aqua regia* solution is used for Au etching. Here we preferred an iodine based solution for etching the gold layer as it does not etch transition metals such as *Co* or *Ni* and because it is characterized by a lower etching rate ($1 \mu m/min$ at *RT*) compared to *aqua regia* solution ($10 \mu m/min$ at *RT*). Gold and iodine form gold iodide via the following equation:



The solubility of *AuI* is improved by adding KI to the solution obtained in the mixing ratio $I_2 : KI : H_2O \text{ DI} = 10 \text{ g} : 2.5 \text{ g} : 100 \text{ ml}$.

Furthermore, adhesive tape can be used to prevent the etching solution to diffuse within the pores containing the upper Au segment of the HNWs. Once the Au layer is etched, the template should be quickly rinsed thoroughly in DI water, again to prevent the unintentional etching of the bottom Au segment of the HNWs and the template becomes transparent as only the adhesion layer remains¹. Also, it is preferable to remove also this adhesion layer, otherwise it would form residues during the deposition process. This can be easily etched in a specific solution. Once, the template was rinsed and dried in a N_2 flux, it is ready for being dissolved in pure dichloromethane.

Assuming a circular synthesis area of 5 mm of diameter, the (maximum) number of NWs in solution is about $N_{NW} \approx 10^8 \#$. As the goal is

¹Generally, a $5 - 10 \text{ nm}$ thick adhesion layer is deposited on top of the PC membrane before the *Au* electrode.

to deposit single NWs homogeneously on a substrate, the density of the solution has to be controlled by the amount of solvent and generally, for all non segmented NWs (metallic NWs, CNT, etc...) a sonication step is performed to homogenize the solution [230] but sonication has to be avoided when the solution contains HNWs. Finally, the solution is only stirred and slightly heated ($T \approx 45^\circ\text{C}$) to favor the dissolution reaction. From a solution of 100 ml, a drop of 1 μl contains a maximum of 1000 NWs. Depending on the chosen approach for contacting NWs, this density can be further decreased. Among these NWs, the observation of dispersions of tri-segmented 90 nm diameter Au-PPy-Au HNWs on oxidized substrate has shown that around 50 % were missing one metallic segment. This proportion of broken NWs depends of course on the diameter of the deposited NWs due to the stronger polymer/metal adhesion for higher diameter HNWs, but also on their length. It was noticed that short Au-PPy-Au HNWs -that is typically 12 μm long and below, are often in one piece. Also, PEDOT-based HNWs are much robust with better mechanical Metal-CP interfaces as only less than 25 % of the tri-segmented HNWs are broken when freed from the template [70]. This could stem from the optimized synthesis parameters and the strong interaction between the Au segments and the sulfur atoms present in the EDOT monomer.

4.2.2 Bottom-Contact Approach

Once the solution containing the NW is obtained, the simplest way to make a contact to a single NW is to deposit directly a small quantity of the solution containing the NWs on top of a substrate with predefined electrodes. The procedure is exemplified in the Fig. 4.2.(a). Because of their low weight ² the position of HNWs in a solution is dictated mainly by the forces induced by the different flux occurring in the solvent drop due to its evaporation and the interaction of the solvent with the substrate. In the two following sections, we present the simplest dropcast deposition method and the dielectrophoretic assembly.

The dropcast deposition is a passive method, which requires a high concentration of NWs to increase the probability that a single NW falls *correctly* onto more than one electrode. In order to further increase this probability, a high surface density of electrodes is desired. As a result, we designed 180 μm long electrodes with different spacing from 1 μm to 5 μm . The increase of the electrode density is limited by the smallest dimensions (smaller than $150 \times 150 \mu\text{m}^2$ is not reasonable) of the pads required to contact the device to the measurement system.

²The weight of a typical 100 nm diameter, 15 μm long HNW is about 1 pg.

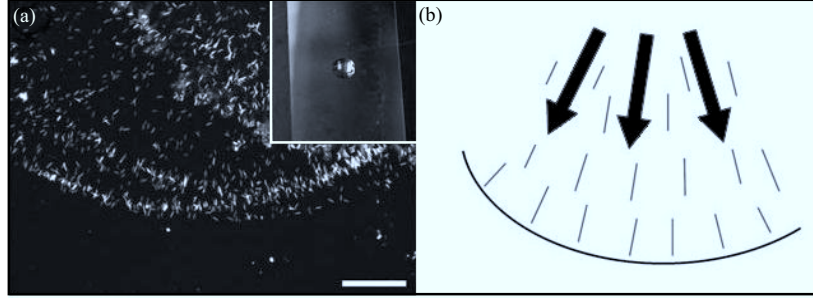


Figure 4.1: Evaporation induced deposition and alignment of NWs at the solvent-substrate contact line. (a) CCD image showing a typical pattern of metallic NWs formed upon drying a $10\text{-}\mu\text{l}$ droplet of solution in methylene chloride onto a hydrophilic glass slide. (b) Schematic illustration of the deposition of NWs at the edge of a drying droplet on a horizontal substrate. From reference [22].

While RT measurements can be performed with a probe system, low- T measurements require the devices to be contacted to the sample holder and the measurement system by hand using silver paint and gold wires. The Fig. 4.2 gives a 3D view of a typical device designed for contacting NWs by the dropcast method. Typically, 50 sets of four gold electrodes with the corresponding pads are easily defined on a $6 \times 8 \text{ mm}^2$ substrate.

The Fig. 4.1 gives CCD pictures of a deposition of NWs obtained by the evaporation of the solvent. This is the simplest way to deposit NWs onto a substrate. The global alignment of the NWs is induced by the shape of the solvent-substrate contact line during the evaporation of the solvent [214] and this process can be influenced by structuring the substrate. For instance, trenches - obtained by dry etching of the SiO_2 layer could be advantageously used to trap HNWs. Unfortunately, this dropcasting is not selective as it deposits onto the electrodes HNWs but also the dirt present in the solvent. We will show below other techniques that can be used to improve the deposition. Let's first detail the electric devices and their fabrication process.

A schematic diagram of the process given in the Fig. 4.2.(c) and more details are given in the appendix C. Essentially, a $360 \text{ }\mu\text{m}$ thick, 3 inches Si highly doped wafers (Si $\langle 111 \rangle$, $3\text{-}5 \text{ m}\Omega\text{m/sq}$) are oxidized in a dry atmosphere to obtain high quality and uniform SiO_2 layer (step 1). Gold or platinum pads and electrodes are defined by an optical or e-beam lithography (steps 2 & 3) followed by the evaporation of a 100 nm thick Au or Pt layer with a typical adhesion layer of 5 nm of Cr or Ti (step 4). Then a lift-off is performed generally in acetone followed by

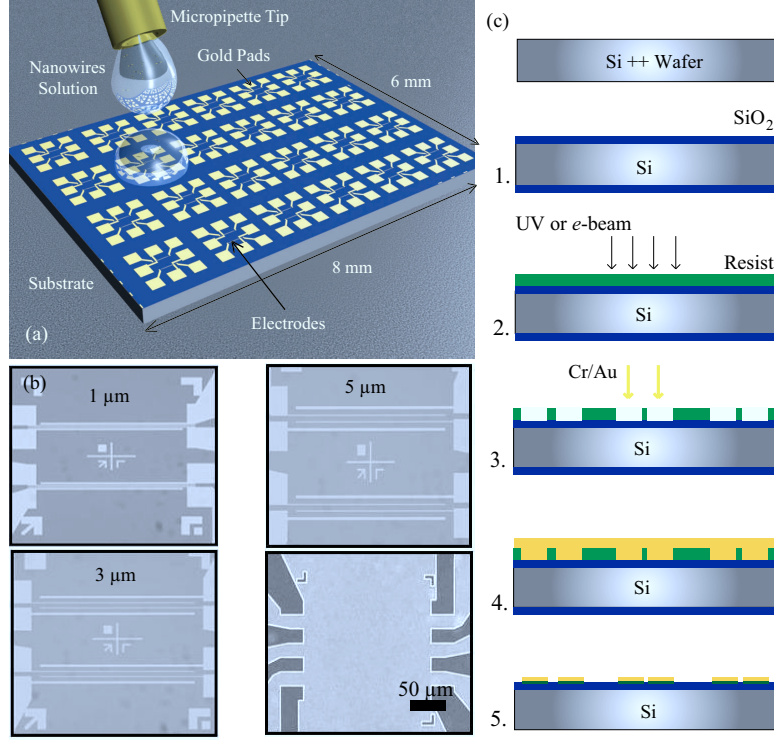


Figure 4.2: (a) 3D view of an electrical device designed for contacting NWs by the dropcast method. (b) CCD images of the electrodes area designed for the dropcast deposition. (c) Schematized fabrication process of electrical devices.

rinsing the wafer in isopropanol and water. Wafers are diced to obtain single devices with typical dimensions of $6 \times 8 \text{ mm}^2$ (see Fig. 4.2.(a)).

Once a drop of solution is deposited onto the substrate, it has to completely evaporate to allow the NWs to enter in contact with the substrate (SiO_2). As the solvent evaporates, the volume of solvent decreases but with a constant number of NWs and impurities coming from the dissolution of the membrane. Consequently, if nothing is done, various dirts such as broken NWs and PC residues are concentrated and will be deposited together with NWs as shown in the Fig. 4.3.(g) and (h). This situation has to be avoided as the dirts have a huge impact on the measured electrical properties of deposited NWs. Even if a single NW seems correctly deposited onto gold electrodes according to optical inspection, only electrical measurements could reveal the quality of the electrical contact obtained. For example, the two HNWs given in the panel (c-d) presented highly nonlinear and non reproducible ($I - V$)

characteristics at RT while comparable HNWs given in the panel (a-b) present Ohmic characteristics.

Short sonication can be used for cleaning the surface, when the density of NWs deposited in the region of interest (electrodes) is high. But in the special case of HNWs, sonication is prohibited as it is the best way to break them in pieces.

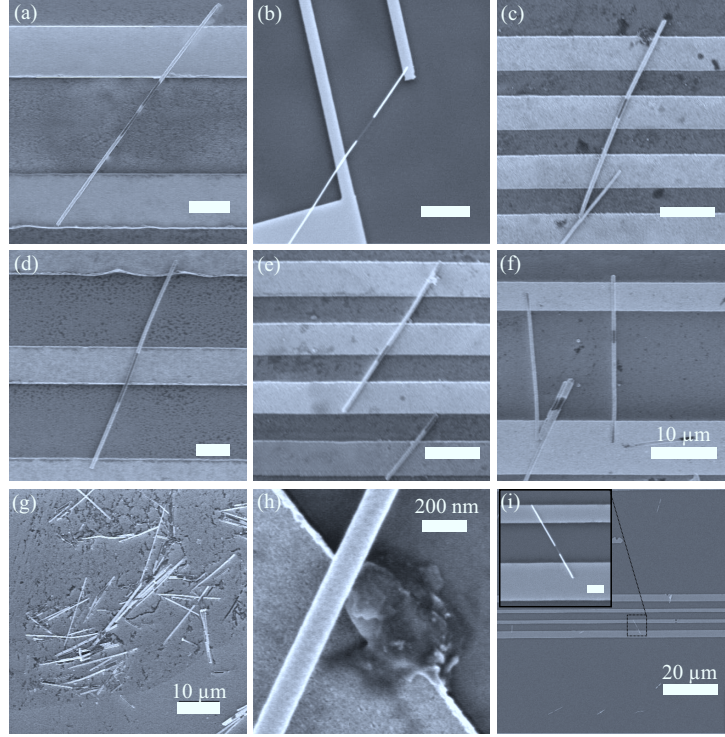


Figure 4.3: SEM pictures of HNWs contacted by the bottom-contact approach. The scale bars are $2\ \mu m$ otherwise indicated.

Remarkably, the experience has shown that the deposition process is greatly improved by changing the condition of the dropcast. Indeed, when performed on a heated substrate above $40^\circ C$ - the boiling point of the solvent, the deposition of NWs onto the substrate occurs homogeneously while the PC and the other impurities stay dissolved in the solvent drop which can be easily removed by a nitrogen flux. Then, presence of NWs is checked by optical inspection before rinsing thoroughly with pure solvent. Thanks to this procedure, single isolated NWs are obtained with very few impurities, dirt and PC. For comparison, pictures of a hot dropcast and a normal dropcast are shown in the panel (i) and (g) of the Fig. 4.3, respectively. With the *hot dropcast*, the

deposited NWs are not glued together by PC residues and are homogeneously dispersed onto the substrate. This *hot dropcast* is essential for the deposition of NWs onto membrane-based devices for which sonication is not allowed (see section 4.4) and was used also for the dispersion of HNWs contacted by a top-contact approach.

Besides the random spatial distribution of deposited NWs onto the substrate obtained by the dropcast method, the orientation or the alignment of the deposited NWs to electrodes is not always the *good* one. Indeed, it is driven mainly by a shear force during solvent evaporation [214] which are not easy to control. As a result, the probability to deposit *correctly* a unique NW onto electrodes is further decreased. Here, *correctly* means that the NW is contacted by at least two electrodes at both extremities and exhibit linear ($I - V$) characteristics at RT with low contact resistances. Interestingly, as it will be shown in the section B.2, this probability can be enhanced by the use of an external electric field to trap NWs directly onto the electrodes.

4.2.3 Top-Contact Approach

Because top-contact approaches allow to perform several cleaning steps, they appear more interesting in the point of view of electrical characterization of single HNWs despite the higher cost (time and resources) associated to these techniques. The contacting procedure of the top-contact approach can be summarized as follows. Prior to the electrodes fabrication step, the dispersed HNWs are deposited onto a substrate by the *hot dropcast* technique. Here, the substrates are identical to those used within the bottom-contact approach but the central part of the device containing the electrodes is left empty. A CCD image of an empty device is given in the Fig. 4.4.(a). The device is then thoroughly rinsed with pure solvent in a home made soxhlet like system in which solvent is evaporated from a heated bath and condensed to flow on top of the device continuously. The panels (b-c) of the same figure gives two examples of 110 nm diameter HNWs as observed after the cleaning procedure. Then electrodes are deposited on top of NWs. While many techniques (shadow mask, optical lithography,...) can be used for the deposition of the electrodes, only the EBL-based technique gave satisfactory results and was used for the RT measurement of single HNWs (see section 5.3). Another top-contact technique was used in this work for contacting single HNWs. This technique allows to deposit Pt electrodes directly on top of the NW by the chemical decomposition of a gaseous precursor similarly to a local chemical vapor deposition process. This technique is briefly presented in the appendix B together with a few measurements

obtained for single HNWs.

Once the HNWs are deposited onto a substrate by the *hot dropcast* technique, the device is then thoroughly rinsed with pure solvent in a home made soxhlet like system in which solvent is evaporated from a heated bath and condensed to flow on top of the device continuously. The device is then dried in a nitrogen flux. Careful observation with an optical microscope determines the presence of entire HNWs. The positions of the extremities of the HNW gold segments are measured relatively to the electrodes and/or alignment marks, directly on an image taken at high magnification such as the one given in Fig. 4.4.(b-c).

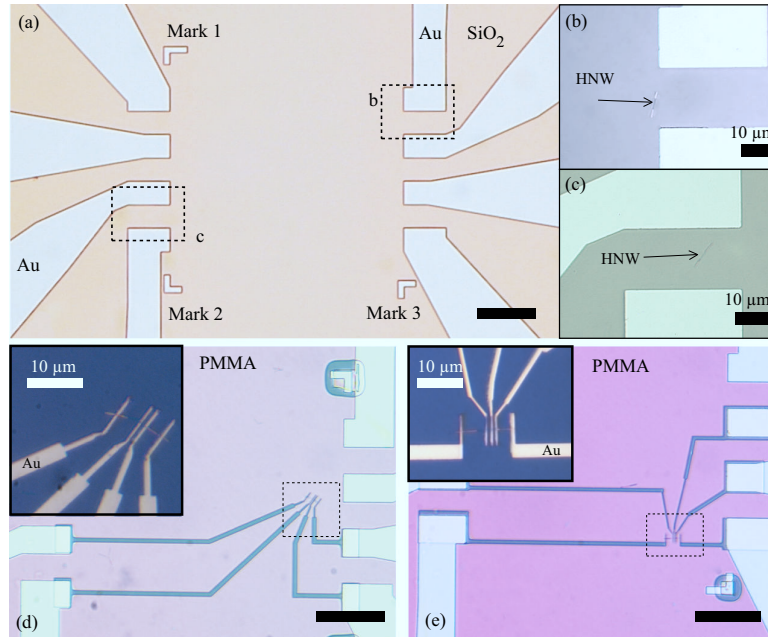


Figure 4.4: CCD images of SNWs devices at different steps of the EBL processing. The scale bars are $50\ \mu m$ unless otherwise indicated. (a) view on a device's central part with 8 contacts and 3 alignment marks ready for the dropcasting of HNWs. (b-c) Examples of high resolution CCD images taken for the position measurements of HNWs.

These coordinates are used for drawing a set of electrodes adapted for each HNW and fitting in the contacts pads shown in the Fig. 4.4.(a). For high precision in the measurement of the position of the HNWs which is required for the placement of a lateral gate for instance, SEM imaging can be used. The drawback arises from the unavoidable e-beam exposure of the NW to be contacted. It is thus preferable to observe cautiously the sample as little as possible, preferentially at low magnification and

using a very low beam current in order to limit as far as possible the exposure of the NW. Once the NW spotting is performed, the EBL resist is deposited on top of all the sample. PMMA is generally most commonly used as a high resolution positive resist for direct write e-beam as well as x-ray and deep UV microlithographic processes [231]. In this work, high molecular weight PMMA (950 *k*), dissolved in chlorobenzene (2 – 7 %) was spincoated at moderate rotating speed and acceleration, typically $\dot{\omega} \approx 2000 \text{ rpm}$ and $\ddot{\omega} \approx 2000 \text{ rpm.s}^{-1}$ and baked in an oven at $T = 120 - 140 \text{ }^{\circ}\text{C}$ under nitrogen atmosphere for at least 30 min. Depending on the electrodes thickness, width and spacing, the EBL resist thickness should be adapted to allow an easy removal of the lift-off procedure. In all cases, the resist thickness should be at least three times higher than the metal thickness. The best results were obtained with the use of a bilayer resist made with the followed spincoating of layers of a copolymer PMMA-MAA @ 4.5 % and PMMA 950 k @ 4 % (in chlorobenzene) with typical thickness of 150/600 nm spincoated at $2000 \text{ rpm} / 2000 \text{ rpm.s}^{-1}$. This bilayer produces nice undercut profiles helpful in the lift-off process. Examples of developed EBL are given in the Fig. 4.4.(d-e).

Generally, the exposure is performed with a dose varying between 350 and 450 $\mu\text{C}/\text{cm}^2$. The value could be adapted to the conditions, equipment and developer used [231]. Prior to the EBL exposure, two point and three point alignments are performed to ensure a good overlap of the designed electrodes onto the predefined pads. The experience has shown that marks reading procedure is mandatory to reach high accuracy in the positioning of the electrodes, especially when several contacts are deposited on a single HNW. In this work, an accelerating voltage of 30 *keV* was used for all exposures. The effect of the e-beam exposure is to break the long PMMA chains into several fragments which are soluble and thus can be removed in a proper solvent. In this work, PMMA was developed in a 3 : 1 mixture of isopropanol alcohol (IPA) to methyl iso-butyl ketone (MIBK) for 90 s and then rinsed in pure IPA for 60 s and dried with filtered nitrogen³.

Prior to the deposition of the Au electrodes, a short cleaning oxygen plasma is performed to remove all PC and resist residues that could remain on the NWs due to the previous processing steps. The plasma is performed with a K1050X Plasma etcher/cleaner⁴ an applied power of 20 *Watts* at a pressure of 2 *mbar* of O_2 during 20 seconds. This ensures a clean NW-to-electrode interface, removing all the residual PMMA which

³The detailed process is given in the appendix.

⁴Quorum Technologies Ltd. Charlswoods Road, East Grinstead, West Sussex, RH19 2HL, United Kingdom

translates into a good electrical contact. Of course, this step can be questioned when contacting a single CP NW as conjugated polymers could be sensitive to plasma exposure. Actually, the parameters of the plasma (time, power) were optimized to etch only a few nm of PMMA⁵. To really check the influence of this cleaning steps on the CP segments, single HNWs should be measured before and after a O_2 cleaning plasma.

4.3 Measurement Techniques

All the electrical measurements of NWs presented in this manuscript (resistivity, current-voltage characteristics, magnetoresistance, transistor transconductance, etc...) can be resumed to voltage and current measurements performed simultaneously as a function of a parameter such as the temperature or the magnetic field. The figure 4.5.(a) gives a schematic view of a homogeneous sample contacted by several electrical probes. These probes are characterized by several geometrical and physical parameters (width d , thickness t , resistivity ρ_{probes}) and define at the same time, the interface with the sample. The quality of the resulting interface can vary widely depending on the technique and the conditions used for defining the electrodes. A good electrical characterization of the intrinsic properties of a sample requires clean and controlled interfaces to inject properly electrical charges through the metal/sample interfaces. Otherwise, the intrinsic electrical properties of the sample could be hidden by interface related mechanisms that limit the charge transport. Contrary to the case of inorganic materials where Ohmic contacts are obtained by a doping procedure consisting often in a diffusion of dopant, organic materials are directly contacted by metal electrodes [232]. We will see that the simple resistivity measurement is not as trivial as it seems especially when the sample is not homogeneous and presents nanoscale dimensions. Let's briefly review the measurement techniques.

4.3.1 Two-Probe Measurement

The so-called two-probe resistance measurement technique consists in injecting a known current I through the sample between two leads, and to measure the resulting voltage drop ΔV_{2C} using the same leads (see Fig. 4.5.(b)). The sample resistivity ρ_{2C} can be easily deduced assuming the section (S) and the length (L_{2C}) of the sample are known: $\rho_{2C} = \Delta V_{2C} S / I L_{2C}$. The two-probe measurement technique was widely

⁵Which is the typical thickness of potential PMMA residues on the NWs

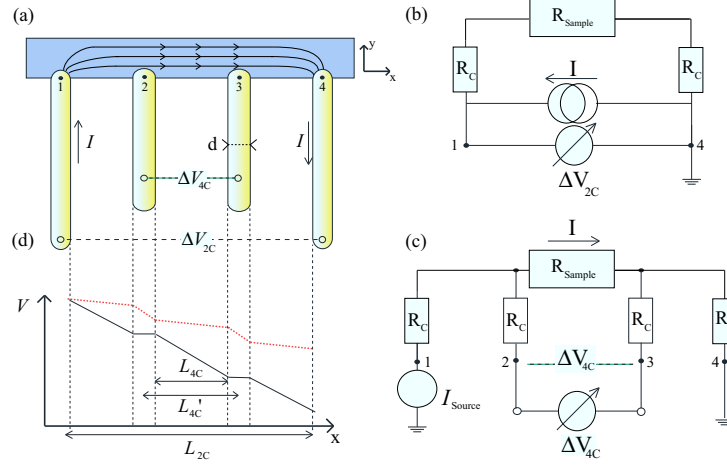


Figure 4.5: (a) Schematic view of a NW like sample contacted by four electrical probes. (b) Equivalent circuit of a two-probe measurement. The measured resistance includes the contact resistances R_c . The influence of the interface mechanisms are included in the measurements. (c) Equivalent circuit of a four-probe measurements. (d) Voltage drop along the sample in the case of metallic and highly resistive probes (red curve).

used and is still often performed but presents two main drawbacks. First, the sample resistance is over-estimated as it includes a total contact resistance $2 R_C$ that may not be always neglected. Especially, care should be taken when measuring low resistive samples such as metallic NWs. secondly, as the ΔV_{2C} is measured at the same point where the current is injected, in the case of a *bad* lead-sample interface, ΔV_{2C} could contain an important voltage drop due to charge injection issues which could result in non-linear characteristics. This could happen for oxidized or contaminated sample surface with PC residues or other materials present in the solvent or because of a work function mismatch (see section 4.3.3). Almost all the HNWs contacted by the bottom contact approach were characterized by two-point measurements. The main reason is simply that two good (Ohmic) electrical contacts to a single HNWs is statistically much more probable and easy to obtained with the dropcast method, than four.

4.3.2 Four-Probe Measurement

A solution to fix these problems is given by the four-probe technique. As exemplified in the Fig. 4.5.(c), besides the current-injection leads (1

and 4), two more leads (2 and 3) are used for measuring the voltage drop ΔV_{4C} . In the case of a perfect voltmeter (with an infinite impedance), no current flows in the leads 2 and 3. As a consequence, ΔV_{4C} is exactly equals to the voltage drop between the point 2 and 3 of the sample and all the measured current I goes through the sample. The resulting resistivity $\rho_{4C} = \Delta V_{4C} S / I L_{4C}$ is not affected by the charge injection mechanisms occurring at the lead-sample interfaces.

Despite the apparent simplicity of the four-probe technique, a few precautions should be taken for avoiding errors. Firstly, as shown in the Fig. 4.5.(a), the presence of the voltage probes could influence the voltage drop along the sample (shown in the Fig. 4.5.(d)) when the probes width d is comparable to distance L_{4C} . In such a case, it becomes difficult to define precisely L_{4C} . This translates in an error in the estimated resistivity ρ_{4C} . Furthermore, when the resistivity of the probes is comparable or higher than the resistivity of the sample, the voltage drop occurring along their width induces an error in the measured voltage ΔV_{4C} which can combine to other errors, the calculation of the resistivity ρ_{4C} that can not be neglected. Obviously, all the samples are not homogeneous in their length as the one depicted in the figure 4.5. Consequently, it is preferable to put more than two voltage probes along non-uniform samples to be able to track the resistivity change along the sample. For uniform samples, this will give the possibility to check the consistency of the measurements by performing several four-probe measurements with various sample length L_{4C} .

4.3.3 Contact Resistance

The contact resistance R_C , of a device can be determined by subtracting the four-point resistance R_{4C} from the two-point value from the inner electrodes of the four-point contact. Generally R_C includes the resistance of the leads R_{Leads} and an eventual interface resistance R_{Ci} . The specific contact resistivity is then defined as [233]

$$\rho_{RC} = R_C A_C, \quad (4.1)$$

where A_C is the area of the contact which can be assumed to be half of the total NW surface area lying under the metal lead [234]. Noteworthy, the contact area on nanoscale samples are often 2 or 3 orders of magnitude lower than for conventional devices, therefore, typical R_C values obtained in a single NW device could be hundred or thousand times higher [233].

Many measurements of single HNWs presented in this thesis were performed in a two-probe configuration. This implies that the measured

resistances also include an unavoidable contact resistance R_C in series with the NW. R_C cannot be determined only from a single two-point measurement, nevertheless, several two-point measurements of single *Au* NWs, performed in both contacting approaches (top and bottom contact) exhibited resistances lower than a few hundred ohms. This suggests that a two-probe measurement of a single HNW performed by contacting its metallic segments, should present negligible contact resistances ($R_C < 10^2 \Omega$) Compared to the resistance of a single HNW $10^6 < R_{HNW} < 10^8 \Omega$.

When the interface is between a metal and a semiconductor, R_C can result from Schottky type contacts. In this case, the zero-voltage specific contact resistivity can be written as follows

$$\rho_{RC} = \frac{k}{A^*eT} \exp\left(\frac{e\Phi_S}{k_B T}\right), \quad (4.2)$$

where, A^* and Φ_S are the Richardson constant and the Schottky barrier height (SBH), respectively. As it will be shown later for HNWs, the contact resistance can often be modified by doping [235].

4.4 Micromachined Devices

4.4.1 Overview

In the recent years, many studies were devoted to the structural and electronic characterization of low dimensional materials. Among them, nanowires (NWs) and nanotubes were intensely scrutinized because of their potential use in various applications requiring miniaturization. Besides the well-known CNT, many species of NWs-like nanomaterials can be synthesized from inorganic and/or organic materials and offer an impressive applicative potential from bio-environmental sensing and energy harvesting to ultra-low power electronic devices and high density memories. Nevertheless, the use of single NW in real applications asks for identifying their intrinsic behavior and requires to manipulate and contact them properly. At the nanoscale, a simple resistance measurement can revealed itself quite challenging.

Moreover, as the intrinsic properties of materials depend on their microstructures, their elemental composition and the nature of their surfaces, the understanding of nanoscale materials should be improved by combining the structural characterization with the electrical measurements on the same sample. Hence, devices that enable the correlation between structural properties - as contemplated, for instance, by trans-

mission and scanning electron microscopies - and electrical properties of single NWs are requested.

In the following section, we present the fabrication of a multipurpose platforms, fabricated via Si micromachining techniques and state-of-the-art nanoscale processing which offer a unique tool for studying single nanostructures. Despite the useful information that could bring such tool, only a few publications proposed membrane-based devices for studying properties of nanomaterials such as CdS nanorods or CNT [221, 222, 223, 225]. Here, the platforms were used with a multitude of contacting techniques such as the standard e-beam lithography (EBL), dielectrophoretic trapping and electron-beam induced deposition (EBID) (see section 4.2). The microdevices are plasma cleanable and exhibit a very good chemical stability against various substances (acids, bases, oxidizing agent,...) but also present an excellent thermal stability up to very high temperature ($T > 800^\circ\text{C}$). All the features of the microdevices stem from the very thin (30-80 nm) Si_3N_4 membrane which is transparent to electrons, thus making the device compatible with TEM analysis including the high resolution imaging in bright/dark field mode, the selected area electron diffraction (SAED), Electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX) analysis [225]. This analysis can be coupled to the topology of the samples observed by AFM and correlated to T -dependent electrical measurements. Furthermore, because of the good thermal properties of the Si_3N_4 membrane, the Seebeck coefficient and the thermal conductivity measurements of a single nanostructure are possible (see appendix C).

In the following section, we describe briefly the fabrication of membrane-based devices.

4.4.2 Device Fabrication

We have used Si micromachining techniques for batch-producing devices based on Si_3N_4 membranes on top of which are deposited the NWs to be analyzed. They are compatible with both bottom and top-contact planar approaches for contacting single NWs (see section 4.2).

Figure 4.6 gives the schematic view of a single device at each step of the fabrication process. The detailed fabrication process is given in the appendix C. The relatively small dimensions ($4800 \times 4800 \mu\text{m}^2$) of the final device are imposed for being compatible with various sample holders (AFM, TEM). The fabrication process can be described as follows. Essentially, 200 μm -thick (100) Si wafers are oxidized to obtain a high quality 20 nm thick SiO_2 layer. Then a low pressure chemical vapor deposition (LPCVD) Si_3N_4 layer is then deposited on both side

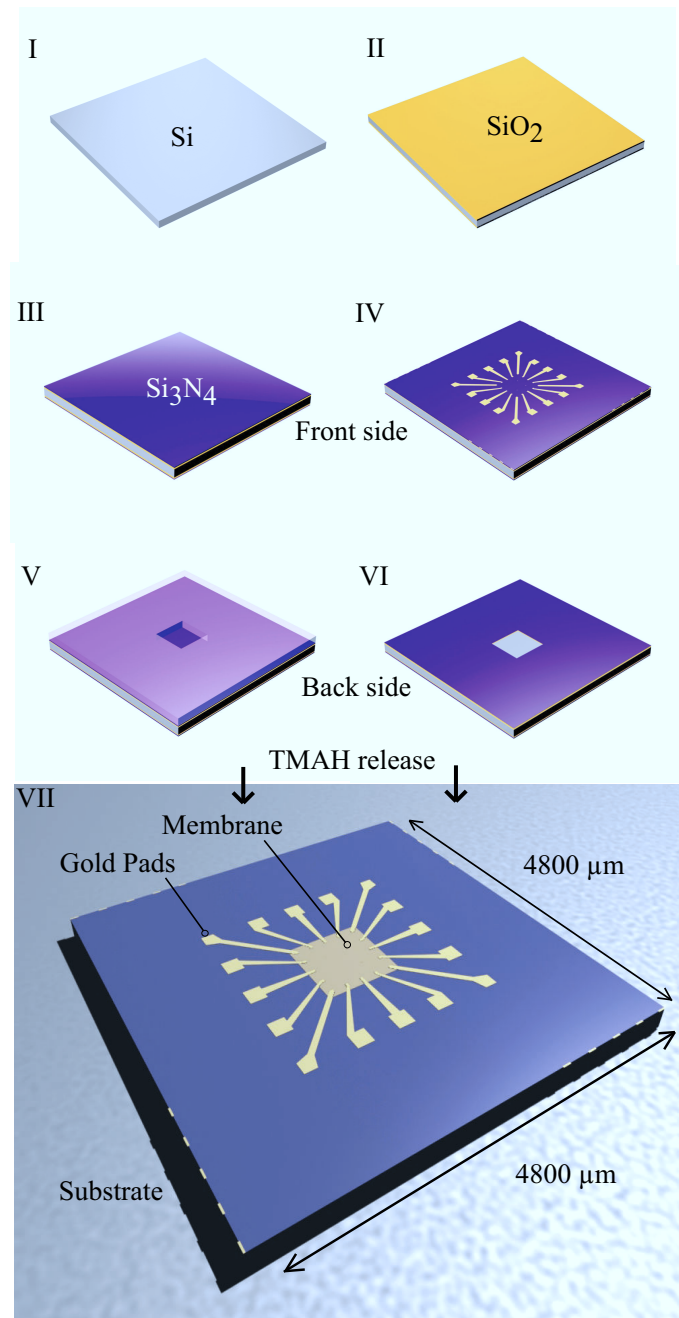
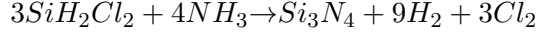


Figure 4.6: Schematic view of each important steps of the fabrication process of microdevices.

of the wafers according to the following reaction of dichlorosilane and ammonia



with a typical thickness between 30 and 80 nm. This layer is crucial to the microdevice as its intrinsic properties (the most important are its electrical and mechanical properties) will determine mostly the properties of the final device's membrane. Because of the LPCVD furnace limitations, only stocheometric Si_3N_4 was used. The deposition of stocheometric nitride is performed at a average rate of 7 nm/min with a gas flow ratio of 3 to 1 of ammonia and dichlorosilane respectively at a temperature of $T \approx 800^\circ C$ and a pressure of $P \approx 370$ mTorr. Nevertheless, it is known that Si-rich Si_3N_4 layer with far better mechanical properties can be obtained by modifying the deposition conditions. while the stocheometric nitride present a tensile stress of 0.8 – 1.2 GPa [236], it could be decreased until values as low as 100 MPa with gas flow ratio of 1 to 6 ammonia and dichlorosilane respectively.

Afterward, 24 Pt or Au pads, 100 nm thick, are defined by optical lithography. Generally, the lift-off technique is avoid as it can lead to irregularities of the contact edges when defined by optical lithography. These irregularities can be problematic for the quality of the electrical contact with thin samples like EBID Pt line [237]. Thus, another technique is used and consists in the wet etch of the metal layer (deposited on the full wafer) covered by a thick resist mask defined by optical lithography. Then, openings in the nitride layer on the back side of the wafer are created by a double side alignment photolithography followed by dry etching of the exposed areas in an SF_6 plasma. These two previous steps can be interchanged, nevertheless, the mask for the first optical lithography performed on the wafer should be carefully aligned against the flat of the wafers.

Membranes are then released by an anisotropic etching of the Si all through the wafer in Tetramethylammonium hydroxide (TMAH) solution 10% at $T=90^\circ C$ at an average etch rate of 0.8 $\mu m/min$. The etch rate depends on the TMAH concentration, the doping level of the silicium and is quite sensitive to contaminations of the solution [238]. Because the wafer thickness is given only within a $\pm 25 \mu m$ margin, the total etch times often over exceeds four hours. Because the etching time is important, care should be taken to do not etch unintentionally other materials present on the device. TMAH etching present an excellent selectivity for noble metals such as Pt and Au while Si_3N_4 and SiO_2 are considered as etch stop layers exhibiting very low etch rates (typically 3 nm/hour in a 10% at $T=90^\circ C$). But even such low etch

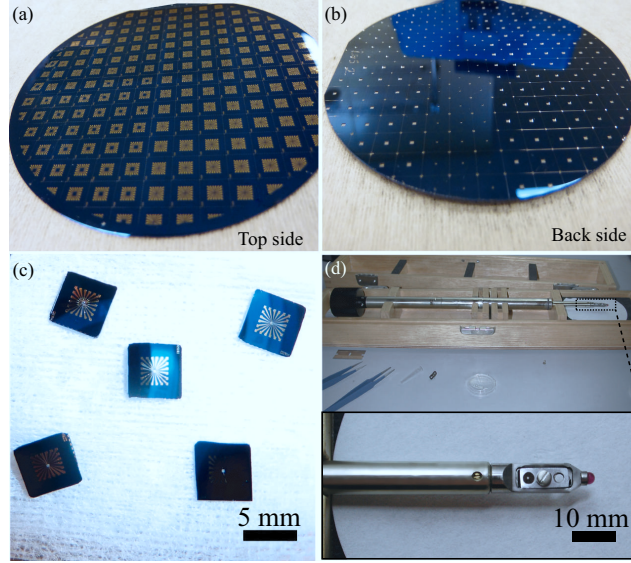


Figure 4.7: (a-b) Front and back view of a 3 inches wafer during the fabrication process. (c) Single devices obtained after the TMAH etching. (d) Mounted microdevice on the TEM sample holder.

rate should be taken into account for determining the final membrane thickness, especially for very thin membranes.

The centering of the membrane is important for the compatibility with the TEM sample holder shown in the Fig. 4.7.(d). Nevertheless, the usual dicing process is prohibited for TMAH etched wafers because of the fragility of the membranes. Auto-alignment of the membranes is performed by defining long trenches on the back side of the wafer as shown in the . The TMAH etching is often followed by the removal of the 20 nm thick SiO_2 layer in a HF @2% solution. After the SiO_2 etching, the devices are carefully and thoroughly rinsed in a DI water and then dried in nitrogen flux. Consequently, wafer can be easily cut by hand after the TMAH etching to obtain the devices ready for the deposition of NWs as shown in the panel (c).

The optical masks were designed with three types of devices characterized by a different empty central area, each are associated with 3 different membranes dimensions $100 \times 100 \mu m$, $250 \times 250 \mu m$ and $500 \times 500 \mu m$.

4.4.3 Nanowire Integration into Microdevices

The experience has shown that compared to others techniques, the EBL top-contact approach gives better results, i.e. more NWs are contacted with very low contact resistances. As a result, this technique is often preferred for microdevice integration, furthermore it allows custom design of the electrodes for each addressed NW as shown in the Fig.4.8. Also, because the top-contact approaches allow to perform several cleaning steps, they appear more interesting in the point of view of electrical characterization of single HNWs despite their higher cost (time and resources).

The deposition of NWs onto the microdevices is performed by the *hot dropcast* technique which gives the better results concerning the dispersion of the NWs (see section 4.2.3). The Fig. 4.8 schematically presents the NWs integration process onto microdevices and gives several CCD images of the integration of HNWs onto microdevices by EBL process. After the dropcast, the device is then thoroughly rinsed with pure solvent in a home made soxhlet like system in which solvent is evaporated from a heated bath and condensed to flow on top a the device continuously. Then, the relative position of both extremities of each HNWs are noted down for designing the electrodes layout and the PMMA resist is deposited onto the samples. Based on these information the layout of the electrodes can be drawn in the *Elphye* layout editor to fit to the Cr/Au pads design of the microdevice. Often a metal line is added to the layout as, measured in a four-probe configuration, it allows to estimate precisely the electrical conductivity of the deposited electrodes (as shown in the panel d of the Fig. 4.8). Interestingly, after calibration, this line can also be used as thermometer which benefits thanks to the SiN membrane, of an excellent thermal link to the HNWs. Prior to the deposition of the Au electrodes, a short cleaning oxygen plasma was performed to remove all PC and resist residues that could remain on the NWs due to the previous processing steps. This ensures a clean nanowire-to-electrode interface, which translates into a good electrical contact.

Due to the specificity of the substrate⁶, the dose is slightly increased compared to a standard EBL process to ensure a good developing of the resist. The resist used is a bilayer made with a copolymer PMMA-MAA @ 4.5% and PMMA 950 k @ 4% (in chlorobenzene) with typical thickness of 150/600 nm spincoated at 2000 *rpm* /2000 *rpm.s*⁻¹. In order to avoid the shadow-like evaporation effect due to the presence of NWs, the deposited Au leads must have a thickness of at least 100 nm

⁶A 100 nm thick Si_3N_4 membrane is almost transparent for 30 *keV* electrons.

to be continuous. Examples of NWs integration onto microdevices are given in the Fig. 4.8.

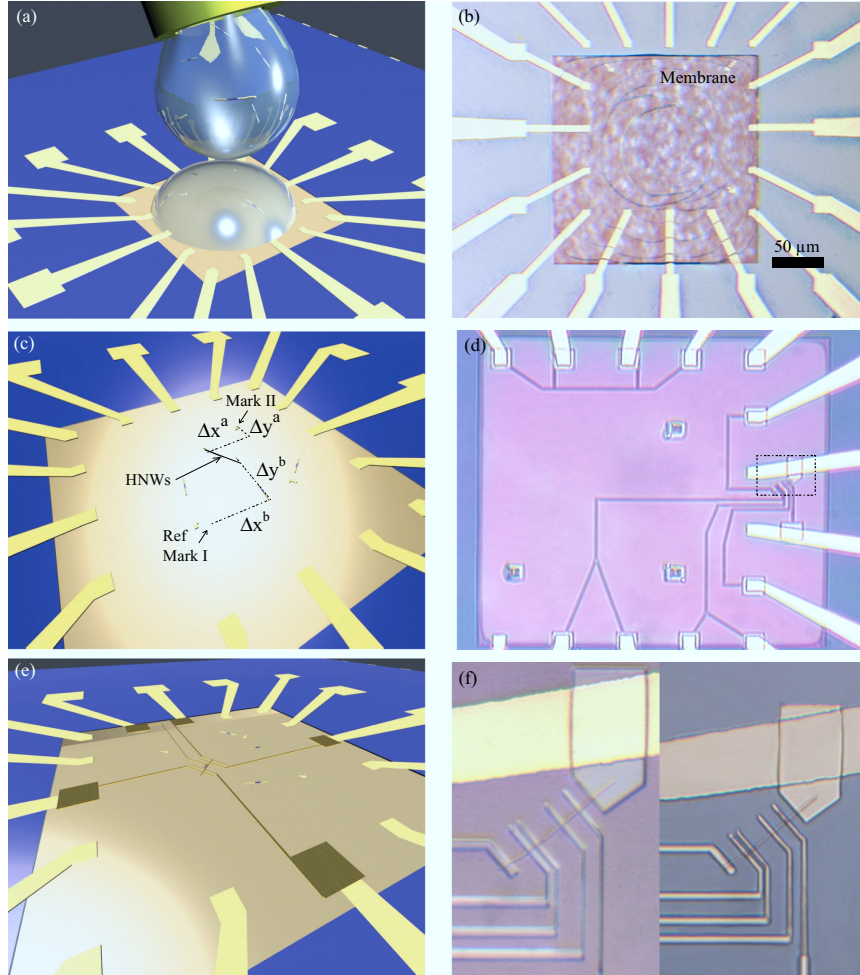


Figure 4.8: The top-contact approach is used for contacting NWs. (a) The deposition is performed by the *hot dropcast* technique. (b) CCD picture of a real device before rinsing. (c-d) After a thorough cleaning in pure solvent, the positions of several candidate NWs are noted down to perform the EBL. (e-f) View on schematized and real sample after the lift-off procedure.

The panel (f) of the same figure gives a zoom of the highlighted region in (d) where of a 110 nm diameter Au-PPy-Au HNWS is contacted and observed after the PMMA developing and the lift-off procedure.

4.4.4 Correlated Characterization

In the following sections, we present briefly the various analysis allowed by the use of microdevices. The main idea is to combine the possibilities given by powerful instruments that are TEM and AFM microscopes and to correlated the obtained structural information to electrical or thermal measurements performed on a single nanostructure (film, wire, particle...). To exemplify the possibilities offered by the microdevices, the results of the correlated characterization of Pt-C NWs are presented in the section 4.4.4.5 whereas the results obtained for HNWs will be detailed in the chapter 5.

TEM pictures and SAED patterns were obtained using a LEO 922 transmission electron microscope (Carl Zeiss SMT Inc.) operating at 200 *kV* while SEM imaging were performed using either a LEO 982 Field emission scanning electron microscope (FE-SEM, Carl Zeiss SMT Inc.) or a Philips-FEI XL-30 SFEG microscope combined to a Raith Elphy Plus hardware module, working at an accelerating voltage varying between 1 and 15 *keV*. The AFM imaging was performed with a *Nanoscope IV* from *Veeco* microscope. The electrical measurements were performed with an *Agilent B1500* Semiconductor Parameter/Device Analyzer equipped with high current resolution (0.1 *fA*) Source Measure Units and a *Süss-Microtech* Probe Station.

4.4.4.1 Electronic Imaging

Transmission, scanning electron and atomic force microscopes (TEM, SEM and AFM) together offer the most complete imaging tool available for the characterization of materials and especially nanoscale samples. Both electron microscopes can be equipped with X-ray spectrometers which information about the elemental composition of observed samples with a nanometer resolution. Compared to usual SEM, TEM imaging benefit of a much higher imaging resolution and present other capabilities such as electron spectrometry electron energy loss spectroscopy (EELS). The main counterpart of these techniques is the exposure of the sample to the high energy electron beam which damage (mainly by amorphization) organic materials such as CP but also inorganic samples such as thin Si NWs [239]. On the other hand, AFM offers the atomic resolution and is much less harmful for the sample. Furthermore, the AFM gives information on the third dimension of the sample which is not or not well represented in the SEM/TEM observations. Microdevices are designed to be compatible with all these techniques and thus deliver a large set of data that can be correlated to the electrical (and

thermal) measurements performed on the same sample.

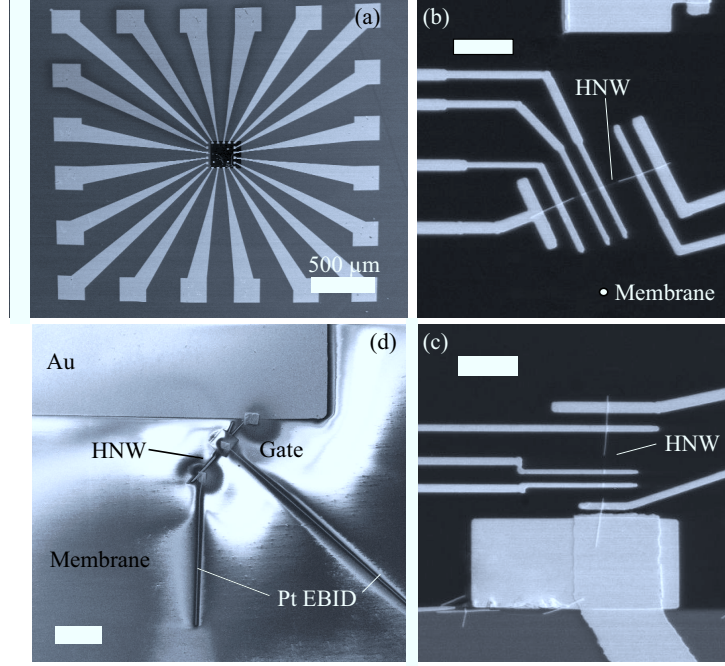


Figure 4.9: SEM pictures of a samples contacted on top of the membrane of microdevices. The membrane is $200 \times 200 \mu m$ wide. (a) View of a typical microdevice. (b-c) SEM pictures of two tetra-segmented HNWs contacted on top of a membrane. (d) Single PEDOT NW contacted in a FET configuration by EBID on top of a membrane. The scale bars are $5 \mu m$ otherwise indicated.

4.4.4.1.1 SEM Characterization The SEM characterization is easy to perform and is very useful to check the presence of HNWs deposited on a microdevice and offers several advantages compared to optical microscopes. It allows to determine with much higher precision than optical microscopes their length and to record the positions of both ends of HNWs to be connected.

Nevertheless, the information given by SEM observation is limited because of the size of typical HNWs. Indeed, the interesting features of the microstructure of HNWs are below usual SEM resolution. Because the microdevice membrane are excellent electrical insulators, charging effects or sample drift further limits the actual resolution of the microscope as exemplified in the panel (d) of the Fig. 4.9 which gives the SEM

image taken after the EBID deposition of EBID Pt leads.

Similarly, to the SEM pictures of the tetra-segmented HNWs given in the chapter 5 (see Fig. 5.5), The SEM micrographs shown in the panels (b-c) of the Fig. 4.9 do not allow the identification of each segment of the HNWs. Thanks to the development of the microdevices, TEM imaging is accessible as shown in the following section.

4.4.4.1.2 TEM Characterization TEM imaging allows to obtain structural information well beyond the resolution limit of a SEM. The only requirements concern the thickness of the sample which should be thinner than 150 nm. Because of the possible amorphization of sensitive samples, the TEM experiments are made as short as possible in order to minimize the effects of beam damage. Generally, the focusing is performed on an adjacent region of the sample, very close and the HRTEM micrographs are then quickly recorded.

Obviously, higher resolution micrographs are obtained for decreasing sample thickness and the membrane thickness should be as low as possible for enhanced resolution. The structuring of the membrane by making openings between electrodes which could be implemented only with low-stress nitride would offer better quality imaging but unfortunately the structuring of stoichiometric nitride membrane fails due to its very high tensile stress.

The example of a tetra-segmented HNWs imaging on a microdevice is given in the Fig. 4.10. Only based on TEM observations, it is possible to discriminate both metal-CP junctions which turned out to be impossible with SEM imaging. Indeed, the metal segment of the inset II exhibits a typical roughness of Pt NWs produced by chronoamperometry [49]. Furthermore, the metal segment of the inset I exhibits the typical morphology of a (second grown) *metal-onto-polymer* segment with a pronounced meniscus whereas the inset II exhibits the typical flat shape of the bottom *polymer-onto-metal* interface [145].

When a doubt still persists concerning the identification of the observed nanomaterials, the local elemental composition can be given by an energy dispersive X-ray (EDX) analysis performed locally. Complementary, to the information given by the imaging mode and the EDX analysis, the diffraction and selected area diffraction mode can reveal important and local informations concerning the structural properties of the observed materials such as its crystal type, its symmetry and orientation, the presence of defects.

4.4.4.2 AFM Characterization

Atomic force microscope allows to map surface topography with nanometer precision and thus offers, conjointly to the TEM and SEM analysis very complementary informations for observing and studying the morphology of nanoscale samples. Here, we present an example in the Fig. 4.11.(b) giving a topographic AFM image of the tetra-segmented HNWs (sample A) shown in the Fig. 5.8. The AFM imaging was performed with a *Nanoscope IV* from *Veeco* microscope operated in tapping mode with commercial Si cantilevers with a spring constant of 42 N/m and resonance frequency close to 300 *kHz*.

While electron beam based microscopies could obviously damage nanoscale CP materials deposited on microdevices, AFM offers the atomic resolution and is harmless for samples. As already mentioned, AFM gives information on the third dimension of the sample which is not or not well represented in the SEM/TEM observations. Interestingly, AFM could be used as a scanning gate microscope in which the conductive tip is used as a movable gate to modify locally the electronic charge transport within HNWs like what was performed for inorganic samples [240]. Microdevices are compatible with this technique and thus could deliver a large amount of original data that can be correlated to the electrical (and thermal) measurements performed on the same sample.

Interestingly, the AFM can also be used to study the mechanical properties such as the tensile elastic modulus of NWs like systems [241, 242]. Simple modifications of the microdevices would allow to correlate the mechanical measurements to structural and electrical data sets.

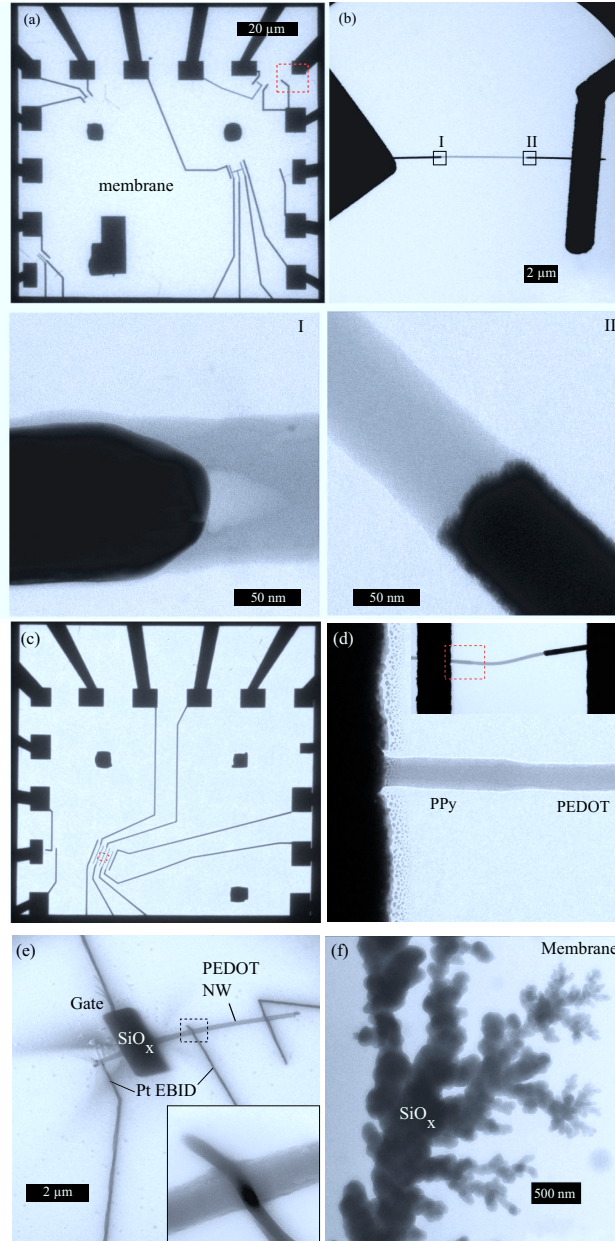


Figure 4.10: (a) BF TEM picture of the whole membrane of a microdevice containing HNWS circuitry at low-magnification. (b) Picture of a tetra-segmented HNWS (Pt-PANi-PPy-Au) with the two insets giving TEM pictures showing the different morphologies of each metal-CP junction. (c-d) Single tetra-segmented HNWS contacted by several probes with identifiable PEDOT-PPy junction. (e) View of a NWFET based on a PEDOT NW contacted by EBID Pt leads and a EBID SiO_x gate dielectric. (f) SiO_x nanotree produced during the oxide deposition.

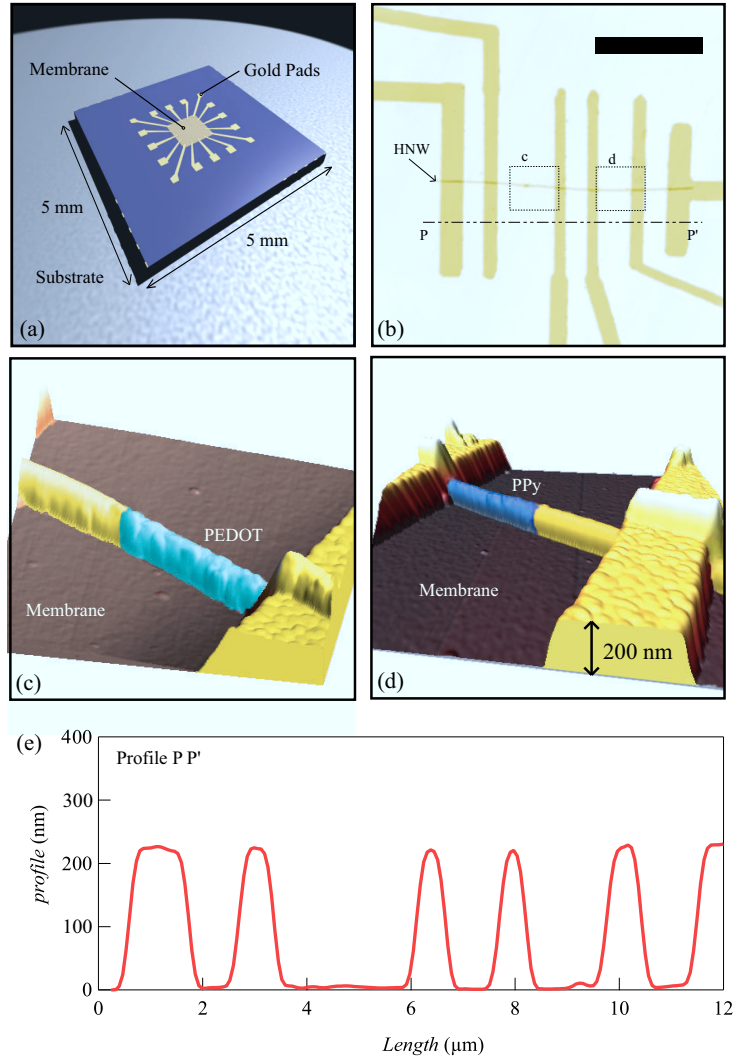


Figure 4.11: (a) 3D schematic view of a membrane-based device. (b) AFM image of a single tetra-segmented HNW (sample A) connected on top of a microdevice. The scale bar is 5 μm . (c-d) Perspective views of $2 \times 2 \mu\text{m}^2$ AFM images of each metal-CP junction. (e) profile of the electrodes along the HNW as shown in (b).

4.4.4.3 Energy Dispersive X-ray

The X-ray spectrometry, associated to the electron microscopes gives qualitative and quantitative elemental analysis capabilities covering almost the whole periodic table⁷, with a spatial resolution to the nanometer scale and analytical sensitivity close to the single-atom level [243]. In this thesis, energy dispersive X-ray (EDX) was applied as one of the principle characterization techniques. It allowed for instance, to determine the composition of each segment of the measured HNWs. EDX experiments were carried out with the *LEO 922* TEM equipped with an *INCA* x-sight detector from *Oxford Instruments*.

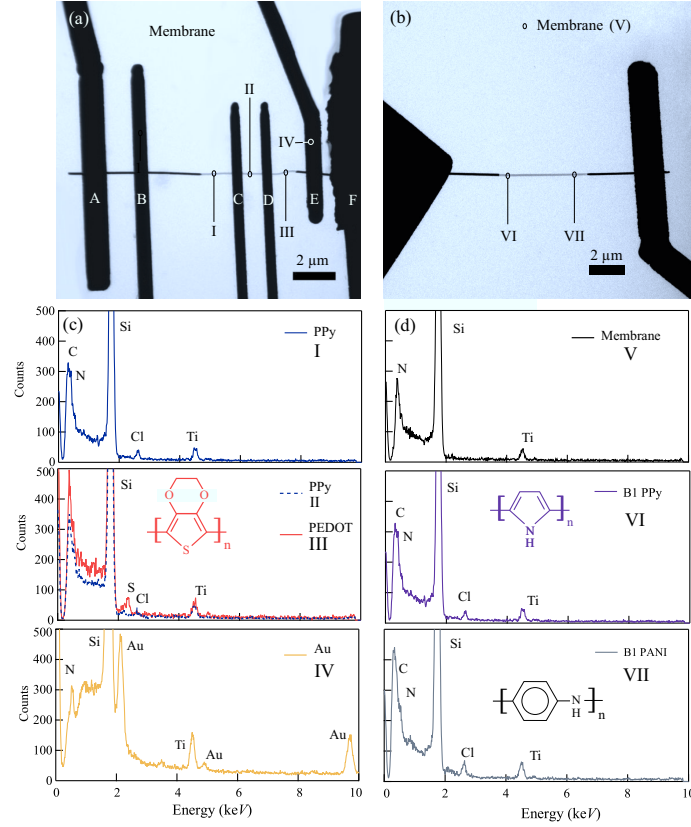


Figure 4.12: TEM pictures of a Au-PEDOT-PPy-Au (a) and Pt-PANi-PPy-Au (b) HNWs deposited on top of a microdevice membrane and connected with several electrodes. (c) Energy dispersive X-ray spectra measured at different positions on the microdevices shown in (a) and (b) (left and right column respectively).

⁷For elements with atomic number above $Z = 2$.

The basic principle of EDX is the following [244]: X-rays are formed from the interaction between the focused high-energy electron beam and the sample atoms. Inner shell electrons of the sample atom are excited and ejected from the shell. The atom subsequently relaxes to its ground state by means of a transition of an electron from an outer shell to the inner shell vacancy. This transition is accompanied by the emission of a X-ray photon characteristic of the sample atom and the particular transition which occurred. This allows the elements in the sample to be identified through the analysis of the spectrum. Every spectrum contains a continuum radiation contribution (*Bremsstrahlung*) [245] due to the deceleration of the electrons from the beam in the sample and a Ti peak stemming from the TEM sample holder used for the characterization. Also, every spectrum taken on microdevices contains the silicium (Si) and nitride (N) peaks because of the presence of the nitride membrane underneath the samples.

The Fig. 4.12 gives several spectra taken from the samples shown in the TEM micrographs of the panels (a-b). Recently, we have successfully demonstrated the formation of the PEDOT-PPy heterojunction within Au nanowires, using high-resolution TEM and EDX analysis performed on HNWs dispersed on a TEM grid [70].

Here, we reproduced the same EDX analysis of several HNWs contacted on top the microdevices. In the Fig. 4.12.(c) are shown the EDX spectra recorded on two different tetra-segmented HNWs: a Au-PEDOT-PPy-Au HNW and a Au-PANi-PPy-Au one (see panel (a) and (b) respectively) and whose measurements are presented in the section 5.4.1. Each spectrum corresponds to spots marked with roman numerals in the panels a and b.

The EDX measurements showed several peaks present in every spectrum and that can be ascribed to Si, N and Ti, in all samples. While the N and Si peaks correspond to the nitride membrane, the Ti peaks are induced by a contamination coming from the TEM sample holder. These spectra reveal also the presence of sulfur atoms - characteristic for PEDOT, only in the segment III while on the other hand, the segment I and II exhibit the presence of Cl atoms - characteristic for PPy. Therefore, two consecutive segments of PEDOT and PPy are present in the sample and could be ascertained by EDX analysis. This is further confirmed by the curved feature of the segment III which is typical of PEDOT.

Nevertheless, it appears that the information given by the EDX spectra is not always enough as exemplified by the case of the Pt-PANi-PPy-Au HNW shown in the Fig. 4.12.(a). where both EDX measurements exhibit the same spectrum as PPy and PANi do not differ in their el-

emental composition as shown in the insets. Hopefully, the position of each metal was identified by high magnification imaging of the metal-CP junction as detailed in the section 4.4.4.1.

Element	Energy	Line	Intensity
-	(keV)	-	(%)
⁶ C	0.277	K $\alpha_{1,2}$	147
⁷ N	0.2924	K $\alpha_{1,2}$	150
²⁴ Cr	5.4141	K α_1	111
⁸ O	0.5249	K α_1	151
¹⁴ Si	1.7400	K α_1	100
¹⁶ S	2.3078	K α_1	100
¹⁶ S	2.3066	K α_2	50
¹⁶ S	2.4640	K β_1	50
¹⁷ Cl	2.6208	K α_2	100
¹⁷ Cl	2.6224	K α_1	100
²² Ti	4.5049	K α_2	50
²² Ti	4.5108	K α_1	100
⁷⁸ Pt	2.0505	M α_1	100
⁷⁸ Pt	9.4423	L α_1	100
⁷⁹ Au	2.1229	M α_1	100
⁷⁹ Au	9.7133	L α_1	100

Table 4.1: Energy position, in *keV*, and relative intensities of principal K-, L-, and M-shell lines for usual elements. An intensity of 100 is assigned to the strongest line in each shell for each element. From reference [26].

4.4.4.4 Selected Area Diffraction

The SAED patterns were obtained using a LEO 922 transmission electron microscope (*Carl Zeiss SMT Inc.*) operating at 200 kV and with a constant camera length of 300 mm. The analysis of the diffraction patterns was performed using the program *ProcessDiffraction* [246]. SAED was performed with a 100 nm diameter circular selected area using the 5 μm condenser aperture. Generally, before performing the SAED of the sample, a SAED pattern through the membrane is performed to check that no (poly)-crystalline impurities are present which could eventually superimpose unwanted spots on the SAED patterns. A typical SAED pattern of the SiN membrane is given in the Fig. 4.13 and clearly exhibits the typical rings of amorphous materials. To demonstrate the possibi-

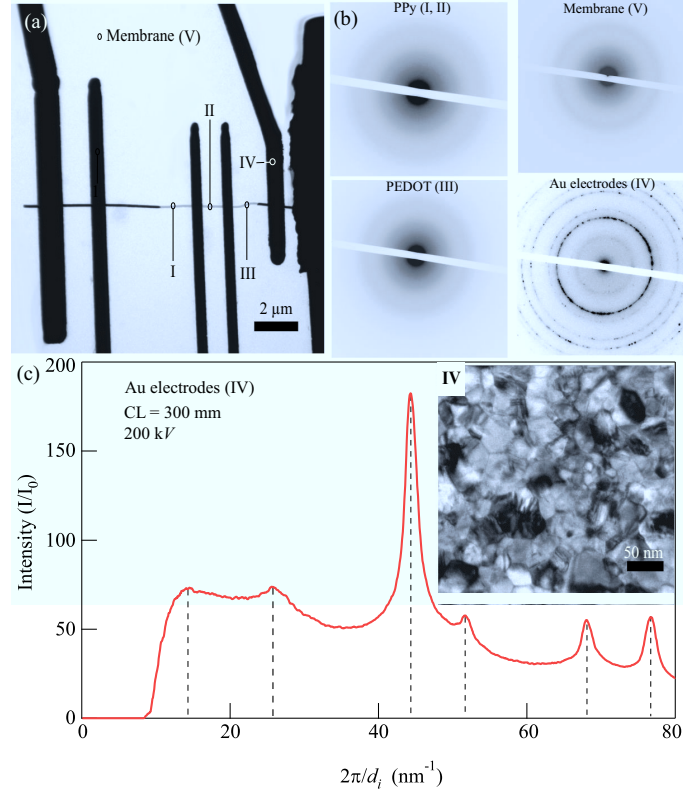


Figure 4.13: (a) TEM micrograph of the contacted HNW. (b) SAED patterns taken at various positions along the NW, membrane, and on top of the electrodes, marked in the picture given in (a). (c) Diffraction spectra obtained for the SAED pattern of the Au electrodes (IV).

ties of electron diffraction of the microdevice, we first briefly discuss the

results obtained on EBID Pt deposited on a membrane of a microdevice provided with several Au electrodes in a configuration that allows thermopower measurements. A SEM picture of an EBID Pt NW deposited on Au electrodes of a microdevice is given in the Fig. B.3.(a) A high resolution bright field (BF) TEM micrograph is given in the panel (c). The deposited materials is composed by dark granular regions of 5 nm in diameter separated by brighter regions showing an amorphous like pattern. As Pt is characterized by a higher electro-optical contrast than a-C [247], this BF TEM picture suggests that the deposited materials is composed by nanometer-sized Pt grains (typically 5 nm wide) embedded in an amorphous carbon (a-C) matrix. To confirm the presence of platinum, we performed a SAED of the deposited materials. The diffraction pattern of the same region is given in the panel (d) of the Fig. B.3. The SAED pattern demonstrates the existence of poly-crystalline Pt. Indeed, the observed diffraction rings translate into interplanar d-spacings of 0.21, 0.19, and 0.13 nm which are in good agreement with the literature [247] values for fcc bulk Pt (see table 4.2).

We performed the same SAED analysis on several microdevices with HNWs contacted by an EBL process. The figure 4.13 presents the typical results obtained for a tetra-segmented HNWs. Here, during the exposure of the CP segment, the beam current should be kept as low as possible to prevent any modification of the CP. Indeed, polymers are often very sensitive to TEM electron beam and could even become unstable under high electron beam which could cause important Joule effect and even amorphization. The SAED performed on both CP exhibits the same amorphous circular pattern than empty membrane which is not surprising for CP electrochemically synthesized. On the other hand, the SAED pattern of the Cr/Au electrodes (point IV) exhibits nice rings demonstrating a poly-crystalline form for the deposited electrodes. The corresponding TEM image is given in the inset of the Fig. 4.13.(c) which exhibits clearly the polycrystalline structure of the electrodes. Several d-spacing values are obtained from the indexing of the SAED pattern. From the comparison with the crystallography database [27], the obtained d-spacing values (2.37, 2.06, 1.45, 1.24, 1.18) can be attributed to the Au cubic closest packed and Cr Body centered cubic, structures.

Element	Intensity (%)	d-spacing (nm)	(H K L)
Au	100.00	2.35	1 1 1
Au	47.94	2.039	2 0 0
Au	28.39	1.441	2 2 0
Au	31.32	1.229	3 1 1
Au	8.95	1.177	2 2 2
Pt	100.00	2.265	1 1 1
Pt	47.55	1.961	2 0 0
Pt	27.67	1.387	2 2 0
Pt	30.79	1.182	3 1 1
Pt	8.87	1.132	2 2 2
Cr	100.00	2.039	1 1 0
Cr	13.20	1.441	2 0 0
Cr	23.21	1.177	2 1 1

Table 4.2: D-spacing values obtained from X-rays powder diffraction and their relative intensity for different substance [27].

4.4.4.5 Application to EBID Pt Single NW

In this section, we present the correlated characterization of a sample presented in the section B.1.2 of the appendix B.1.2. The Fig. 4.14.(b) gives the RT ($I - V$) characteristics of the Pt NW shown in the SEM micrograph of the panel (a). This EBID Pt was deposited on the membrane of a microdevice, thus, enabling TEM imaging SAED and EDX analysis of the measured Pt NW. As shown in the panel (c), the deposited materials contains darker regions with a typical diameter of 10 nm which could correspond to Pt nanoparticles. The presence of Pt was further confirmed by EDX measurements given in the panel (e) of the Fig. 4.14. EDX spectra were taken on the Pt NW (spot 1) and on the membrane very close to it (spot 2), to identify the components coming from the membrane and the sample holder. It can be seen that several elements are common in both spectra (i.e. Si, N, C and Ti). While the Si and N peaks can be attributed to the stocheometric nitride membrane of the microdevice, the presence of Ti is a well known contamination peak stemming from the TEM sample holder. On the other hand, the M_α and L_α peaks at 2.05 and 9.44 keV present only on the spot 1, can be ascribed to Pt (see Table 4.1). The presence of carbon in both spot results from the decomposition of the precursor gas $(Me)_3MeCpPt$. While Pt is confined in approximately 60 nm (the width of the deposited NW), the distribution of carbon is much wider and should be mainly responsible of the *halo* that can be seen around the deposited NW in the SEM and TEM micrographs given in the panels (a) and (e) respectively. The SAED pattern shown in the panel (d) contains several rings characteristic of polycrystalline materials overlayed on the typical amorphous pattern of the nitride membrane. According to the crystallography database [27], the d-spacing values obtained from the indexing of the SAED pattern ⁸ can be attributed to the face centered cubic (fcc) structure of Pt.

In the chapter B.1.2, we briefly discuss about the ageing effects on the deposited Pt NWs. The four-probe measurement demonstrated no degradation of the materials (even a slight improvement was noticed) upon exposure to air whereas other works showed that the deposited materials deteriorate quickly (even after a few hours) when samples are exposed to air. It was suggested that the diffusion of Pt nanocrystals could be responsible of the deterioration. Thus, after each electrical measurement, TEM imaging was performed to check the eventual structural change.

⁸Using the *ProcessDiffraction* software.

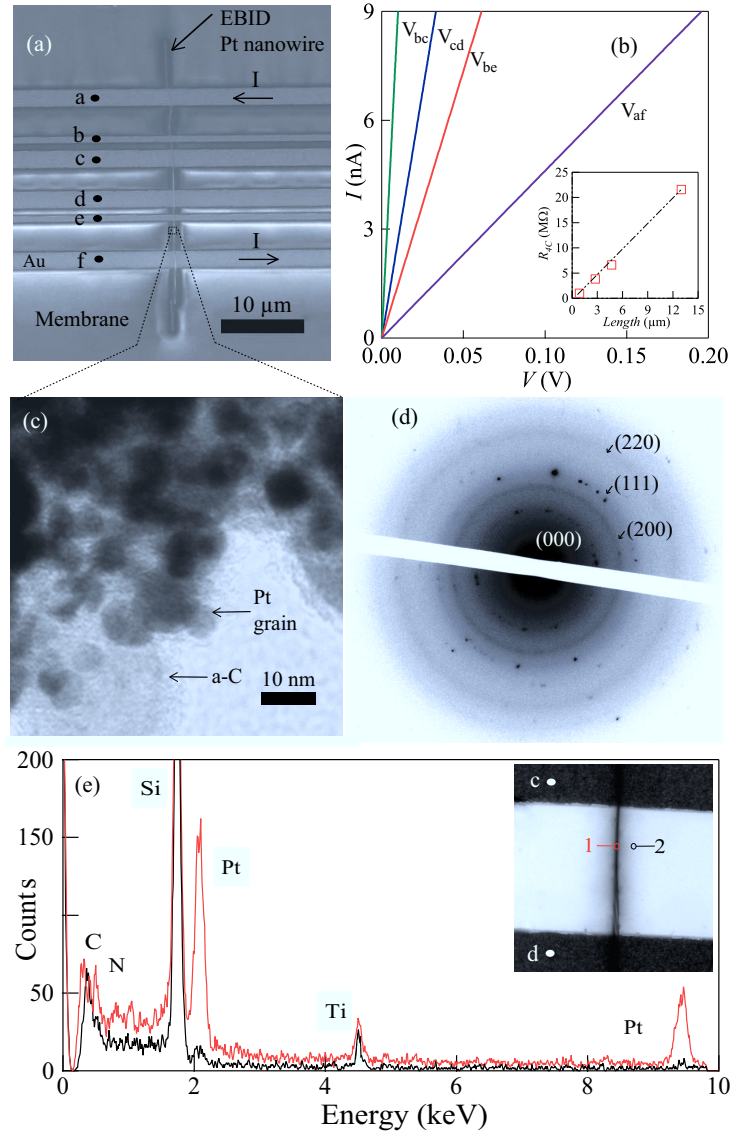


Figure 4.14: (b) ($I - V$) characteristics of a single Pt NW shown in (a). The inset gives the dependence of the measured resistance as a function of the NW length. (c) TEM micrograph of the same Pt NW where Pt nanocrystals are visible. (d) SAED of the Pt NW. (e) EDX spectra taken in spot mode at two different positions of the membrane.

4.5 Summary

In this chapter, we presented the fabrication of a multipurpose platforms, fabricated via Si micromachining techniques which offer a unique tool for studying single nanostructures. While these membrane-based microdevices were used for correlated studies of NWs, the extension to other nanomaterials (organic, inorganic or hybrid films, nanoparticle) is straightforward. Standard EBL based technique was mainly used to interrogate single HNWs but microdevices are compatible with other techniques such as dielectrophoretic trapping or electron-beam induced deposition. We demonstrated the possibilities of the microdevices by correlating the electrical measurements with high resolution TEM imaging, selected area electron diffraction, and energy dispersive X-ray analysis on the same sample. We have seen that this analysis can be coupled to the topology of the samples as observed by AFM. Furthermore, the membranes-based devices were designed to allow also thermal measurements and more specifically, thermopower measurements.

Several improvements of the platforms could be envisaged. Concerning the microdevices, many new experiments can be envisaged and several improvements of the devices are possible. The mechanical behavior of the membrane could be improved by using low stress (Si-rich) nitride available with the new LPCVD oven. The decrease of the mechanical stress of the membrane would allow to structure it by removing the nitride layer between electrodes. This will further increase the resolution of TEM imaging allowing true HR-TEM. This would also suppresses the unavoidable nitride membrane component in the SAED and EDX signals.

The second possible improvements of microdevices, aims to build improved NW-FET. Indeed, in order to improve the coupling between the gate and the NW, the definition of gates on the back side of the membrane of the microdevice, would allow a gate dielectric thickness as small as 30 nm (the membrane thickness) which is much better than what can be obtained by EBL processing.

Chapter 5

Characterization of Single Hybrid Nanowires

Et s'il n'en reste qu'un, je serai celui-là!

Ultima Verba, Victor Hugo

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5.1 Overview

In this chapter are presented the electrical characterization of HNWs performed in a single NW configuration. The first part of this chapter focus on low- T transport properties of HNWs based on PPy and Au segments. We show that the electrical transport properties observed on single HNWs measured in planar configuration are consistent with the measurements of HNW arrays presented in the chapter 3. Similarly to the measurements of HNW arrays, apparent power-law behavior (APLB) of the conductance and the current-voltage curves of single HNWs were observed. These results are discussed and compared to HNW arrays measurements and recent experimental works where APLB were reported for CP systems [120, 18, 35, 210] and attributed to tunneling in Luttinger liquids.

Then, the following section focuses on RT tunable transport properties of HNWs. We present the detailed analysis of two main types of HNWs the tri- and tetra-segmented HNWs which exhibit very distinctive response upon chemical treatment. An interesting feature of the tetra-segmented NWs compared to tri-segmented NWs is the switching of their electrical characteristics in function of the probes configuration and of the redox state of the two conjugated polymer blocks. A simple model of two back-to-back Schottky diodes is proposed to explain their distinctive behavior.

Finally, the last section deals with the correlation characterization of HNWs performed using microdevices. The results obtained with microdevices further consolidate the proposed explanations of the behavior of the tetra-segmented (Au-PEDOT-PPy-Au) HNWs presented in the previous section.

5.2 Low- T Transport Properties of single HNWs

Here, we present T -dependent electrical measurements for three single HNWs based on Au and PPy segments: two tri-segmented HNWs S70A and S70B with $\phi = 70$ nm and a 90 nm diameter penta-segmented HNW S90. While S70A has a nominal PPy segment length of 1500 nm, the PPy segment is reduced to 300 nm for samples S70B. Sample S90 present two identical 1250 nm long PPy segments separated by a 300 nm Au island. The HNWs were contacted by the dropcast method presented in the section 4.2.2 and measured by a two contact technique. An example of T -dependence of the two probe resistance (measured with a fixed applied bias of 5 mV) of an single Au NW contacted by the dropcast technique

is given in the inset of the Fig. 5.1.(b). It exhibits a clearly metallic behavior even after cycling T , suggesting that electrical contact are not contaminated by any residues. The room-temperature total resistance (including leads and contact resistance) measured for a $3\ \mu\text{m}$ -long Au NW with diameter of 70 nm is less than $300\ \Omega$. Using a standard bulk value of resistivity for Au, it can be deduced that the contact resistance between the Au segment of the NW and the Au contact pads is less than $200\ \Omega$, which is negligible compared to the resistance of one single HNWs ($\approx 10^8\ \Omega$).

$(I - V)$ characteristics for each sample are given in the figure 5.1 for several temperatures. Generally, the level of the current measured through single HNWs is roughly 3 orders of magnitude lower than the current measured for HNW arrays. Nevertheless, the T -dependences of the measured currents are essentially the same in both cases with an ohmic $(I - V)$ relation observed at RT whereas S-shaped curves are recorded in the low- T regime. Like for the electrical characterization of HNW arrays, resistance values $R(T)$ are deduced from the $(dI/dV)^{-1}$ values at zero bias and are shown in the inset of Fig. 5.1.(c) and are clearly divergent as the temperature is lowered demonstrating a clear insulating behavior. RT conductivities of 0.04 , $0.05\ S.\text{cm}^{-1}$ and $0.5\ mS.\text{cm}^{-1}$ were recorded for samples S70-A, S70-B and S90 respectively.

5.2.1 3-D Hopping Charge Transport in HNWs

These data can be analyzed similarly to HNW arrays data within the framework of the VRH mechanism. Indeed, if the VRH applies, the resistance is expected to follow the relation given in the equation 2.17. As for HNW arrays, The best fits to our data were obtained with $d = 3$. The $\ln[R(T)]$ versus $T^{-1/4}$ plots are given for each HNWs in the panel d of the Fig. 5.1. From these plots we extract the parameter $T_0 = 1.4 \times 10^8$, 5.0×10^7 and 1.8×10^8 for samples S70A, S70B and S90 respectively. Remarkably, these values (listed in the table A.2) are consistent with the values reported for HNW arrays (see chapter 3).

To further confirm that the electrical transport properties of single HNWs are consistent with the 3D-VRH model, we analyzed the non-Ohmic 3D hopping transport observed at low- T . As for HNW arrays, the parameter $\beta = eF\xi/k_B T$ is used to define two different hopping transport regimes. For all the samples, $\beta \gg 1$ is obtained at sufficient low- T ($T < 100\ K$). The plot of $\ln I$ versus $F^{-1/4}$ is given in the upper inset of Fig. 5.1.(a) for several temperatures. Clearly, a linear behavior is observed at the lowest temperatures, which remains almost unchanged upon further decrease of T showing that the electric field

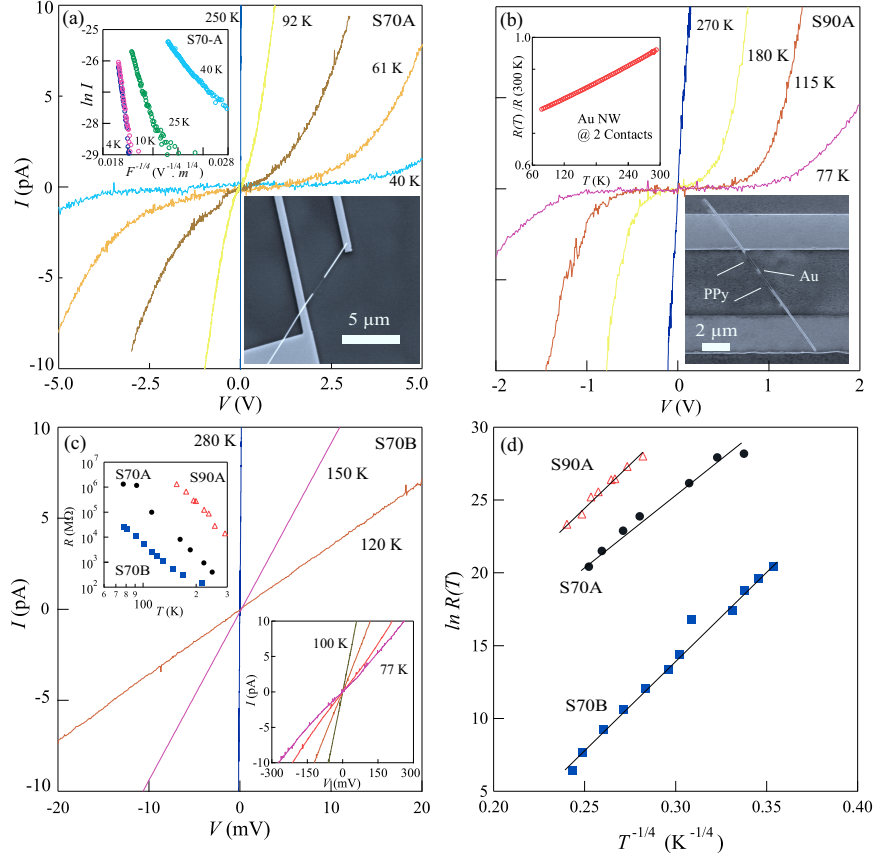


Figure 5.1: T -dependent data analysis for single HNWs made up of Au and PPy segments. ($I - V$) characteristics of single HNWs measured by the two probe technique, taken at various temperatures. (a-b) 70 nm diameter tri-segmented HNWs (Au-PPy-Au). (b) shorter PPy segment and (c) 90 nm diameter penta-segmented HNWs (Au-PPy-Au-PPy-Au). (d) 3D-VRH plots for samples S70A, S70B and S90. The solid lines are the 3D-VRH fits to the data (see text).

F dependence of the resistance of sample *S70-A* follows the 3D-electric field-induced hopping regime (see chapter 2). The value of the critical electric field $F_0 = 1.5 \times 10^{13} \text{ V/m}$ found from the linear fit to the data is consistent with the values obtained from the HNW array measurements. This confirms once again that despite the unavoidable average effect in the HNW arrays samples, the intrinsic behavior of PPy NWs can be probed and the extracted parameters are the same as those deduced for planar single NWs.

In the following section, we analyze the T -dependent data obtained

for single HNWs within the same framework than for HNW arrays (see section 3.4.2), taking into account the electron-electron interactions (EEI) which could result in the possible formation of a Luttinger liquid (LL).

5.2.2 1-D Charge Transport in Single HNWs

Low dimensional and 1-D structures are of great interest for investigating transport mechanisms on the nanoscale, where the quantum confinement effect, Coulomb charging energy, EEI, and disorder all play important roles [20]. Especially, EEI are strongly affecting the transport in 1D systems by leading to phases different from conventional Fermi liquid [120]. While the effects of dimensionality on interacting electrons were predicted for a long time [205, 206] it is only recently that they were demonstrated experimentally in Molybdenum Selenide NWs [166] and CNTs [164]. Over the past decade, an increasing number of authors reported data suggesting LL effects in CP systems [120, 35, 13].

Here we present similar data for 70 nm diameter tri-segmented HNWs (Au-PPy-Au) and 90 nm diameter penta-segmented (Au-PPy-Au-PPy-Au) HNW as a function of temperature and voltage that agree with predictions for tunneling into a LL. Then, we discuss briefly the data in light of the recent work of Rodin and Fogler [210].

Generally, the suppression in differential conductance around the zero-bias voltage - as shown in the Fig. 5.2.(a) for sample S70-A, is caused by the depletion of the density of states at low energies. Recently, several works have demonstrated that for different organic systems (eg. CP films [35], single CPNWs [20] and CPNWs arrays [18]), this gap could be induced by the formation of a LL which results from repulsive short range EEI [73, 120].

According to a simple version of the LL theory, which takes into account EEI in (quasi) 1-D system and describes spinless electrons scattered by a single potential barrier [248], power-law dependencies of the conductance $G(T) \propto T^\alpha$ and of the current $I(V) \propto V^\beta$ are expected at low ($eV \ll k_B T$) and high applied voltage ($eV \gg k_B T$), respectively. Figure 5.2.(c) gives G as a function of T on a double logarithmic scale for samples S70-A, S70-B and S90. The measured data show approximate power-law behavior, $G \approx T^\alpha$, for the three samples. The field dependence of the current for all samples are similar to the dependence given in the panel (b) of the Fig. 5.2 for sample S70-A. The parameters α and β are listed in the table A.3.

The $(I - V)$ characteristics should follow the equation 2.28 for tunneling in a LL. As a result, $(I - V)$ curves should collapse into a single

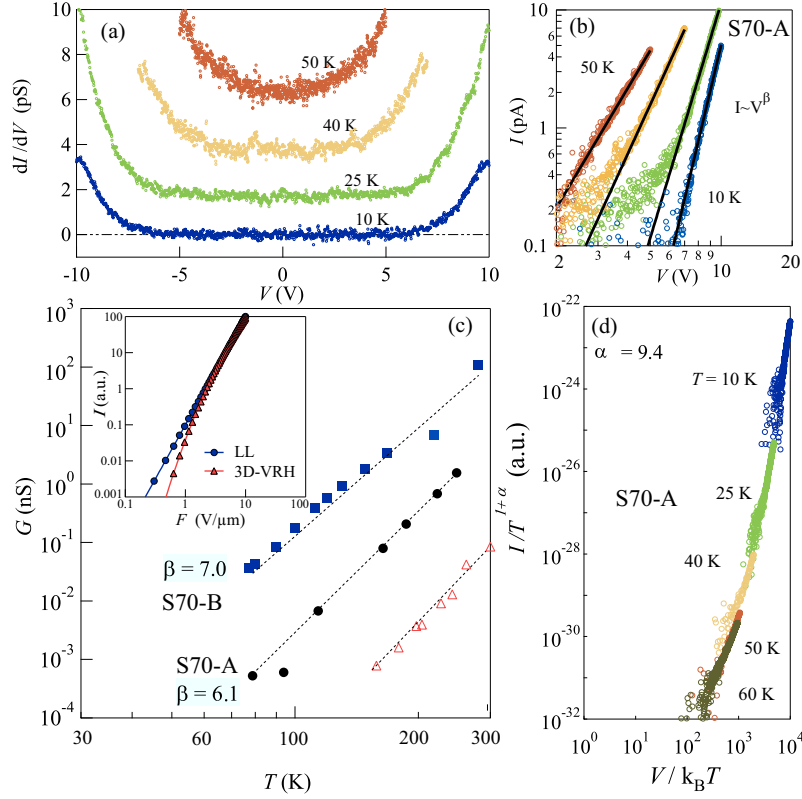


Figure 5.2: (a) differential conductance and power-law current dependence (b) for sample S70-A. (c) Conductance vs T for Single NWs samples. The dashed lines are guides for the eye. The inset gives typical $(I - V)$ dependences given by the equations 2.28 and 2.20 for the LL and the field-induced VRH models respectively. (d) $(I - V)$ data plotted as $I/T^{\alpha+1}$ vs $eV/k_B T$ for a 70 nm diameter single HNW (Au-PPy-Au).

curve if $I/T^{\alpha+1}$ is plotted as a function of $eV/k_B T$ [119]. This plot is shown in the panel (d) of the Fig. 5.2 for sample S70-A using the parameters estimated by the power-law dependences. The curves collapse pretty well into a single curves suggesting together with the power law dependence that in the low- T range, the charge transport in single HNWs correlates with the LL theory for quasi-1D system. It was proposed by Aleshin *et al.* that CP can be seen as several LLs linked with one another and that conduction is due to carriers tunneling along LLs through barriers produced by impurities in the LLs and tunneling between the LL chains [119].

While $\beta = \alpha + 1$ is expected in the case of a single chain of LLs, the

values for CP NWs (our samples included) always exhibit $\beta \neq \alpha + 1$ [120]. Moreover, β is less than α in many cases, which contradicts the previous relation between the exponents. These discrepancies were found also in inorganic 1D-systems [166] and may depend on the impurity distribution or the presence of disorder which have an impact on the properties of LL [163] and the interactions between the CP chains [119].

We have seen in the previous section that the single NW Data are consistent with the 3D-VRH. This could seem contradictory. It is worthy of note that at low- T , in the high-field regime, the field dependences of the current are very similar for both LL and 3D-VRH models. To exemplify this, the field dependences of the current of the equations 2.28 and 2.20 for both models respectively and using usual parameters (β , F_0 , F) are given in the inset of the Fig. 5.2.(c). Clearly, within the voltage range used in the experiments, both models result in the same ($I - V$) dependence.

It is to my great relief that very recently, Rodin and Fogler emphasized in a very interesting paper [210], that in specific conditions and within narrow T and V intervals, the VRH conductance could deviates from the usual exponential formula $G(0, T) \propto \exp[(-T_0/T)^{1/d+1}]$ (equ. 2.17), to exhibit the collapse onto the universal curve of Eq. 2.28 and an apparent power-law behavior (equ. 2.27). More precisely, this may be observed in hopping systems, in case of the hopping distance is not much smaller than the length L of the CP segment. While the CP length is not exactly known in HNW array measurements, in single HNW measurements, the length of the CP segments are well known and typical values are about $1.5 \mu m$. Remarkably, from the equation 2.15, and assuming a reasonable value $\xi = 2$ nm, the hopping distance ($\bar{R}'_{hop} = 154$ nm at $T = 4$ K for sample S70A) is less than one order of magnitude smaller than L . Thus, it seems possible that hopping process in our sample is dominated by hopping paths made up by a few hops.

To further clarify this point and to confirm the explanation of Rodin *et al.*, it should be possible to test the predict numerical values and relations among γ , β and δ given by the proposed model. Furthermore, in the the experimental point of view, thermoelectric power (Seebeck coefficient) measurements performed on single HNWs could further discriminate the charge transport mechanism, as the thermoelectric power is a linear function of T in the framework of Luttinger liquid theory whereas it varies as a power of T for the VRH mechanism [249, 122].

In the following section, we focus on several classes of HNWs based on poly(3,4-ethylenedioxythiophene) (PEDOT) and PPy. We investigate the RT electrical transport of tri-segmented (Au-PEDOT-Au) and

tetra-segmented (Au-PEDOT-PPy-Au) HNWs synthesized by an all-electrochemical template method [70] (see section 3.2), all with a nominal diameter of 110 nm. Contrarily to the previous work, here, HNWs were contacted using a top-contact approach based on an EBL system, described in the section 4.2.3. This technique allows the deposition of several contacts on the same HNW with low contact resistance. In the following, we show that the tetra-segmented NWs present an interesting feature compared to tri-segmented NWs as they switch to rectifying behavior by exposure to oxidative solution $FeCl_3$.

5.3 Tunable Transport Properties of HNWs

In this second part of the chapter dealing with single HNWs, we present the electrical characterization of tri-segmented and tetra-segmented HNWs made of PEDOT and PPy and with an average diameter of 100 nm. The measurements were performed in a two and/or in a four-probe configuration at a constant RT . In the first part of this section, we show how the electrical properties of tri-segmented and tetra-segmented HNWs are modified upon chemical treatment. Then, based on XPS measurements and on correlated characterization of HNWs, a detailed explanation of the chemical treatments was proposed and a simple model based on Schottky diodes was developed to explain the observed difference in tri- and tetra-segmented HNWs which reproduces quite well the rectifying behaviors of tetra-segmented HNWs.

5.3.1 Electronic Behaviour of Tri-segmented HNWs

Here, we present the R - T characterization of as-synthesized single tri-segmented Au-PEDOT-Au NWs. We focus on the results obtained for several samples (NW1, NW2, NW3, NW4 and NW7) with PEDOT segment lengths of 0.6, 1.2, 4.2, 3.7 and 4.1 μm , respectively. The two-point current-voltage ($I - V$) characteristics of the samples NW1, NW2 and NW3 are given in Fig. 5.3.(a). All samples exhibit symmetrical and linear ($I - V$) characteristics, consistent with Ohmic contacts between the PEDOT and the gold segments [16, 12].

Room- T conductivities of 4.3, 2.5, 450, and 11 $mS.cm^{-1}$ were deduced from the slopes of the two-probe¹ ($I - V$) curves for NW1, NW2, NW3, NW4 and respectively. These values are much lower than typical values reported in the literature (up to 550 S/cm) for pure PEDOT

¹Contacting the metallic segments.

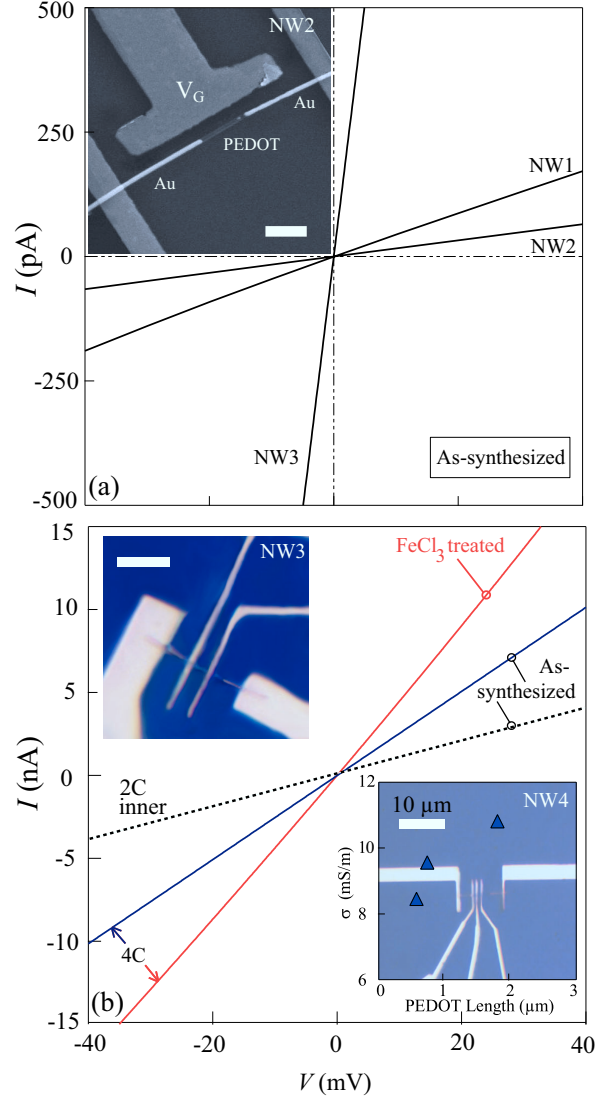


Figure 5.3: (a) ($I - V$) characteristics of tri-segmented Au-PEDOT-Au NWs measured in a two-point configuration. The upper inset is a SEM picture of sample NW2. The scale bar is $1 \mu\text{m}$. (b) Four-point ($I - V$) characteristics of NW3 measured before (blue curve) and after (red curve) FeCl_3 treatment. The upper inset gives a CCD view on the HNW. The scale bar is $5 \mu\text{m}$. The dashed curves is the two-probe measurement of sample NW3 as-synthesized. The lower inset gives the resistivity variation vs PEDOT length for sample NW4.

NWs [12] or Au-PEDOT-Au HNWs ($\approx 200 \text{ S/cm}$) [16]. The low conductivity of our HNWs were confirmed with the measurement of several samples. Strikingly, the two-probe conductivity of HNWs given in the Fig. 5.4.(a), exhibits a rather large variability. This could be due to the presence of high and variable contact resistances R_C along the path of the two-probe measurement. The existence of such high R_C would also explain the low conductivity observed for as-synthesized samples. To check the presence of such contact resistance, we therefore, measured several tri-segmented Au-PEDOT-Au HNWs in a four-point configuration (see Fig. 5.4.(b)). This configuration eliminates the contact resistance issues and actually gives the conductivity of the CP segment defined by the two inner probes.

Interestingly, the observed conductivities given in the Fig. 5.4.(b), are very similar to the values deduced from the two-probe measurements and spread out over four orders of magnitude. This result suggests that the low values and the variability of the conductivity observed for HNWs are intrinsic to the CP segment of HNWs and not stemming from contact resistance. This variability is probably due to the unavoidable postsynthesis processing, including the number and the position of the contacts.

As it will be shown later, the variability and the high values of resistivities of HNWs could be explained by taking into account the presence of substantial metal-CP interface resistances, included in the path of the two-probe measurements and not in the four-probe measurements.

While very low contact resistances are expected with outer probes contacting Au segments, thanks to good electrical metal-metal² interfaces (see section 4.3.3), the situation is totally different when measuring through the two inner probes with metal-PEDOT interfaces.

The two-probe measurements performed with the inner probes, often exhibit non-linear ($I - V$) characteristics and include important contact resistances R_C . Indeed, for inner probes, R_C can be estimated by comparing the two and four-probe measurements. For instance, the contact resistance deduced for the inner probes of samples NW3 and NW7³ represent 24 and 54 % of the four-probe resistance, respectively. These values are quite high as they are comparable to the sample resistance.

Despite the high R_C value for the two inner probes of sample NW3, the two-probe ($I - V$) characteristic performed, with the outer probes is linear (see the panel (b) of the Fig. 5.3), demonstrating that there are no charge injection issues for this sample. From these results, one can

²(Au electrode)-(Au segment)

³For sample NW7, R_C is bias dependent as the ($I - V$) curves are non-linear as shown in the Fig. 5.6.(a).

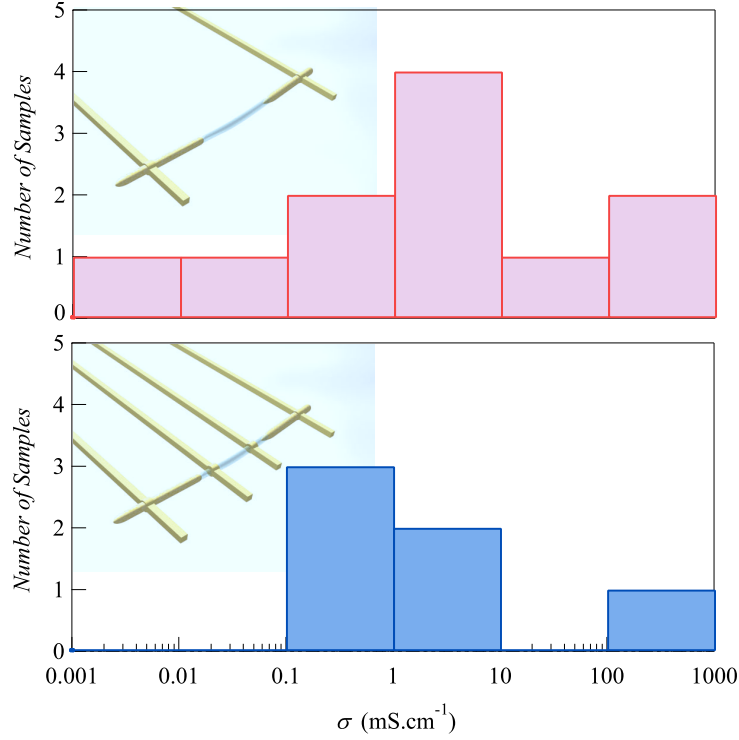


Figure 5.4: Histogram of the observed conductivities of tri-segmented HNWs (Au-PEDOT-Au) as measured in a two-probe (a) and four-probe configuration (b).

conclude that

- a simple and efficient way to measure a single HNW is to contact the outer metallic segments as they exhibit much lower contact resistances.
- Compared to pure CP NWs, the HNWs structure with its two metallic segments, offer an excellent configuration to perform a two-probe electrical measurement of a CP NW.

We also probed the electrical conductivity in a four-probe configuration of the PEDOT segment of a Au-PEDOT-Au HNW at various lengths. Contrarily to what is expected intuitively, the measured conductivity is not constant along the PEDOT segments HNWs as we observed an increase of the conductivity with the length of the PEDOT segment, as shown in the lower inset of the Fig. 5.3.(b). This length dependence of the conductivity was already reported for electrochemically

template-synthesized PPy NWs [11]. Obviously, the conductivity of CP can be strongly influenced by sample synthesis parameters, the template removal or the EBL processing. This behavior partly explains the high conductivities of long PEDOT blocks in tri-segmented HNWs but is not enough to explain the large variability of the conductivity observed for single HNWs.

Another source of variability of the measured resistance, could be the resistance associated to the CP-metal junctions of the HNWs. This resistance should play a key role in the two-point resistance (with outer probes) of HNWs and its variability. Indeed, this junction resistance which is stemming from the existence of a carrier-injection barrier, whose height depends on the intrinsic parameters of the CP and the type of metal. Interestingly, it was shown recently that the barrier height (the work function of the CP), and thus the junction resistance between a metal and a CP (see equation 4.2) can be decreased by up to three orders of magnitude by modifying the doping level of the CP [235].

It is worthy to note that generally an increase of the doping level of a CP, is accompanied by an increase of the work function of the CP [250]. Considering a high work function metal (e.g. Pt, Au), this directly translates into a decrease of the resistance of the metal-CP junction.

To check the influence of the doping level on the properties of tri-segmented HNWs, we performed a post-doping treatment of HNWs by immersing the samples in a $FeCl_3$ 0.5 M (oxidative) solution for 1 h. As shown in Fig. 5.3.(b), we observe as expected, a conductivity increase ($G/G_0 \approx 190\%$) of the polymer segment measured in a four-probe configuration. We repeated the experiment and the same result were obtained for several HNWs contacted in a four-probes configuration. This increase of the four-probe conductivity upon oxidative treatment can be easily understood as PEDOT is a typical p-type conjugated polymer (CP) which are known to exhibit a conductivity increase (decrease) upon oxidation (reduction). It is known that the interaction of CP such as PEDOT or PPy with electron acceptors causes variations in both the carrier density and mobility, leading to significant changes in the conductivity [147, 47].

The effects of this post-doping treatment on the PEDOT properties will be discussed in details later. Let's first present the results obtained with on another class of HNWs: the tetra-segmented HNWs Au-PEDOT-PPy-Au.

5.3.2 Electronic Behaviour of Tetra-segmented HNWs

In this section, we present the electrical measurements of tetra-segmented HNWs Au-PEDOT-PPy-Au containing a PEDOT-PPy junction. Strikingly, as it will be developed below, the tetra-segmented HNWs present specific features compared to tri-segmented NWs, provided by their ability to switch their electrical behavior in function of the redox state of the two conjugated polymer blocks.

The synthesis of such HNWs was briefly presented in the section 3.2. More details about the synthesis can be found in reference [70]. The same top-contact approach using EBL was employed for contacting tetra-segmented HNWs. The Fig. 5.5 presents the symmetrical and linear ($I - V$) characteristics of two single tetra-segmented Au-PEDOT-PPy-Au specimens (NW5 and NW6) measured in their as-synthesized state (blue curve) and after a post-doping treatment (red curve). Noteworthy, the resistance observed for the tetra-segmented samples in their as-synthesized state (blue curve) is much higher than that of tri-segmented samples NW1, NW2, NW3 and NW4. Despite this increase of the resistance, the ($I - V$) characteristics are linear.

Similarly to tri-segmented HNWs, we tried to increase their doping by performing the same chemical oxidative treatment. We thus immersed single NW devices in a $FeCl_3$ 0.5 M solution for 1 h. Surprisingly, after this chemical treatment, tetra-segmented HNWs exhibited a highly non-linear ($I - V$) characteristic, accompanied by an important current increase which depends on the sign of the bias voltage V . Roughly speaking, the gain in current is enhanced by a factor of two at negative bias compared to positive bias. It is important to notice that the electrical measurements were performed by varying the voltage sweeping rate, the number of points to be sure that the observed asymmetry is not a measurement artefact. Also the effect was confirmed on a second independent sample for which the same protocol were used. The same results were obtained and both are given in the Fig. 5.5.

In one hand, the increase in the current level can be explained by a usual *p-type doping* of both PPy and PEDOT segments consecutively to the oxidative treatment as confirmed above for PEDOT segment of tri-segmented Au-PEDOT-Au NWs. Like PEDOT, PPy is well known to exhibit an increase (decrease) of its conductivity after an oxidative (reduction) treatment (for details see chapter 1). The chloride ions inserted during the chemical oxidative treatment effectively adjust the low-dimensional carrier hopping network on the backbone of the polymers inducing an enhanced charge transport [147].

On the other hand, this doping effect - which is usual for CP, does

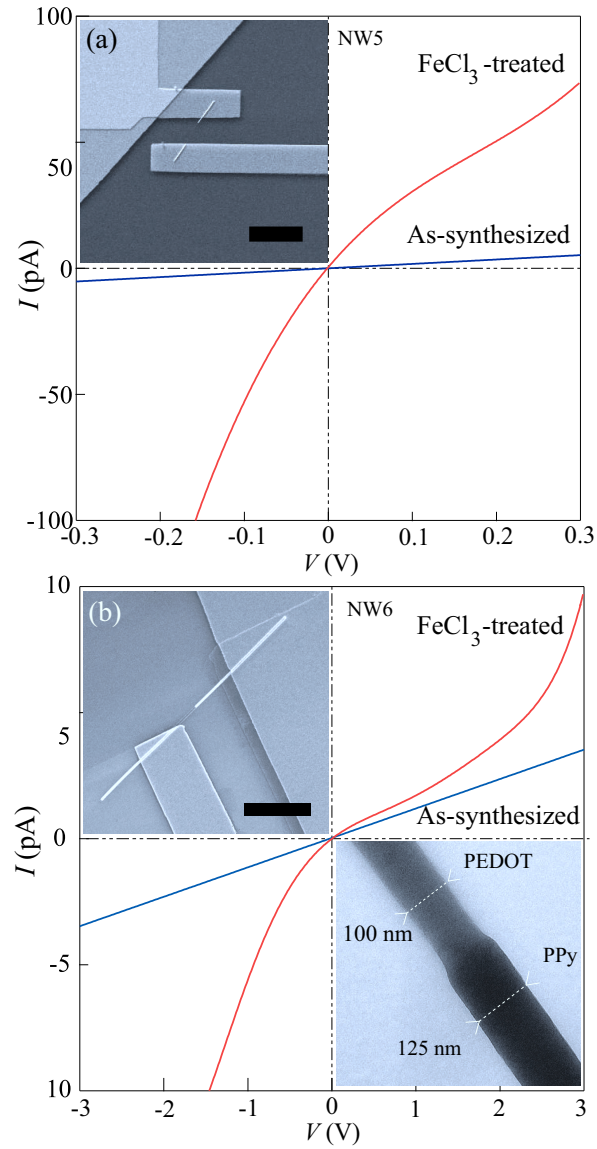


Figure 5.5: ($I - V$) characteristics of a single tetra-segmented Au-PEDOT-PPy-Au NW measured before post-treatment (blue curve) and after post-treatment (red curve). The upper insert is a SEM picture of a connected tetra-segmented NW. The scale bar is $10\ \mu\text{m}$. The lower insert shows a TEM micrograph of a typical PEDOT-PPy junction.

not explain the observed asymmetry. At the first glance, and because of the specific feature of the tetra-segmented HNWs - the presence of the PEDOT-PPy junction shown in the inset of the Fig. 5.5, and the huge

modification of both CP after the chemical treatment shown by XPS measurements (see section C.1), it is tempting to say that the asymmetry of the $(I - V)$ curves, reminiscent of the p-n junction⁴, stems from the PEDOT/PPy junction. Indeed, one can imagine that the junction defines an abrupt shift or variation of an intrinsic parameter of the CP which could be responsible for the observed asymmetry. Nevertheless, no convincing physical explanation was found to give credence to such hypothesis.

After FeCl_3 treatment, the effect is very different for tri- and tetra-segmented HNWs. We have already seen that an increase of conductivity was observed for several HNWs contacted in a four-probes configuration, that is when measuring only a portion of the PEDOT segment. Strikingly, the results are quite different when measuring the same HNW in a two-probe configuration. Let's first examine in details, the behavior of tri-segmented HNWs (Au-PEDOT-Au).

5.3.3 Analysis of the Results Using a Back-to-back Schottky Diodes Model

The Fig. 5.6 gives the $(I - V)$ characteristics for tri-segmented HNWs measured with two probes before (green curves) and after (red curves) FeCl_3 treatment. The observed $(I - V)$ characteristic is linear for the HNW in its as-synthesized state. Clearly, after the FeCl_3 treatment, the $(I - V)$ characteristic become highly non-linear and the conductivity around the zero-bias is decreased roughly by a factor of 10 (for $V = 0.5 \text{ V}$). Nevertheless, compared to the tetra-segmented HNWs, the $(I - V)$ curves are still symmetric.

Remarkably, the panel (b) shows that when the two-probe measurement is performed with the probes deposited directly on the PEDOT segment, slightly non-linear curves are obtained even in the as-synthesized state. Even if a possible dedoping effect induced by the e-beam exposure of the CP segment could be responsible of the observed non-linearity with the inner-probe measurements, the most probable is that the thin (3-5 nm) Ti adhesion layer⁵ - which is a low work function metal (see table 5.1), induces a small Schottky barrier at the electrodes-CP interface. So, the comparison of the inner and the outer probes only demonstrates the good quality of the *as-synthesized* electrical contacts between the CP and the Au segments despite their nanoscale. For comparison, the four-probe measurement of sample NW7 is also given.

⁴Of course, both PEDOT and PPy are p-type CP.

⁵Normally this adhesion layer is not continuous when deposited in the range of a few nm.

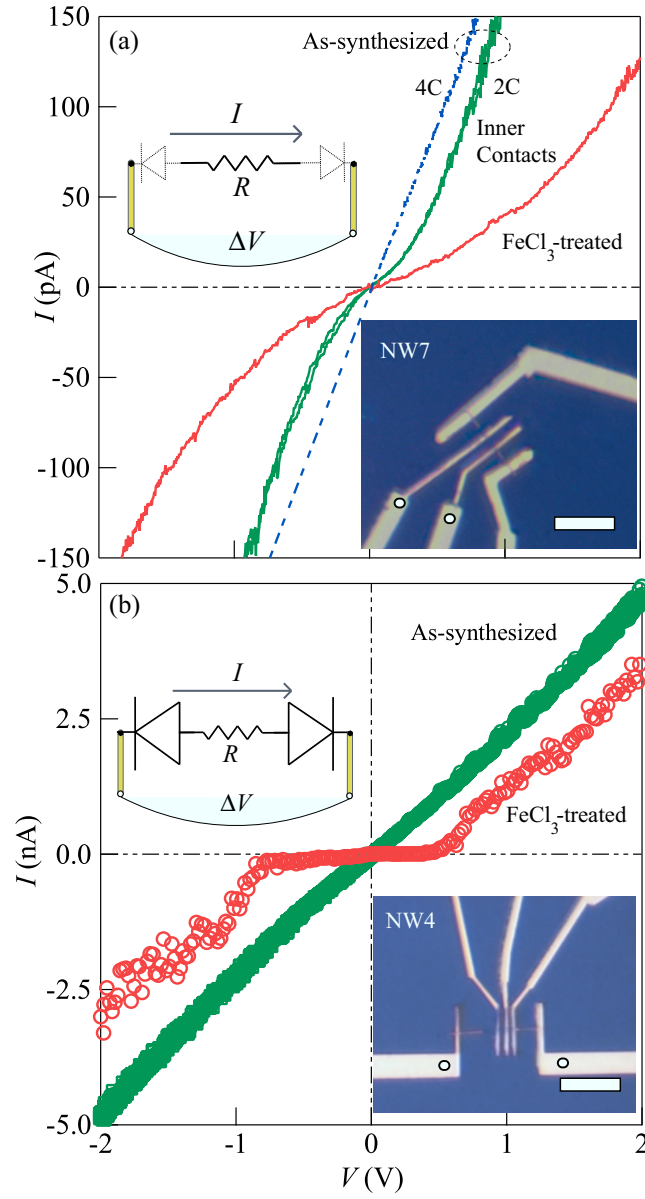


Figure 5.6: ($I-V$) characteristics for two Au-PEDOT-Au samples measured in a two-probe configuration using the electrodes marked by white circles, before (green curves) and after (red curves) FeCl₃ treatment. (a) The probes are deposited on the PEDOT segment and on the Au segments in (b). The scale bars in the insets are 10 μm .

Strikingly, after the oxidative treatment, in most of the cases, the

Element	Au	Pt	Ti	PEDOT	PPy	PANi
Φ_{WF} (eV)	5.1-5.6	5.1-5.8	4.3	5.0-5.6	5.0-5.2	3.5-5.5

Table 5.1: Typical values of Φ_{WF} for several materials of interest as reported in the literature. Noteworthy, the exact values especially for metals, vary depending on their surface cleanliness and crystal plane.

two-probe measurement exhibit a decrease of the conductivity around the zero-bias point and the appearance of non-linearity or an increase of existing non-linearities. Obviously, this behavior seems contradictory with the previous four-probe measurements presented earlier (see Fig. 5.3). Actually, we are not measuring the same things in a four-probe configuration as the two-probe measurements include the two metal-CP junctions present in every HNW.

Indeed, upon chemical (oxidative or reductive) treatment, charges are transferred to the CP chains which consequently modify the Fermi level by either a decrease or an increase in the doping level of the CP [251, 252]. As it was shown by XPS analysis (see section C.1), the FeCl_3 treatment, modifies the doping level but also replace the initial counterion (ClO_4^-) of PEDOT films by a smaller anion (Cl^-).

This shift of the Fermi level is reflected in the change of the work function (Φ_{WF}) of the CP [53, 253]. The doping (oxidation) of p-type CP results in an increase of Φ_{WF} while the de-doping (reduction) induces a decrease of this value [251].

This effect is well known and was used in various sensing devices of analytes such as NH_3 or H_2 and high sensitivity as low as 10 ppm [251, 252]. Consequently, the chemical treatment performed here, results in the modification of the Φ_{WF} of the CP segment which translates into the formation of Schottky barriers. PEDOT and PPy are a p-type CP. When Φ_{WF} of a such p-type semiconductor is greater than that of the metal contact, a Schottky barrier is formed. Conversely, when the work function of the metal is greater than that of a p-type CP, an ohmic contact is observed [253].

For all tri-segmented HNWs as those presented in the Fig. 5.6, the symmetric ($I - V$) curves demonstrate that identical Schottky barriers height (SBH) are induced at both metal/CP interfaces. Also, the observed decrease of the conductance is an artefact as it is only due to the higher resistance of contact at the metal/CP junctions resulting from the induced Schottky barriers. As shown in the Fig. 5.3, the induced Schottky barrier differs with the metal/CP interface configuration and shape. Indeed, it seems that the induced SBH are much more important

for the metal/CP interfaces that were exposed more intensively to the oxidative solution, namely the electrochemically synthesized metal/CP interfaces, as the decrease of the current is much more pronounced in this case.

Consequently, it can be said that what is measured in a two-probe configuration really depends on the metal/CP interfaces. We suggest the existence of metal/CP Schottky barriers which can be tuned by chemical treatment. In the next section, based on the observation of tri-segmented HNWs, we develop a diode model to explain the behavior of the tetra-segmented HNWs Au-PEDOT-PPy-Au.

In the following we show that the observed asymmetry in the tetra-segmented HNWs Au-PEDOT-PPy-Au genuinely stems from the presence of both PEDOT and PPy segments, but not from their junction. Tri-segmented and tetra-segmented HNWs are schematically represented in the Fig. 5.7.(a-b) and corresponds to the common metal-semiconductor-metal (MSM) structures often encountered in the two-probe electrical measurements [254, 255, 218, 233]. Such NW-based MSM structure presenting non-linear and asymmetric ($I - V$) characteristics can be modeled as two back-to-back Schottky diodes [255, 218, 256]. The electrical models for the tri-segmented and tetra-segmented HNWs are obtained by adding the intrinsic resistance of the CP segments as shown in the panels (a-b) of the Fig. 5.7.

In their *as-synthesized* state, HNWs present always Ohmic contacts at both metal-semiconductor interfaces and the charge transport is not electrode-limited as demonstrated by the T -dependent measurements (sections 5.2 and 3.3.2). As a result, the total resistance measured in a two-probe configuration is the sum of the intrinsic resistance R_{PPy} or R_{PEDOT} (see Fig. 5.7) of the CP segments and the equivalent resistances of the diodes which are negligible⁶.

When the two diodes present balanced SBH, the ($I - V$) curves are symmetric, even after the chemical treatment. On the other hand, when SBH are unbalanced, asymmetric characteristics are observed.

Thus, while the Au-PEDOT-Au HNWs contains two identical Schottky diodes (Au/PEDOT), their ($I - V$) curves are always symmetric and no rectification effect is expected. On the other hand, after the oxidative treatment, the tetra-segmented HNWs contains two different Schottky diodes (Au/PEDOT) and (Au/PPy) characterized by two different SBH Φ_{PPy} and Φ_{PEDOT} . A rectification effect in the ($I - V$) curves is expected for SBH ratio $\Phi_{PPy}/\Phi_{PEDOT} \neq 1$. Assuming

⁶Or could be equivalent to a simple resistance placed in series and included in the total contact resistance R_C .

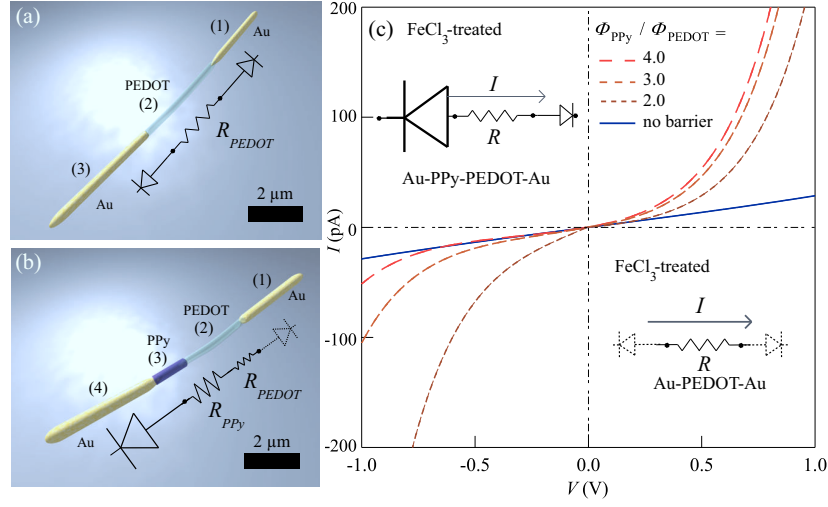


Figure 5.7: (a-b) Schematic view of single tri- and tetra-segmented HNWs with their equivalent circuits. (c) ($I - V$) curves calculated for two back-to-back Schottky diodes with various SBH ratio (red dashed curves). The blue curves was calculated with Ohmic contacts at both interfaces (i.e. zero SBH). The insets show the equivalent circuit of a tetra-segmented (upper inset) and a tri-segmented HNW (lower inset) after the FeCl_3 treatment.

that current dependence for Schottky contact follows the thermionic model [103, 100] (equation 2.2), the data shown in the figure 5.5 is simply explained and the ($I - V$) curves are well reproduced by considering the two back-to-back reverse-biased Schottky diodes presenting two different SBH. For understanding the effect of the SBH ratio, the Fig. 5.7 gives three ($I - V$) curves calculated with three different SBH ratio $\Phi_{\text{PPy}} / \Phi_{\text{PEDOT}} = 2, 3, 4$.

The previous proposed model based on two asymmetric Schottky diodes even being simple, explains quite well the observed change in the ($I - V$) characteristics. Nevertheless it does not explain why an increase of the current is observed in tetra-segmented HNWs while a decrease (even a suppression around the zero bias point) of the current level is recorded for tri-segmented HNWs. Actually, it is possible that other reasons such as the shape of each metal/CP interface, contribute to the observed behaviors. Indeed, the geometry of the second grown (CP/metal) interface differs with the CP (PPy or PEDOT). Furthermore, the redox doping-dedoping process is accompanied by a consequent change in the

volume of the CP [257, 258]. For instance, PPy undergoes a mechanical contraction when oxidized, whereas its volume increases when it is reduced, depending on the mobile ion present in PPy [257]. This mechanical response is different for PEDOT than PPy and should obviously affect the interfaces of each metal-CP junction differently by modifying the contact surface between the metal segments and the CPs. Nevertheless, these modifications are not easy to estimate and measure.

Another cause could be found, again in the different response of PPy and PEDOT to the chemical treatment. Indeed, it was predicted that at the nanoscale, the conventional description of the Schottky diodes no longer holds. Smit *et al.* have shown that high tunneling current is expected through nanoscale Schottky barrier. The level of the tunneling current depends on the Schottky barrier thickness which decreases with the doping level of the CP. For sufficiently small diode, the tunneling current can even exceed the thermionic emission current [106]. So the observed ($I - V$) asymmetry could be caused by an asymmetric tunneling component stemming from the difference in the barrier thicknesses of the Au/PEDOT and Au/PPy junctions. This difference in the barrier thicknesses could result from the distinct responses to the chemical treatment of PPy and PEDOT, as demonstrated by the XPS analysis (see section C.1). The interest of considering the tunneling current is that it provides an explanation for the enhanced conduction in small Schottky diodes without the necessity of assuming a modified Schottky barrier height.

The back-to-back Schottky diodes model explains quite well the observed ($I - V$) characteristics without the necessity of considering other mechanisms. Nevertheless, in the Fig. 5.7 we have modeled the effect of the chemical treatment by asymmetrical SBH, choosing the PPy/Au junction with the higher SBH. Actually, the real orientation of the contacted HNWs shown in the Fig. 5.5 cannot be determined by simple inspection (optical, SEM). To further understand the effect of the chemical treatment on HNWs, we developed and present in the chapter 4, microdevices that allow local and precise characterization of the measured HNWs by correlating the electrical measurements to several analysis such as EDX and SAED which allows to determine the localization of each segments.

5.4 Correlated Characterization of Hybrid Nanowires

We have seen in the previously that the tetra-segmented HNWs are able to switch their electrical characteristics in function of the redox state of the CP segments. In this section, we show that microdevices offer a unique tool to investigate and correlate the structural and electrical properties of such HNWs. The results obtained with microdevices corroborate the proposed explanations of the behavior of the tetra-segmented (Au-PEDOT-PPy-Au) HNWs presented in the previous section. Furthermore, 110 nm diameter tetra-segmented (Pt-PANi-PPy-Au) HNWs were deposited on microdevices and contacted with the same top contact approach based on the EBL technique. Strikingly, these HNWs exhibited much stronger rectifying effects than Au-PEDOT-PPy-Au. The results are discussed within the back-to-back Schottky diodes model proposed in the previous section.

5.4.1 Electrical Properties of the Metal-CP Junctions of Au-PEDOT-PPy-Au HNWs

Here, we consider two 110 nm diameter tetra-segmented HNWs (Au-PEDOT-PPy-Au) of whom TEM micrographs are given in the Fig. 5.8.(a-b) with the probes configuration. As it was already observed in the section 5.3.2, tetra-segmented HNWs present much higher resistances than tri-segmented HNWs. But as the previous measurements were performed in a two-probe configuration they could include a possibly high contact resistance contribution. The panels (c-d) of the Fig. 5.8 give the RT ($I - V$) characteristics of both samples. The presence of these six probes allow to measure in a four-probe configuration, the electrical charge transport in three different segments (BC,CD and DE) of each HNW.

It is important to notice that in both cases, the TEM pictures were oriented intentionally such as the segment BC corresponds to the Au/PPy junction. To do so, each CP segment was identified by comparing both meniscus shapes as observed by TEM. EDX analysis was carried out directly on each segment after the electrical measurement to confirm the identification of both CP segments (see section 4.4.4.3). Despite its apparent simplicity, the identification of both CP segments is not trivial and becomes even impossible without the use of microdevices. as for the case of the tetra-segmented HNWs presented in the previous chapter (see Fig. 5.5) for which the observation of the meniscus is not possible.

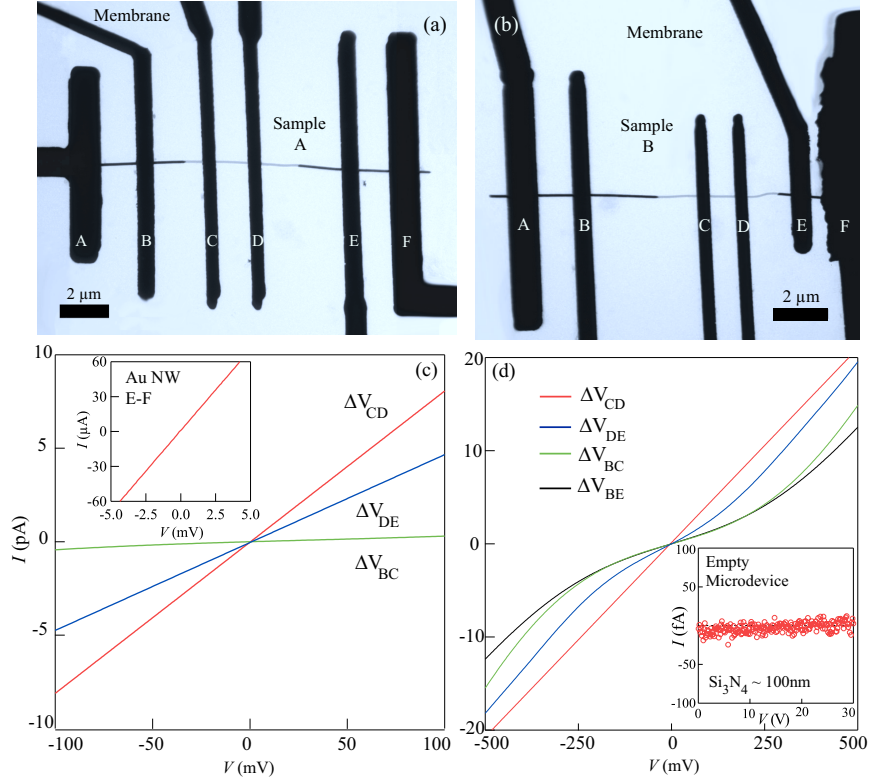


Figure 5.8: (a-b) TEM micrographs and ($I-V$) curves (c-d) of two tetra-segmented HNWs Au-PEDOT-PPy-Au measured by the four-probe technique. The curves are linear around zero bias. The inset in (c) gives the ($I-V$) curve measured for a gold segment and demonstrates the good electrical contact quality.

The Fig. 5.8 gives the ($I-V$) curves for typical tetra-segmented HNWs, which exhibit linear behavior around the zero bias point while at higher bias, the curves become slightly non-linear for segments BC and DE. These segments contain the metal/CP junctions which are responsible of the observed non-linearities. Noteworthy, the non-linear ($I-V$) curves are not symmetric. Resistance values can be deduced for each measured segment (CD, BC, BE and DE) from the slope of the ($I-V$) curves and are listed in the table 5.2 for both samples A and B. Thus, comparing to the values obtained for tri-segmented HNWs, these measurements confirm the intrinsic higher resistance of Au-PEDOT-PPy-Au samples of the chapter 5.3.2.

The RT ($I-V$) characteristic of the Au segment between the probes (E-F) is shown in the inset of the Fig.5.8.(c). The calculated resistance

Resistance [M Ω]	BC	CD	DE	BE
Sample A	2.93×10^5	1.23×10^4	2.13×10^4	3.3×10^5
R_i/R_{CD}	23.71	1.00	1.72	26.7
Sample B	5.97×10^4	2.40×10^4	2.46×10^4	9.08×10^4
R_i/R_{CD}	2.49	1.00	1.025	3.79

Table 5.2: Four-probe resistances for each segment of tetra-segmented HNWs (sample A and B).

which includes the leads resistance is $R_{Leads} = 83 \Omega$. This low value demonstrates the good electrical contact quality obtained by the EBL technique. The 20 nm thick thermal oxide layer ensures a very good insulating layer together with the 80 nm thick nitride membrane. Because of the low level of the measured current (often below the nA range), the noise level and the leakage current are always checked before measurement. Generally, no measurable leakage currents are observed between unconnected pads. The inset of the Fig. 5.8.(d) gives a typical leakage current recorded by sweeping the applied voltage between two contiguous leads of a microdevice.

It was proposed, recently [70] that this high resistance of Au-PEDOT-PPy-Au samples, could be ascribed to the PEDOT-PPy junction, as both PEDOT and PPy are known to form Ohmic contacts with gold. Nevertheless, this assumption is not verified for the nanoscale metal/CP contacts of HNWs because non-linear behavior and high resistances are exhibited by the segments containing the Au-CP junctions (see table 5.2). The Au/PPy junction exhibits a resistance roughly 14 times higher than the PEDOT-Au junction resistance and 24 times higher than the resistance of the CD segment. As the resistances ratios are not proportional to the CP segments lengths, the high resistance of the segment *BC* could be ascribed to the Au-PPy junction itself. Generally, such high junction resistance are modeled within the framework of the thermionic-emission theory where Schottky type contacts result in the following zero-bias contact resistivity for both metal-CP junctions[100, 233]

$$\rho_C^{CP} = \frac{k_B}{A^*Tq} \exp\left(\frac{q\Phi_{CP}}{k_B T}\right),$$

where A^* , k_B , q and Φ_{CP} are the Richardson constant, the Boltzmann constant, the electron charge and the effective Schottky barrier height (SBH), respectively. Considering the model of two back-to-back reverse-biased Schottky diodes presented in section 5.3.2, a junction resistances

ratio of 14 could be attained with two SBH in a ratio of ≈ 2.6 . The observed $(I - V)$ curves are quite far from the ideal Schottky characteristic as the reverse current is very high which is assumed to originate from the low dimensions of the Schottky diode, which result in a tunneling current (through the Schottky barrier) can even exceed the thermionic emission current [106] as mentioned in the section 5.3.2.

These measurements demonstrate that even before any chemical treatment, the metal/CP junctions are not equivalent. As suggested in the section 5.3.2, the chemical treatment of HNWs enhances the existing difference between both junctions. Unfortunately, the electrical measurement of the chemically modified HNWs shown in the Fig. 5.8 has not been performed because of the loss of the electrical contacts before the measurements. Actually, The existence of such barriers and the exact values of both SBH cannot be deduced from the above measurements and should be determined by T -dependent measurements like what was performed in the chapter 3 for HNW arrays.

5.4.2 Enhanced Rectifying Effects with Pt-PANi-PPy-Au HNWs

As the theoretical values of SBH are determined by the CP bandgap E_g , its electron affinity χ_{SC} and the metal work function Φ_M (see chapter 2), if one changes the materials composing the tetra-segmented HNWs, it could be possible to observed a different rectifying effect. Thus, to further confirm the presence and the influence of Schottky barriers on the electrical properties of tetra-segmented HNWs, several tetra-segmented HNWs presenting a MPP'M structure Pt-PANi-PPy-Au (see Fig. 3.3) were contacted and the same protocol was used for integrating these PANi-based HNWs into the microdevice (see section 4.4.3). While oxidative treatment could have been used, it was replaced by an acid treatment (HCl 1 M for 30 min) as it is known to be an efficient way to dope PANi [215].

The Fig. 5.9 gives typical $(I - V)$ characteristics of 110 nm diameter Pt-PANi-PPy-Au HNWs. As for PEDOT-based tetra-segmented HNWs, an increase of the current is observed in a four-probe configuration but here, the effect is stronger as shown in the Figure 5.9.(a). The four-probe measurement demonstrates an increase of the conductivity of the measured CP segment $G/G_0 \approx 440$ %.

The Figure 5.9.(b), gives the $(I - V)$ characteristic of a Pt-PANi-PPy-Au HNW, taken in a two-probe configuration. A TEM micrograph of the HNW is given in the inset of the Fig. 5.9.(b). The voltage is applied to the source (labeled S in the inset) and the drain is grounded.

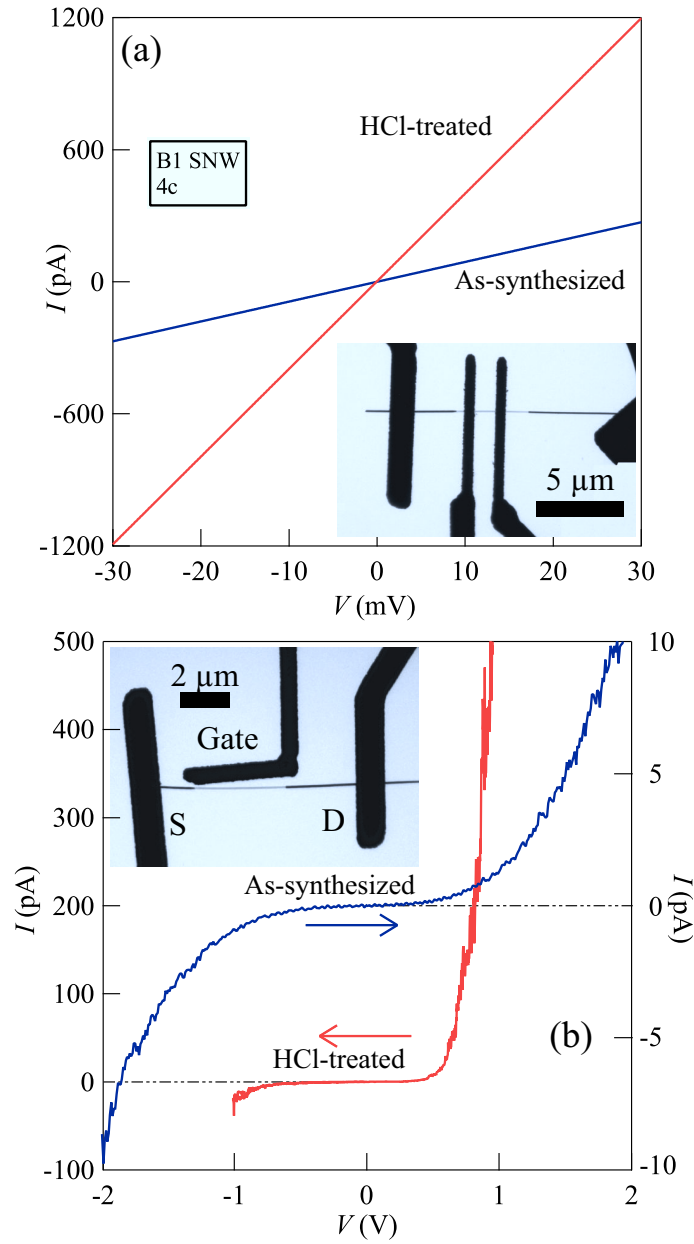


Figure 5.9: (a) ($I - V$) characteristics for two Pt-PANi-PPy-Au single HNWs measured in a four-probe configuration before (blue curves) and after HCl treatment (red curves). (b) The measurements performed in a two-probe configuration exhibit highly asymmetric ($I - V$) characteristics after the acid treatment.

The two-probe measurements configuration includes the two metal-CP Schottky diodes. In its as-synthesized state, the HNW of the panel (b) exhibits a rectifying behavior with clear non-linear but symmetric ($I-V$) curves indicating the existence of two identical Schottky barriers.

As expected, an important increase of current is observed after the acid treatment. Indeed, considering an applied voltage $|V| = 1$ V, highly asymmetric current gains $G = I^{doped}/I$ are obtained for negative $G \approx 20$ and positive applied bias $G \approx 600$. Consequently, this translates, after the HCl treatment into a rectifying ratio ($RR = G = \frac{I^{doped}}{I}$) defined at 1 V $RR \approx 30$.

The data confirm that tetra-segmented HNWs present an interesting rectifying effect which is absent in the tri-segmented samples. Similarly to the Au-PEDOT-PPy-Au HNWs, this effect originates from the metal-CP junctions which exhibit important alterations of their Schottky barrier height after the chemical treatment.

The rectifying effect is in agreement with the model proposed in the section 5.3.2 based on two asymmetric Schottky diodes and can only be measured in a two-probe configuration.

Higher rectifying effects ($RR \approx 30$) obtained with an acid treatment of Pt-PANi-PPy-Au where for oxidative treatment of Au-PEDOT-PPy-Au ($RR \approx 2$). This difference could be ascribed to the different metal/CP junctions that are constituting the HNWs. Indeed, Whereas Au/PEDOT and PPy/Au diodes seem to be more alike (presence of the heterocycle), it seems logical that the Pt/PANi diodes do not exhibit the same modification upon chemical treatment than the PPy/Au diodes.

Interestingly, similar result were obtained by Fowler *et al.* with PANi NWs [253]. In their work, Fowler *et al.* have shown that the response upon exposure to H_2 of Pt-PANi-Pt structures is dramatically different from the Au-PANi-Au structures and that this behaviour is stemming from the formation of different Schottky barriers for Au/PANi and Pt/PANi junctions. As recalled by Fowler *et al.* PANi which is a p-type CP, makes ohmic contacts only with metals exhibiting greater work functions $\Phi_M > \Phi_{CP}$, while metals with smaller work functions result in Schottky barrier formation [253].

The same effect can be invoked to explain our observations for PPy or PEDOT-based HNWs, however several experiments are required to determine the critical parameters that leads to a such high RR values. T -dependent measurements of several classes of tetra-segmented HNWs would confirm the presence of the Schottky barriers and determine their respective height after and before the chemical treatment.

5.5 Summary

The first important conclusion of the work presented in this chapter is that T -dependent data obtained with single HNWs corroborate with HNW arrays data. As a result, the intrinsic behavior of PPy NWs can be probed in the vertical configuration despite the averaging effect as the extracted parameters are the same as those deduced for planar single NWs. Several features characteristic of one-dimensional systems observed for various HNW arrays presented in the chapter 3 were confirmed by single HNWs measurements. The ambiguity stemming from the data interpretation can be resolved by considering large hopping length in CP segments which results in the modification of the usual exponential laws of the Mott variable range hopping into power-law dependences. Consequently, the apparent power-law behavior of the conductance observed for many samples in the low- T data corroborates with the Mott VRH model which thus explains particularly well the T -dependent electrical measurements, including nonlinear current-voltage characteristics and magnetotransport at low temperatures.

Secondly, we presented the electrical properties at room temperature of individual multi-segmented NWs. While the tri-segmented NWs exhibit symmetrical ($I - V$) characteristics, the tetra-segmented HNWs switch to rectifying behavior by exposure to oxidative or acid solutions ($FeCl_3$ or HCl). This interesting feature of the tetra-segmented HNWs compared to tri-segmented NWs is provided by their ability to switch their electrical behavior in function of the work function of the two conjugated polymer blocks. The use of microdevices allowed to confirm the existence of unbalanced contact resistances at both metal-CP interfaces of tetra-segmented HNWs.

A simple model based on the existence of Schottky diodes within HNWs allow to reproduce the rectifying behavior of the tetra-segmented Au-PEDOT-PPy-Au HNWs and to explain the enhanced rectifying behavior observed for Pt-PANi-PPy-Au HNWs.

Conclusions and Perspectives

La confiance est un élément majeur : sans elle, aucun projet n'aboutit.

Eric, Tabarly

Hybrid metal-CP NWs are promising high-tech materials as they combine the enhanced properties stemming from the NW family, to the high applicative potential of conjugated polymers and thus are of direct interest for developing novel multifunctional systems for convergent micro-nano-biotechnology applications. Nevertheless, before dreaming about wonderful HNWs-based applications, the promises of enhanced performances should be thoroughly verified and evaluated by the precise characterization of their intrinsic properties. This is what we try to do in this thesis. We focused on the characterization of the electrical properties of several classes of hybrid nanowires made of Au,Pt,Ni,PPy,PEDOT and PANi.

In the first step, electrical measurements were performed on multiple NWs-contained within the polycarbonate template as this method for measuring is very fast and requires no complex processing of the sample to be measured. Thanks to this technique, it was possible to characterize a large panel of hybrid nanowires presenting a wide range of parameters (diameters, composition). In particular, we have shown that the 3D-Mott VRH model provides a complete framework for the understanding of transport in PPy based hybrid nanowires with diameter down to 50 nm. On the other hand, the 40 nm diameter samples, exhibit a power-law temperature dependence of the resistance, characteristic of the critical regime of disorder-induced metal-insulator transition.

However, we have seen that this *bulk measurement* technique presents several drawbacks annoying for the characterization of nanomaterials such as hybrid nanowires. Besides the limitation inherent to the pseudo

four-probe configuration, an unknown number of hybrid nanowires are measured in parallel and present a wide distribution of their characteristics (diameter, segment length, interface resistance). Obviously, the use of NWs freed from the template is the best choice for the characterization of their intrinsic properties but also for applications oriented purposes. Indeed, the use of CPs specific features for controlled switching of device properties - at nanoscale - in the presence of external stimuli requires the interaction of the CPs with its environment which is almost impossible within the PC template.

We thus developed and adapted several techniques for contacting single hybrid nanowires in a planar configuration. Interestingly, by performing T -dependent electrical measurements of single tri-segmented hybrid nanowires and by comparing the obtained data in both vertical and planar configurations, we have shown that the intrinsic behavior of PPy nanowires are probed correctly in the vertical configuration despite the averaging effect. Strikingly, several features characteristic of one-dimensional systems observed for various hybrid nanowire arrays presented in the chapter 3 were confirmed by single hybrid nanowires measurements. The ambiguity stemming from the data interpretation can be resolved by considering large hopping length in CP segments which results in the modification of the usual exponential laws of the Mott variable range hopping into power-law dependences. Consequently, the apparent power-law behavior of the conductance observed for many samples in the low- T data corroborates again with the Mott variable range hopping model which thus explains particularly well the T -dependent electrical measurements, including nonlinear current-voltage characteristics and magnetotransport at low temperatures.

The second achievement of this thesis, resides in the development of microfabricated tool which allows correlated characterizations of nanomaterials. We demonstrated the possibilities of the microdevices by correlating the electrical measurements with high resolution TEM imaging, selected area electron diffraction, and energy dispersive X-ray analysis performed on the same hybrid nanowire. We have seen that this analysis can be coupled to the topology of the samples as observed by AFM. Among the various techniques used for defining electrical contacts, the top-contact approaches and especially the standard EBL based technique was mainly used to interrogate single hybrid nanowires as it is the one that permits a detailed electrical characterization of single hybrid nanowires by depositing multiple electrical probes on a single hybrid nanowire (up to 7 probes). While these membrane-based microdevices were used for correlated studies of hybrid nanowires but the extension to other nanomaterials (organic, inorganic or hybrid films, nanoparti-

cle) is straightforward. Among the several laboratories of UCL involved actively in nanotechnology, such platform could offer an interesting tool for the correlated characterization of a wide range of nanomaterials and nanodevices.

Together with the development of such sophisticated techniques, the synthesis techniques developed by Sophie Demoustier-Champagne and Vincent Callegari allowed to produce a large family of hybrid nanowires with various structures based on PPy, PEDOT, Au and Pt as principal constituents. Recently, our combined efforts focused on the comparative study of tri- and tetra-segmented hybrid nanowires presenting a CP-CP' junction (PEDOT-PPy or PANi-PPy) which present interesting features upon chemical treatment. While tri-segmented hybrid nanowires exhibit always symmetrical ($I-V$) characteristics, tetra-segmented hybrid nanowires switch to interesting rectifying characteristics by exposure to oxidative and acid solutions. The interesting feature is provided by the existence of two CP blocks which exhibit different responses upon chemical (acid or oxidative) treatment. Based on the XPS measurements and on correlated characterization of hybrid nanowires, a detailed explanation of the chemical treatments was proposed and a simple model based on Schottky diodes was developed to explain the observed difference in tri- and tetra-segmented hybrid nanowires which reproduces quite well the rectifying behaviors of tetra-segmented hybrid nanowires. Obviously, while a few questions have been answered, many others are still opened and plenty of complementary or new experiments could to be performed to gain a better understanding of the properties of hybrid nanowires.

Concerning the microdevices, many new experiments can be envisaged and several improvements of the devices are possible. The mechanical behavior of the membrane could be improved by using low stress (Si-rich) nitride available with the new LPCVD oven. The decrease of the mechanical stress of the membrane would allow to structure it by removing the nitride layer between electrodes. This will further increase the resolution of TEM imaging allowing true HR-TEM. This would also suppresses the unavoidable nitride membrane component in the SAED and EDX signals.

The second possible improvements of microdevices, aims to build improved nanowire-FET. Indeed, in order to improve the coupling between the gate and the nanowire, the definition of gates on the back side of the membrane of the microdevice, would allow a gate dielectric thickness as small as 30 nm (the membrane thickness) which is much better than what can be obtained by EBL processing.

Finally, despite the fact that microdevices were used mainly for the

characterization of metal-CP hybrid nanowires, its extension to other classes of nanowires and nanomaterials is straightforward.

Appendix A

Nanowire Samples

Sample -	Structure -	Φ (nm)	$L_P(L_{P'})$ (μm)	Mes. type -	Ref. Ech.
Au NW Arrays					
Au90	Au NWs	90	-	IV, R(T,F)	CV530
Au90	Au NWs	90	-	IV, R(T,F)	
Au70	Au NWs	70	-	IV, R(T,F)	CV236
Au70	Au NWs	70	-	IV, R(T,F)	
Au40	Au NWs	40	-	IV, R(T,F)	CV47
Au40	Au NWs	40	-	IV, R(T,F)	CV190
Au40	Au NWs	40	-	IV, R(T,F)	CV191
Au40	Au NWs	40	-	IV, R(T,F)	CV192
Au40	Au NWs	40	-	IV, R(T,F)	CV193
Au30	Au NWs	30	-	IV, R(T,F)	CV194
Au30	Au NWs	30	-	IV, R(T,F)	CV195
Bi-segmented NW Arrays					
B1	PPy-Au	90	2	IV, R(T,F)	
B2	PPy-Au	90	2	IV, R(T,F)	
B3	PPy-Au	90	2	IV, R(T,F)	
B4	PPy-Au	90	2	IV, R(T,F)	
B5	PPy-Au	90	2	IV, R(T,F)	
Continued on next page					

Table A.1 – continued from previous page					
Sample	Structure	Φ	$L_P(L_{P'})$	Mes. type	Ref.
E1	PPy-Au	70	2.5	IV, R(T,F)	
E2	PPy-Au	70	2.5	IV, R(T,F)	
Tri-segmented NWs - PPy or PEDOT					
M160-A	Au-PPy-Au	160	2	IV, R(T,F)	554
M160-B	Au-PPy-Au	160	2	IV, R(T,F)	557
M160-C	Au-PPy-Au	160	2	IV, R(T,F)	557b
M160-D	Au-PPy-Au	160	2	IV, R(T,F)	581
M90-A	Au-PPy-Au	90	2	IV, R(T,F), MR	269
M90-B	Au-PPy-Au	90	2	IV, R(T,F), MR	269b
S70-A	Au-PPy-Au	70	1.5 (-)	IV, R(T,F)	
S70-B	Au-PPy-Au	70	1.5 (-)	IV, R(T,F)	
M70-A	Au-PPy-Au	70	1.5	IV, R(T,F)	
M70-B	Au-PPy-Au	70	1.5	IV, R(T,F)	
M50-A	Au-PPy-Au	50	1.5	IV, R(T,F)	480
M50-B	Au-PPy-Au	50	1.5	IV, R(T,F)	560
M40-A	Au-PPy-Au	40	1	IV, R(T,F)	075
M40-B	Au-PPy-Au	40	1	IV, R(T,F)	078
M40-C	Au-PPy-Au	40	1	IV, R(T,F)	139
M40-D	Au-PPy-Au	40	1.5	IV, R(T,F)	140
M40-E	Au-PPy-Au	40	1	IV, R(T,F)	156
M40-F	Au-PPy-Au	40	1	IV, R(T,F)	157
M30-A	Au-PPy-Au	30	1.5	IV, R(T,F)	603
S110-A	Au-PPy-Au	1100	3	IV, R(T,F)	806
M70P'-A	Au-PEDOT-Au	70	3	IV, R(T,F)	482
Tri-segmented NWs - Pt					
M90Pt-A	Pt-PPy-Au	90	2.5	IV, R(T,F), MR	250
M90Pt-B	Pt-PPy-Au	90	2	IV, R(T,F)	231
M90Pt-C	Pt-PPy-Au	90	2	IV, R(T,F)	288
M70Pt-A	Pt-PPy-Au	70	2	IV, R(T,F)	307
Continued on next page					

Table A.1 – continued from previous page					
Sample	Structure	Φ	$L_P(L_{P'})$	Mes. type	Ref.
M70Pt-B	Pt-PPy-Au	70	2	IV, R(T,F)	308
Tri-segmented NWs - PPy and Thiols					
M70Thiol-A	Au-Thiol-PPy-Au	70	2	IV, R(T,F)	185
M90Thiol-A	Au-Thiol-PPy-Au	90	2	IV, R(T,F)	211
Tri-segmented NWs - Nickel Segment					
M110Ni	Ni- $C_7H_9NO_2$ -PPy-Au	106	2	IV, R(T,F)	237
M90Ni	Ni- $C_7H_9NO_2$ -PPy-Au	90	2	IV, R(T,F), MR	273
Tetra-segmented NWs - PPy and PEDOT					
M90PP'A	Au-PEDOT-PPy-Au	90	2.5(2)	IV, R(T,F)	472
M90PP'B	Au-PEDOT-PPy-Au	90	2.5(2)	IV, R(T,F)	472b
S110PP'Ai	Au-PEDOT-PPy-Au	110	2.5(2)	IV, R(T,F)	807
S110PP'Bi	Pt-PANi-PPy-Au	110	2.5(2)	IV, R(T,F)	808
Penta-segmented NWs - PPy					
M70PMP-A	Au-PPy-Au-PPy-Au	70	1(1)	IV	179
S90PMP-A	Au-PPy-Au-PPy-Au	90	1(1)	IV, R(T)	200
M90PMP-A	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F), MR	254
M90PMP-B	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F), MR	261
M90PMP-C	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F), MR	276
M90PMP-D	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F)	278
M90PMP-E	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F), MR	285a
M90PMP-F	Au-PPy-Pt-PPy-Au	90	2(1)	IV, R(T,F), MR	285b

Table A.1: Characteristics of samples measured in a vertical and planar configurations. The polymer length is estimated by the number of scans performed during the synthesis.

Label	E_a (meV)	T_0 (K)	$N(E_F)$ (eV ⁻¹ .cm ⁻³)	F_0 (10 ¹² × V/m)	R_R
M160-A	91	4.9×10 ⁷	-	1.2	3.78×10 ³
M160-B	58	2.4×10 ⁸	-	1.5	6.21×10 ³
M160-C	97	4.6×10 ⁶	-	-	0.26×10 ³
M160-D	57	9.7×10 ⁷	-	-	9.47×10 ³
M90-A	130	2.1×10 ⁸	8.9×10 ¹⁷	18	6.17×10 ⁴
M90-B	92	5.6×10 ⁷	1.1×10 ¹⁸	15	4.82×10 ⁴
S70-A	121	1.4×10 ⁸	-	1.5	1.04 × 10 ⁴
S70-B	92	5.0×10 ⁷	3.9×10 ¹⁷	1.5	0.29 × 10 ⁴
S90-A	140	1.8×10 ⁸	-		0.71 × 10 ⁴
M70-A	133	2.4×10 ⁸	2.3×10 ¹⁷	-	2.22 × 10 ⁴
M70P'-A		1.3×10 ⁶	-	2.1	-
M50-A	98	7.6 × 10 ⁶	-	15	498
M50-B	48	4.19 × 10 ⁶	-	15	64
M40-A	3	580	-	-	1.8
M40-B	4	1608	-	-	1.5
M40-C	-	19	-	-	5.6
M40-D	-	1.3×10 ⁵	-	2.1	10.2
M40-E	-	2.1×10 ⁷	-	2.4	∞
M30-A		2.98×10 ⁷	-	-	193
M90Pt-A	52	6.2×10 ⁷	2.6×10 ¹⁸	0.1	310
M90Pt-B	91	5.4×10 ⁷	-		2500
M70Pt-A	49	9.59×10 ⁶	-		170
M70Pt-B	69	4.14×10 ⁷	-		900
M70Thiol	135	4.1×10 ⁸	-		3.9 × 10 ⁵
M90-PP'-A	59	1.4×10 ⁷	-	0.28	231
M90-PP'-B	55	1.5×10 ⁷	-	1.64	254
M90-PMP-A	76	1.4×10 ⁷	-	2.0	2.1 × 10 ³
M90-PMP-B	73	1.5×10 ⁷	-	3.1	7.7 × 10 ³

Table A.2: Data analysis for various HNW arrays. The Mott temperature T_0 and characteristic field F_0 were extracted from linear fits (see text). The parameter $N(E_F)$ is estimated within the 3D VRH model.

Label	α	β ($T = 77\text{ K}$)
M160-A	6.3	2.9 - (7.7 at $T = 4\text{ K}$)
M160-B	4.32	2.6
M160-C	4.1	3.3
M160-D	6.9	2.6
M90-A	4.1	3.5 (at $T = 4\text{ K}$)
M90-B	4.4	3.5 - (8.6 at $T = 4\text{ K}$)
S70-A	7.3	2.4 - (7.2 at $T = 4\text{ K}$)
S70-B	5.7	1.3
S90A	7.5	3.5
M70-A	9.6	2.8 - (4.7 at $T = 5\text{ K}$)
M50-A	5.0	1.1 - (5.9 at $T = 4\text{ K}$)
M50-B	3.3	3.2
M40-A	0.6	1.1 (at $T = 4\text{ K}$)
M40-B	0.4	1.3 (at $T = 4\text{ K}$)
M40-C	0.27	1.15 (at $T = 4\text{ K}$)
M40-D	1.37	5.7 (at $T = 5\text{ K}$)
M40-E	4.72	6.9 (at $T = 5\text{ K}$)
M30-A	4.7	4.2
M90Pt-A	3.9	2.1 - (6.0 at $T = 4\text{ K}$)
M90Pt-B	6.1	3.4 - (5.9 at $T = 4\text{ K}$)
M90Pt-C		5.2 (at $T = 4\text{ K}$)
M70Pt-A	3.9	5.0 (at $T = 4\text{ K}$)
M70Pt-B	5.8	5.9 (at $T = 4\text{ K}$)
M70Thiol	4.9	2.5
M90-PP'-A	3.2	1.3 - (5.6 at $T = 4\text{ K}$)
M90-PP'-B	4.7	1.6 - (7.7 at $T = 4\text{ K}$)

Table A.3: Exponent α and β for various HNW samples. β values were obtained from power law fits of the $(I - V)$ curves for current levels higher than the resolution of the measurement system, for $T = 77\text{ K}$ otherwise indicated.

Appendix B

Other Contacting Techniques

In this chapter, we present two other techniques that were used to contact single HNWs to electrodes.

B.1 The Electron Beam Induced Deposition Technique

In this section, we present a top-contact approach based on a direct-write nanopatterning technique that allows the deposition of various materials such as platinum (Pt), tungsten (W) or silicon dioxide SiO_x and the etching of materials present on the substrate [259, 260, 261]. The interesting feature of this technique stems from the high deposition and etching resolutions which are related to the electron beam size [262]. When a gas flux is directed toward a substrate together with a focused electron beam, the decomposition of adsorbed gas molecules takes place mainly due to the *SE*. When a suitable gas containing a metal or a semiconductor, the decomposition induced by the focused electron beam results in the local deposition micro and nanostructures of the materials [263]. This process is called *electron beam induced deposition* (EBID). With a reactive gas such as fluorine, water vapor or chlorine, selective etching of some materials is achieved [263]. This process is called *electron beam induced etching* (EBIE).

The process for EBID contacting of HNWs can be described briefly as follows. First, the gas injection system (GIS) can be started heating the heater of the reservoir and capillary to obtain the ideal temperature conditions for the deposition. After a two-point alignment, a SEM inspection is then performed to find a candidate for being contacted, a

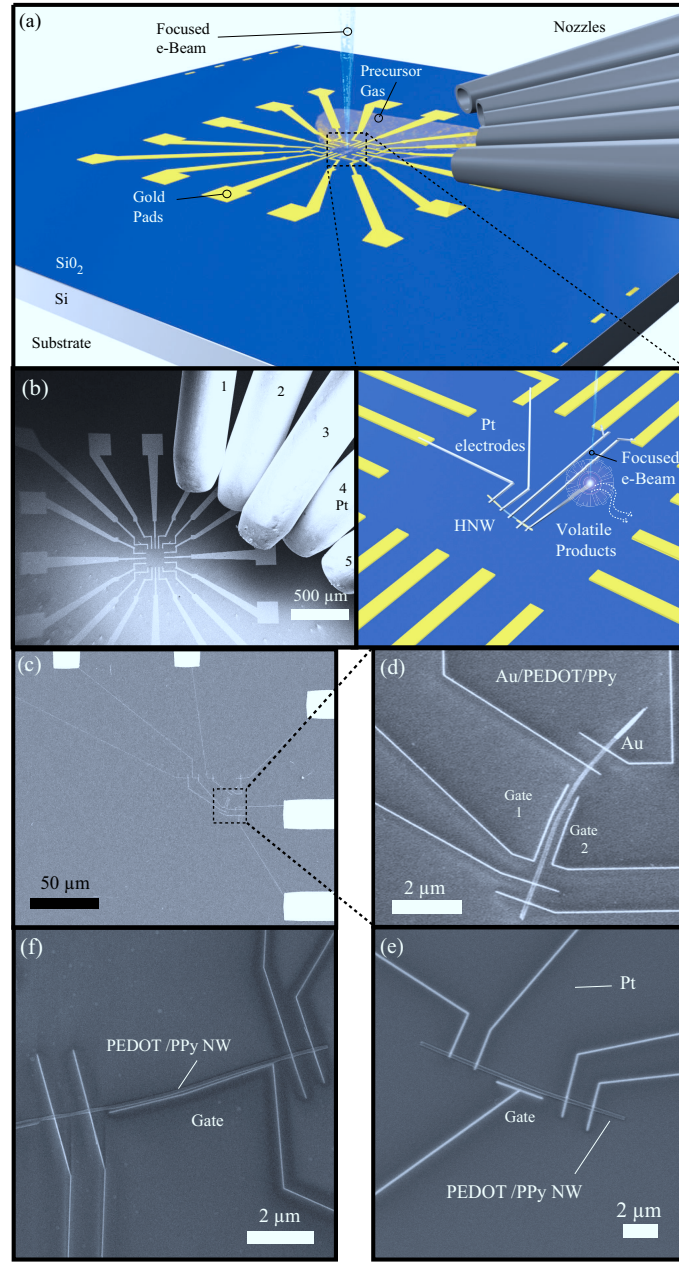


Figure B.1: (a) 3D schematic view and (b) SEM picture of a typical single NW device used for contacting HNWs by Pt contacts. (b) The five GIS nozzles are in position to feed the *MeCpPtMe*₃ precursor into the SEM chamber. (c-f) SEM pictures of HNWs (PEDOT/PPy contacted in a FET configuration).

Precursor	(Me) ₃ MeCpPt	Pt(PF ₃) ₄
Tension (<i>kV</i>)	3	5
Current (<i>pA</i>)	150	900
Step size (<i>nm</i>)	10-15	10-20
Dwell time (<i>ms</i>)	50-100	50-100
Loops (#)	1	1
Pressure (<i>mbar</i>)	1 – 4.0 × 10 ⁻⁶	1 – 4.0 × 10 ⁻⁶
Conductivity ($\mu\Omega.cm^{-1}$)	10 ⁵ – 10 ⁷ [259, 247, 264]	250-2000 [262]
this work	4.0×10 ⁵ -4.8 × 10 ⁶	

Table B.1: Pt Deposition parameters obtained with the standard precursor ((Me)₃MeCpPt) and a new carbon-free platinum precursor (Pt(PF₃)₄).

SEM image is taken of the exposure area and the layout can be directly drawn in the previous picture. Prior to the exposure, an outgas procedure is run to obtain the optimal pressure conditions for the EBID process.

In this work, the EBI technique was mainly used for the deposition of metallic lines (Pt) for contacting single HNWs deposited on a substrate and insulators *SiO_x* for producing the gate dielectric of single NW Field effect transistors (FET). Three examples of NWFET produced by the EBID are given in the Fig. B.1.(d-f). All EBID depositions were carried out at a working distance (WD) of 10 mm and the chamber base pressure was kept below 5.0 × 10⁻⁶ *mbar* before Pt fabrication. The Pt structures were produced with the deposition parameters listed in the Table B.1 together with some resistivity values obtained in this work and from various references.

EBID process seems very simple to use and allows the rapid fabrication of electrical contact to NWs and is a promising technique for many applications in nanoresearch [264]. Nevertheless, despite all the superlatives that are generally used for describing the EBID techniques [262, 247, 265], the high resistivity of the deposited materials and the non-negligible observed ageing effects show that the parameters and the conditions need to be further optimized to suit the requirements of single NW measurements as shown by the electrical measurements of single HNWs.

Here we present a few results obtained with the electron beam induced deposition (EBID) of platinum (Pt) carried out with the demon-

stration E-line at Raith lab in Dortmund and at the IMT laboratory, Romania. First we present a characterization of the deposited materials prior to the electrical measurements of HNWs contacted with EBID Pt. We performed EBID deposition on *classical* electrical devices and also on membrane-based micro-electromechanical systems (MEMS). The interest of such MEMS is that they are specially designed for the characterization of nanomaterials as they allow to correlate the structural informations given by several analysis and techniques such as AFM, SEM, TEM to electrical measurements of the same deposited materials (see section 4.4.4.5 of the Chapter 5).

In the following section, we briefly present the basic theoretical considerations of the electron beam interactions with the substrate and the sample as they are key features of the EBID technique.

B.1.1 Electron Beam Interactions

An electron beam impinging on a solid surface undergoes a series of complex interactions with the electrons and the nuclei of the atoms of the specimen which result in elastic or inelastic scattering, that is with or without energy conservation, respectively. The inelastic scattering can result in emission of X-rays (characteristic and Bremsstrahlung), light and heat depending on the incident energy of the primary electrons (*PE*) [23]. Depending, on the ratio of the sample thickness and the electron mean free path λ_e , a fraction of the primary electrons (*PE*) can be transmitted through the specimen without interactions. As shown in the figure B.2.(a), electron scattering occurs within a defined volume of the specimen with a characteristic tear-drop shape and is accompanied by the emission of a variety of electrons namely, the Auger electron (*AE*), the secondary (*SE*), back-scattered (*BSE*) and low-loss electrons (*LLE*). Generally, it is considered that all specimen-emitted electrons with $E < 50 \text{ eV}$ are *SE* while electrons with $E > 50 \text{ eV}$ are *BSE* [23, 262].

While the Auger electrons and X-rays emissions are useful to investigate the elemental composition and the structure of the surface of a given specimen (ie. Auger Electron Spectroscopy (AES), Electron Dispersion X-ray spectroscopy (EDX)) as it will be shown in the chapter 5. The *SE* are used too for imaging and in electron beam lithography (EBL) systems to modify a resist such as poly-(methyl methacrylate) (PMMA). Interestingly, *SE* can also be used to deposit specific materials and etch selectively some materials with a high resolution. This technique is shortly presented in the following section.

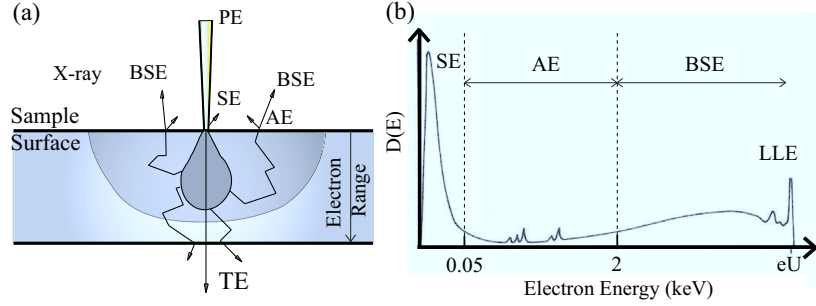


Figure B.2: (a) Schematic view of the diffusion volume where several electron varieties are emitted. (b) Typical energy spectrum of the emitted electrons consisting of secondary electron (SE), backscattered electrons (BSE), low loss electrons (LLE) and peaks of Auger electrons (AE). Adapted from [23].

B.1.2 Pt EBID Characterization

Because, we want to use EBID Pt lines and NWs for contacting HNWs, a primary and useful information is the electrical resistivity of the deposited materials. For its characterization, single Pt NWs and lines were placed on several gold electrodes. We used 70-nm-thick gold electrical contacts defined by EBL as the electrodes should not be too high and present a *clean* profile of the edges¹ to avoid discontinuities of the deposited Pt line [237].

We have thus measured several EBID Pt NWs and lines, all deposited with the parameters given in the table B.1. The lines are 13 to 130 μm long with a typical width of 60-80 nm and presenting a gaussian topographic profile as observed from AFM and TEM measurements [237]. The figure B.3.(b) gives the $(I - V)$ characteristics taken as a function of the length for a 13 μm long Pt NWs. the resistivities measured for different samples are in the range $4 \times 10^5 - 4 \times 10^6 \mu\Omega.\text{cm}$. These values were calculated from four-probe measurements and assuming an equivalent rectangular section of $60 \times 60 \text{ nm}^2$. These values are comparable to values found in the literature for optimized Pt deposition from $(\text{Me})_3\text{MeCpPt}$ precursor [266, 264] (see Fig B.3.(e)).

In this work, one of the main applications of EBID Pt is related to HNWs interconnections, it is therefore quite important to have an idea of the influence of ageing effects on the electrical properties of Pt deposits. Also, we checked the effect of FeCl_3 on the electrical properties of EBID Pt lines as FeCl_3 will be used as an oxidizing agent in the treatment of

¹Which is not always the case in electrodes defined by photolithography.

HNWs (see section 5.3).

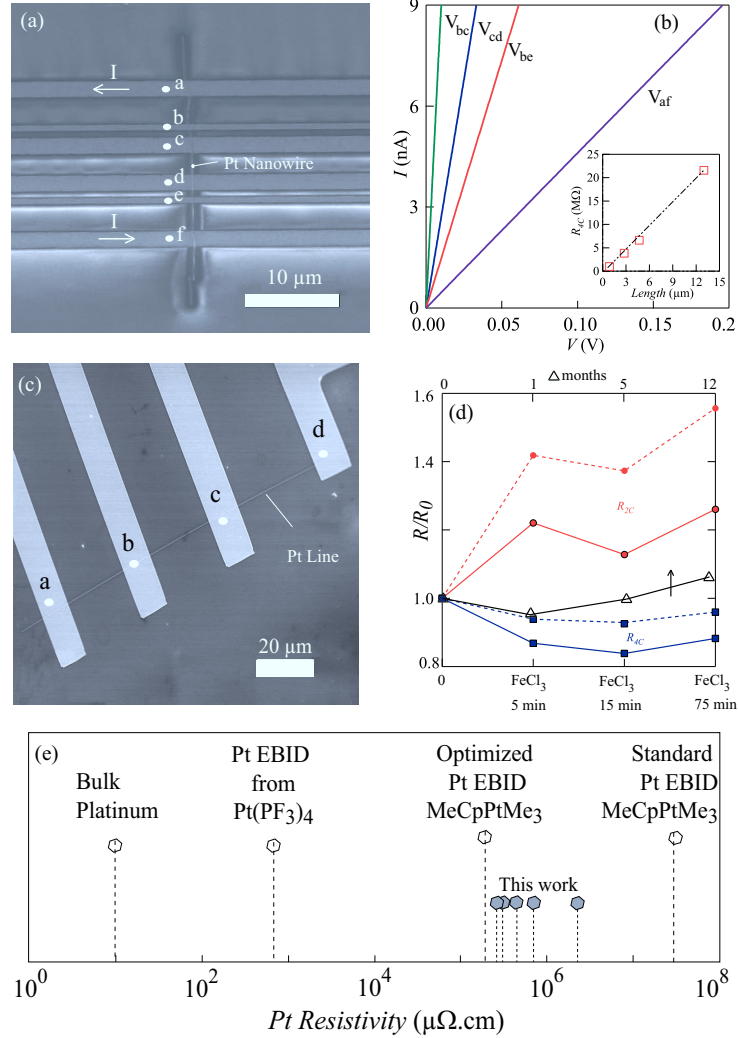


Figure B.3: (b) ($I - V$) characteristics of a single Pt NW shown in (a). The inset gives the dependence of the measured resistance as a function of the NW length. (c) High resolution TEM micrograph of the same Pt NW. (d) Resistance variations of two Pt lines as a function of ageing parameters. (e) Comparison of resistivities values found for several Pt EBID and various values from the literature.

In the Fig. B.3, we compare the relative resistance variations induced on three samples by ageing in ambient air as a function of time and ageing due to oxidative treatment and measured for long EBID Pt lines deposited on four Au probes similar to the one shown in (c), and us-

ing the two (square) and four-probe techniques (circle). Astonishingly, the four-probe resistance of Pt line decreases (triangle) slightly (about 10 %) after the samples were kept in air for 1 month and increases slowly (roughly 13 % after one year), whereas, generally, an increase of several orders of magnitude of the four-probe resistance is expected² only after a few days [265]. In principle, with such low platinum content, the electrical conduction is based on a percolation network of platinum clusters embedded in an amorphous carbon matrix. The ageing process of such structures is often described as a physical modification of the percolation network [267]. Nevertheless, the contact with the oxygen presents in the air could also play an important role in the ageing mechanism [265].

It was proposed that the percolation network of Pt EBID samples could be greatly modified by the migration of Pt particles which would cause Pt cluster growth and thus a decrease of the average distance between clusters, which decreases the conductivity [265]. Nevertheless, it seems that in our (highly resistive) samples, such migration does not occur. This probably because of the low volume of deposited material and its low Pt content. As a result, the four-probe conductivity remains unchanged even upon oxidative treatment. We will see in the chapter 5, that the use of microdevices could improve the understanding of the ageing and migration processes in EBID deposits.

B.1.3 Pt EBID for contacting HNWs

The Fig. B.4 gives the raw data obtained for several HNWs contacted by EBID. The measurements are not very good as the samples exhibit very high resistances and non-linear ($I - V$) curves, suggesting a probable charges injection-limited transport due to high Pt/NWs interfaces resistance. The small section of the Pt leads, (roughly $60 \times 60 \text{ nm}^2$) seems to be responsible of this situation. Pt leads were designed as lines to keep the deposition time within reasonable range. For instance, the time requested for defining the Pt leads for the example given in the Fig. B.1.(c) is about 2 hours using the dwell time and the deposition parameters of the table B.1. This time could have been shorter with closer Au pads as in most of contacted HNWs, the length of deposited Pt leads were more than hundreds of μm long in total. With much shorter leads, it would have been possible to design thicker and wider Pt leads which would have provide better electrical interfaces just like

²Nevertheless, for the comparison, it is important to notice that our samples have not been measured directly in the SEM chamber under vacuum conditions like in reference [265]. They were synthesized in Germany and characterized in the Welcome facilities, the following day. Thus being kept 24 hours in air.

the ones obtained by FIB deposition [144]. Unfortunately, it can be con-

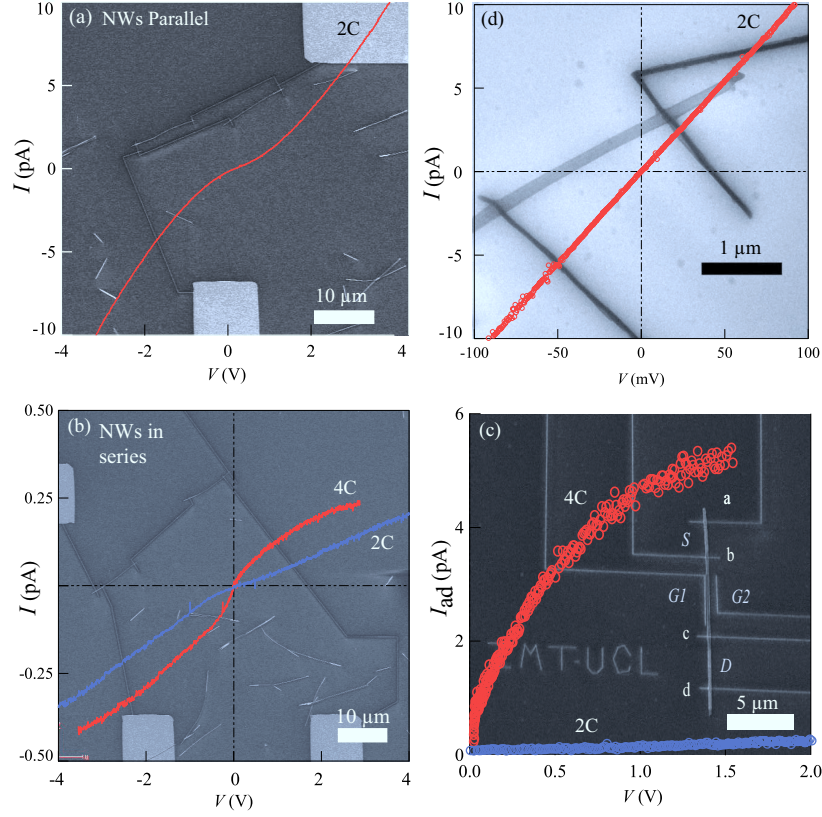


Figure B.4: (I - V) characteristics of a two PEDOT-PPy contacted by EBID Pt lines in different configurations. (a) Two HNWs are contacted in series and in parallel (b). (c) a Single HNW contacted in a FET configuration. (d) Two probe (I - V) curve of a single PEDOT segment. SEM micrographs of the contacted NWs are shown in the background.

cluded that using the same conditions and parameters, Pt EBID is not suited for contacting single NWs and more specifically CP NWs. The conditions and deposition parameters should be optimized to produce thicker Pt leads with higher conductivity within reasonable deposition times.

B.1.4 Effects of Electron-Beam on CP Materials

During a standard EBL process, the resist is chemically modified by the exposure to the high energy e-beam and becomes soluble in the resist developer. When exposed at high doses (Dose $> 500 \mu\text{C}/\text{cm}^2$), the resist

could be inverted becoming insoluble to the resist developer due to the apparition of highly cross-linked chains.

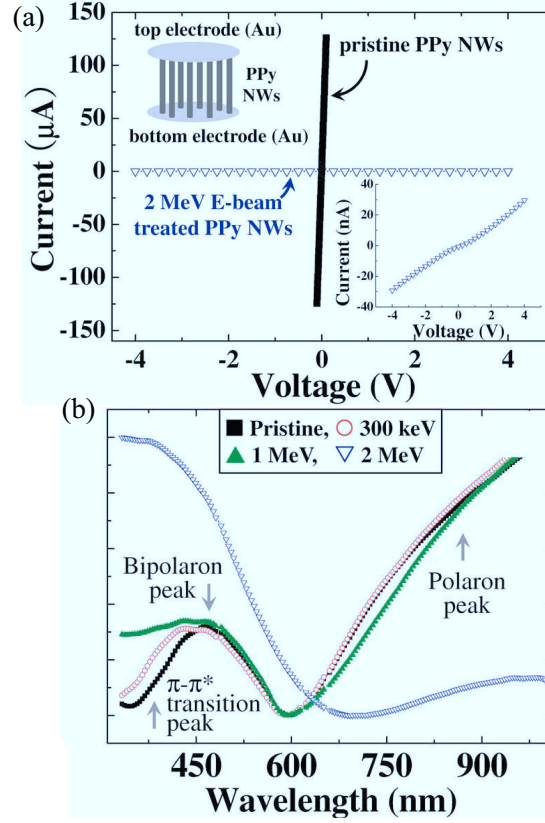


Figure B.5: a) ($I - V$) characteristics of the pristine and exposed PPy NWs (@ 2 MeV $8.0 \times 10^{16} e^-/cm^2$) at RT. Top inset: a schematic diagram of samples and electrodes for the ($I - V$) characteristics measurement by using a two-probe contact method. Bottom inset: the magnification of the ($I - V$) characteristic curve of the treated PPy NWs. (b) A comparison of (a) UV/visible absorption spectra. From ref. [24].

Obviously, e-beam irradiation of other organic materials such as CP could have an impact on their intrinsic properties. Recently, it was observed a dedoping effect and conformational changes on PPy NWs after being exposed to high-energy e-beam irradiations [24]. In their work, Hong *et al.* used 200 nm diameter PPy NWs synthesized through an electrochemical polymerization method. The energy of the e-beam varied from 300 keV to 2 MeV with a constant dose of $D=12800 \mu C/cm^2$. Hong *et al.* have shown that the intercylic rings of the PPy NWs be-

came distorted; the portion of the benzoid structure decreased, while that of the quinoid structure increased and also, the electrical resistance of the PPy NWs dramatically increased by 5 orders of magnitude when exposed to 2 MeV beam (see Fig. B.5). Furthermore, it was shown on PA that the effect of e-beam irradiation depends on the doping process of the CP. More precisely, Yoshino *et al.* have observed that the electrical conductivity shift of PA induced by exposure to an electron beam, differs if the exposure is performed before or after I_2 doping. The authors explained these results by the role of I_2 molecules in the initial stage of radiolysis and the suppression of the cross-linking [268]. More recently, it was shown that the effect of EB irradiation causes both chain scission and cross-linking process in PANi, reducing structural parameters such as inter-chain separation, thermal stability and T_g but increasing crystallinity and solubility [269]. Generally, the effect of e-beam irradiation at low dose on CP is often equivalent to doping while at higher dose, cross-linking mainly occurs reducing the conjugation of the CP and consequently the conductivity and the crystallinity of the CP decrease. Comparing the very low e-beam exposure of a classical EBL process to the previous works where very high energy beams were required to notice an effect, it seems reasonable to conclude that very little effect should result from the EBL processing of our HNWs.

B.2 Dielectrophoretic Assembly

The dielectrophoretic assembly method is a bottom-up assembly approach that relies on dielectrophoresis (DEP) effects. Basically, DEP effects occur when a polarizable microparticle ³ is immersed in a DC electric field gradient [270]. Due to the interaction of the induced dipole and the electric field gradient, a dielectrophoretic force is applied to the particle bearing the dipole [228]. This force which can be either attractive or repulsive depends on the ac bias frequency and on the microparticle and the solvent properties [228]. Assuming the approximation to the first dipole moment contribution, the dielectrophoretic force can be expressed as follows [219],

$$F_{DEP} \propto \epsilon_{sol} V_p \Re(K_\alpha) \nabla |\mathbf{E}|^2 \quad (\text{B.1})$$

where ϵ_{sol} is the permittivity of the solvent, V_p is the volume of the HNw, $\Re(K_\alpha)$ is the real-part of the Clausius-Mossotti factor and $\mathbf{E}$ is the electric Field [270].

³which can be metallic, semiconducting or insulating.

This DEP force can be used also to manipulate dielectric particles that are suspended in liquid media. Especially, DEP was used extensively in biomedical applications [271, 272, 220], where cell microorganisms separation, manipulation, and characterization are essential. Also DEP attracts strong interest, as it could be combined to the emerging field of lab-on-a-chip technology to provide high resolution, low cost, and rapid analysis for a wide range of biological and chemical applications [272].

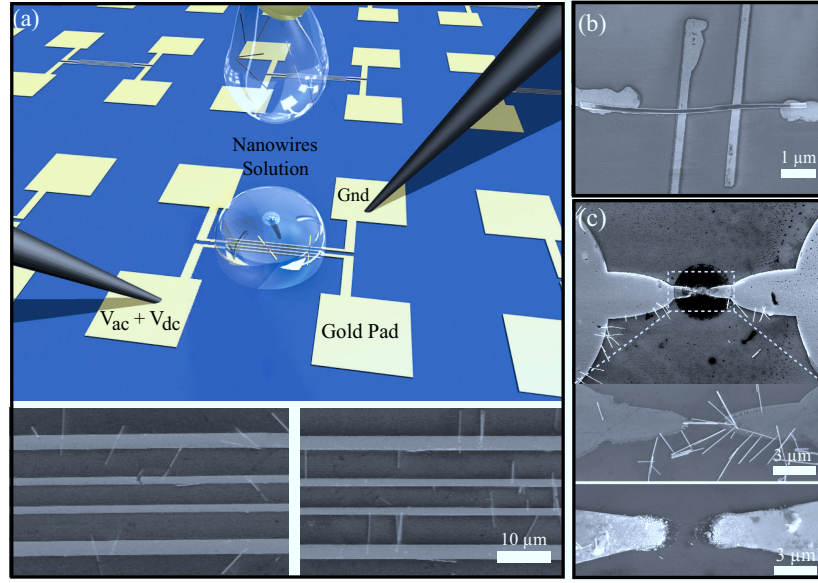


Figure B.6: (a) 3D view of an electrical device during the NW assembly assisted by an external electric field. The lower insets give SEM pictures obtained by dropcasting (left) and dielectrophoretic assembly (right) performed with an applied ac voltage of $5 V_{rms}$ at a frequency of $1 MHz$. (b-c) SEM pictures of HNWs contacted by the dielectrophoretic assembly. (b) 500 nm diameter Au-PEDOT-Au HNWs from reference [16]. (c) SEM picture taken after the assembly process of NWs onto optimized electrodes for enhanced DEP assembly.

Interestingly, DEP can be used also to manipulate and to align metallic and semiconducting NWs between electrodes [273, 226, 227, 274, 275, 228, 219]. Generally, electrodes are immersed in the NW suspension and a composite ac-dc electric field is applied with a high frequency function generator as shown in the Fig. B.6.(a). Once the solvent dried, the nanomaterials are deposited onto the electrodes. After the deposition step, the chip is then rinsed in pure solvent and dried with a nitrogen flux.

Generally, a sinusoidal voltage of $5 - 10 V_{rms}$ is applied through a high resistance larger than $R = 10 M\Omega$ between the two outer electrodes at a frequency of $0.1 - 5 MHz$. The resistance is used to limit the current through the contacted NW as high current can lead to the destruction of both deposited NW and the electrodes pair.

In this work, DEP assembly was firstly performed using the electrodes designed for the dropcast deposition. An example of contacted NW is given in the Fig. 4.3.(f) and in the right inset of Fig. B.6.(a). When comparing the two insets of the Fig. B.6.(a), despite the obvious alignment of the NWs perpendicular to the electrodes, the trapping of NWs is a relatively slow process probably because of the small gradient induced by the non ideal shape of these electrodes.

DEP seems very efficient for contacting HNWs with a different morphology than our samples like the HNWs used in the work of Cao *et al.* [16]. They used DEP assembly for aligning single 500 nm diameter HNWs onto 4 leads in a four point measurement test bed shown in Fig. B.6.(a). Such high diameter HNWs, exhibit mechanically stronger metal-polymer interfaces than in our samples which have a typical diameter of 90 nm. Furthermore, Cao *et al.* characterized HNWs with very small Au segments compared to our samples (about ten times smaller).

From the equation B.1, it can be seen that the DEP assembly can be enhanced by a short electrode distance, a high voltage applied, or by a strong curvature of the electrodes. In order to increase the DEP assembly efficiency, optimized electrodes were produced by EBL with shorter electrodes spacing and radius of curvature of 600 nm. Such optimized electrodes with a spacing of 3 μm are shown in the Fig. B.6.(c).

The result is straightforward as almost all DEP assembly led to electrical contact to HNWs. Unfortunately, the experience has shown that mainly metallic segments of HNWs are trapped between the electrodes. The observation of dispersion has shown that around 50% of hybrid Au-PPy-Au Nws were missing one metallic segments [145]. As a result, a large number of metallic segments, typically 5 μm long, are present on the solution. Consequently, the probability to trap gold segments between electrodes with dielectrophoretic effects is very high as shown in the Fig. B.6.(b) where metallic segments interconnect together to constitute several bridges between electrodes. When the resistance is omitted, large current flows through the system, resulting in the melting of the metallic segment and the destruction of both electrodes as shown in the lower inset of the Fig. B.6.(c).

The presence of a large amount of metallic segments coming from broken HNWs impedes the characterization of a single HNW. Also, it was observed that even when a single HNW was contacted by the DEP

assembly, its electrical measurement could exhibit highly non-linear and non-reproducible features which can be ascribed to high and variable contact resistances. For these reasons, only a few single NWs devices were produced by the DEP assembly and characterized as the DEP assembly seems to be not suited for the assembly of multi-segmented HNWs. On the other hand, the DEP assembly appears to be very efficient when applied to other NWs which exhibit higher robustness and do not break into several pieces in the solution. A few experiments were performed on CuCo multilayered NWs produced by the Group of Pr. L. Piraux, and the DEP assembly seems very promising to contact easily single NW.

Independently from their efficiency, the DEP assembly as well as all the bottom-contact methods present the same inconvenient that the quality of the electrical interfaces between the deposited NW and the electrode can not be controlled by any means. Indeed, once the NW is deposited, it is not possible to clean these interfaces by rinsing in pure solvent or by performing an oxygen plasma for instance. Because a good control of the interfaces is essential to the electrical characterization of HNWs, the work was naturally oriented toward top contact approaches. While photolithography could have been used for defining the top electrodes like what was done for metallic NWs [276], e-beam systems were preferred because of their powerful possibilities (resolution and precision) and their high flexibility (layout design).

B.3 Microfabricated PMMA Template

The usual method used to define contacts to template-synthesized NWs is to remove the NWs from the template or the growth substrate and to deposit them onto a substrate with predefined electrodes. The common technique consists to suspend the NWs in a liquid that is then applied to the substrate. We have seen in the previous section that that contacts to individual NW can be made using other techniques than the ones presented in the chapter 4. Nevertheless, the best results have been obtained using the electron beam lithography, metallization, and lift-off procedure. However, for up-scaling, an approach that does not rely on a random process step is required [81]. If NWs are grown epitaxially on the substrate from defined seed locations, the wires can be left in place and contacts can be post-processed to the top of the wires [217]. Here, we briefly present the characterization of PANi NWs synthesized in a PMMA planar template which have been fabricated by EBL. The chemical synthesis of the PANi NWs has been performed by Yunus, S.

and Atout, A. from the surface group directed by the Prof. Bertrand.

The fabrication of the devices can be resumed as follows. Essentially, a 360 μm thick, 3 inches Si Highly doped wafers are oxidized in a dry atmosphere to obtain high quality and uniform SiO_2 layer (step 1). platinum pads and are defined by an optical followed by the evaporation of a 100 nm thick Pt layer with a typical adhesion layer of 5 nm of Cr or Ti. Then a lift-off is performed generally in acetone followed by rinsing the wafer in isopropanol and water. Wafers are diced to obtain single device with typical dimensions of $6 \times 8 \text{ mm}^2$. Then a thick PMMA (MW) 900 000, 6% in chlorobenzene) layer (500 nm) is deposited onto each single device and subsequently exposed to define directly on the central part of each device, trenches in the PMMA resist through the Pt electrodes with typical lengths of 10 μm and a width varying between 100 nm and 500 nm wide. Interestingly, the shape (width and length) as well as the number of produced NWs can be easily modulated at will prior to the synthesis which allows for example to modify the total resistance between the leads (see Fig. B.8).

These devices are dipped for a given amount of time in an oxygen-saturated solution of aniline (0.4 M) and H_2SO_4 (0.4 M) at 15 °. These devices are then thoroughly rinsed with ultrapure water and then doped with HCl (1M) during 12 h at room temperature. They are then dried with nitrogen. For characterization purposes, the four contact device is freed from its PMMA mask using toluene and ultrasonic agitation [61].

Figure B.7.(a) shows a schematic view of a PMMA template ready for the synthesis. The panel (c) of the figure gives a scanning electron microscopy image of a completed device. As observed in the Fig. B.7.(d), the morphology of the PANi NWs is not perfectly straight. The obtained wire presents necks at the PANi junctions between the electrodes. The experiments on PANI patterning through surface-tension contrast strongly suggest that surface (SiO_2) pretreatments of the substrate could be used to infer on the junction morphology. Electrical bridging is then verified by performing a single current-voltage ($I - V$) measurements. Typical ($I - V$) characteristics of a single polyaniline NW are given in function of the temperature T in Fig. B.7.(d). At RT the ($I - V$) curves are linear and symmetrical and show no rectification effect. As T decreases the current decreases, indicating that polyaniline has a non-metallic behavior found in other CP such as polypyrrole [145].

The measured resistance follows the relation given in the equation 2.17. The best fits to our data have been obtained with $d = 3$. This suggests that the three-dimensional (3D) VRH is the appropriate model of transport in our samples. The $\ln[R(T)]$ versus $T^{-1/4}$ plots are given in the inset of the Fig. B.7 for $T \gtrsim 50 \text{ K}$. From these plots we extract

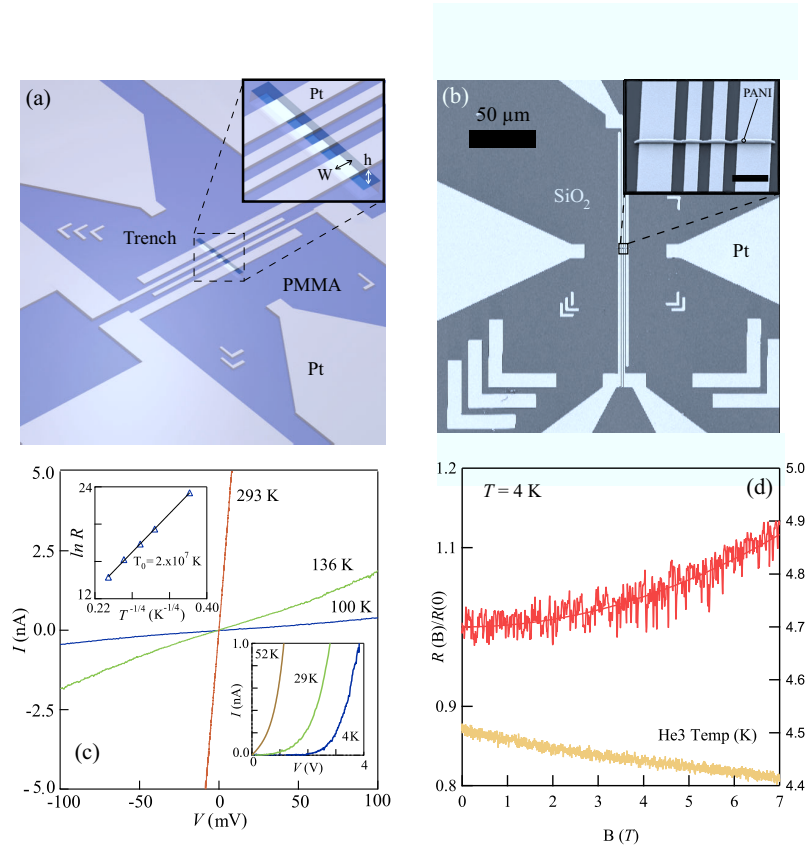


Figure B.7: (a) Schematic view of device designed to realize the PANI NW synthesis. (b) SEM view of a single PANI NW after the removal of the PPMA trench. (c) The corresponding ($I - V$) characteristics taken at RT demonstrate the existence of electrical contacts. d) MR signal taken at $T = 4$ K.

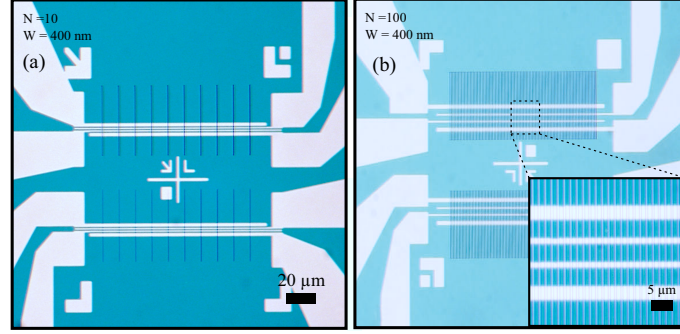


Figure B.8: CCD top view of device with exposed and developed PMMA trenches ready for the synthesis of parallel PANI NWs with a width of 400 nm. (a) 10 NWs are in parallel. The distance between electrodes is $1 \mu\text{m}$. (b) 100 NWs are in parallel with an inter-electrodes distance of $5 \mu\text{m}$.

the parameter $T_0 = 2.0 \times 10^7 \text{ K}$.

Similarly, to what have been done with HNWs arrays, we performed magnetoresistance measurements on single PANi NWs. A typical result is given in the Fig. B.7.(d). The MR measurements are performed with B aligned perpendicular with the NWs axis. The observed magnetoresistance is consistent with the 3D-VRH model, for which a positive MR is expected and is explained by the wave-function shrinkage model (see chapter 2). The MR signal observed at $T = 4 \text{ K}$ is relatively small compared to what has been observed for HNWs arrays.

Appendix C

Supplementary Materials

C.1 X-ray Photoelectron Spectroscopy

Besides the structure of the metal-polymer interfaces, the PPy doping ratio is another key parameter playing on the electrical transport properties of the hybrid nanowires. XPS is a particularly useful tool for gathering information on the doping level of electroactive polymers. In this section, are gathered the XPS measurements performed to characterize HNWs.

C.1.1 Metal Electrodeposition on PPy

Here, we focus on XPS measurements to estimate the doping level of tri-segmented HNWs (metal-CP-metal). Because the CP content of such HNWs, and hence the XPS signal, is too low to obtain a reliable doping ratio, most of the measurements were performed on CP films synthesized under same conditions as for HNWs CP segments described in the chapter 3. A typical N(1s) PS spectrum of a PPy film is shown in Fig. C.1. Two components (green curves)- representing protonated nitrogens-appear at binding energies higher than 400 eV, while two other components, corresponding to aminelike (red curve) and iminelike (blue curve) nonprotonated nitrogens, appear at 399.8 and 397.9 eV, respectively. The doping level in the assynthesized PPy film, estimated by the $[N+]/[N]$ ratio, is close to 22%. Then, XPS measurements were performed for one-component PPy nanowires electrosynthesized under similar conditions Fig. C.1.(d). In this case, the N(1s) curve could be simply fitted by only two components¹. The first peak (green curves)

¹Curve fitting has been done using a Gaussian-Lorentzian (85%-15%) linear combination and a linear background.

Samples	$[\text{N}^{\delta+}]/[\text{N}]$	$[\text{S}^{\delta+}]/[\text{S}]$
As-synthesized PEDOT	-	35
FeCl_3 -treated PEDOT	-	32
As-synthesized PPy	23	-
FeCl_3 -treated PPy	15	-

Table C.1: Doping levels determined by XPS for as-synthesized and FeCl_3 -treated PEDOT ($[\text{S}^{\delta+}]/[\text{S}]$ atomic ratio) and PPy ($[\text{N}^{\delta+}]/[\text{N}]$ atomic ratio).

representing protonated nitrogens is centered at 401.9 eV and the second one corresponding to nonprotonated nitrogens appears at 399.8 eV. The doping level for one-component PPy nanowires was estimated at 13% (one protonated nitrogen out of eight). As already reported for CP NT [180, 14], the lower doping value for template-grown PPy nanostructures compared to PPy films results from the electrosynthesis in nanopores.

For tri-segmented metal-PPy-metal NWs, one expects a lower value of the doping ratio ($< 13\%$) due to the reduction of the PPy segment during the electroplating of the upper metal segment. To flesh out the scale of this reducing process, XPS has been used to estimate the doping in PPy films after application of a post-treatment reproducing the conditions applied for the electrodeposition of the metal segment onto the PPy segment.

Specifically, a potential of -0.2 V was applied to PPy films for 10 or 30 min. As shown in Figs. C.1.(b) and C.1.(c), a progressive decrease of the protonated nitrogen components (green curves) combined with a marked increase of the nonprotonated iminelike nitrogen (blue curve) is observed in the XPS data. This corresponds to a decrease of the doping ratio from 22% to 17% and further to 14% after application of reduction conditions for 10 and 30 min, respectively. Based on these results, we can estimate that for trisegmented metal-PPy-metal NWs, the doping ratio of PPy is only a few percent, in agreement with the electrical behavior described in the chapters 3 and 5.

C.1.2 Chemical Treatment on CP films

The different synthesis and chemical post-treatment conditions used in this study are gathered in Table C.1 and XPS spectra of the four samples are presented in Fig. C.2.

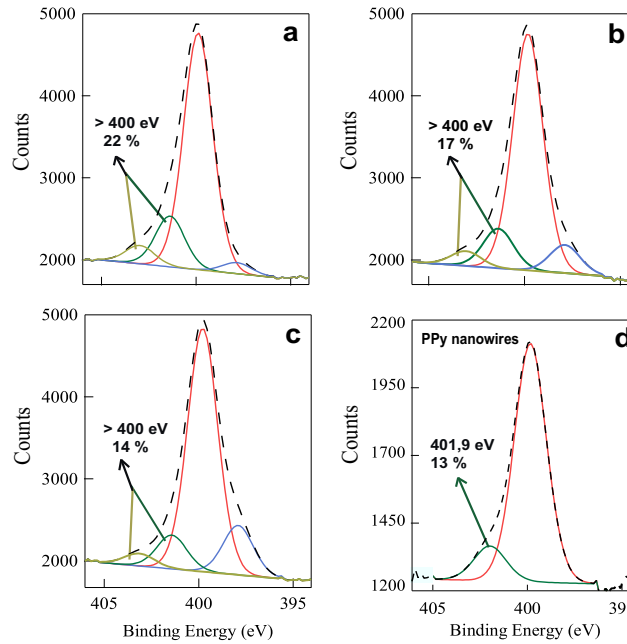


Figure C.1: (N(1s) XPS fitted spectrum of PPy films: (a) as synthesized, (b) after application of a reduction potential of -0.2 V for 10 min, and (c) after post-treatment at -0.2 V for 30 min. (d) N(1s) XPS fitted spectrum of one-component PPy nanowires.

The core level $S(2p)$ XPS spectra of the as-synthesized PEDOT- ClO_4^- film (Figure C.2.(a)) and $FeCl_3$ -treated PEDOT (Figure S1c) can be decomposed into two major doublets, at 162.7 and 163.7 eV and at 163.7 and 165.0 eV, that are attributed to the EDOT sulfur atom in the neutral and partially oxidized state $[S^{\delta+}]$, respectively. The third high-binding energy doublet (> 165 eV) corresponds to the $\pi \rightarrow \pi^*$ shake-up satellite structure. The doping level of the two samples can be determined from the ratio of the positively charged sulfur atoms of EDOT and the total sulfur contribution from PEDOT chains: $[S^{\delta+}]/[S]$ ratios [14]. A doping level of 35% is found for the as-synthesized PEDOT and it slightly decreases to 32% after the $FeCl_3$ post-treatment (Table C.1).

The $Cl(2p)$ core-level spectra of as-synthesized and $FeCl_3$ PEDOT films (Figure C.2.(e)) show clear differences between both samples. Indeed, upon $FeCl_3$ treatment, the characteristic $Cl(2p)$ peak of perchlorate species in the region of 207 eV completely disappears, and two doublets lying at around 196 and 200 eV appear. These binding energy values correspond to the ionic (Cl^-) and covalent ($-Cl$) chlorine species,

Samples	-N= 397.8 eV	-NH- 399.9 eV	N ^{δ+} > 401 eV
As-synthesized PPy	3	74	23
FeCl ₃ -treated PPy	16.5	68.5	15

Table C.2: N(1s) component proportions (%) for as-synthesized and FeCl₃-treated PPy films.

respectively [277]. Though the FeCl₃-treatment only slightly affects the oxidation state of PEDOT, it has a strong impact on the nature of the counter-ion, as all the ClO_4^- anions were replaced by chlorine species.

The N(1s) core-level spectrum of the as-synthesized PPy- ClO_4^- film (Figure C.2.(b)) is best resolved into four components whose positions and assignments are in agreement with the literature data [278]. The two peaks above 400 eV can be attributed to positively charged nitrogen species ($-NH^+-$, abbreviated N^{δ+}), while the amine-like ($-NH-$) and the imine-like ($-N=$) structures are located at binding energies of 399.9 and 397.8 eV, respectively. The doping level of the as-synthesized PPy, estimated from the ratio of the positively charged nitrogen atoms and the total nitrogen contribution from PPy chains, N^{δ+}/[N] ratio, is equal to 23%. The treatment with FeCl₃ (Figure C.2.(d)) results in a strong increase of the imine-like nitrogen (from 3 to 16.5 %, Table C.2), accompanied by a significant decrease of the N(1s) high binding energy peaks (from 23 to 15%, Table C.2). Transformation of a part of $-NH^+-$ to $-N=$ groups may be the result of the nucleophilic attack of H_2O and Cl^- anions on the doped PPy [279, 280]. The Cl(2p) core-level spectra of PPy films (Figure C.2.(d)) show that upon FeCl₃ treatment, all the perchlorate species with a characteristic peak around 207 eV, are replaced by chlorine species (mainly covalent chlorine), as indicated by the appearance of a peak centered at 200 eV. All these XPS data clearly indicate that over-oxidation of PPy occurs during the FeCl₃ treatment. This oxidative degradation of PPy is, of course, affecting the electronic properties and electrical conductivity of PPy.

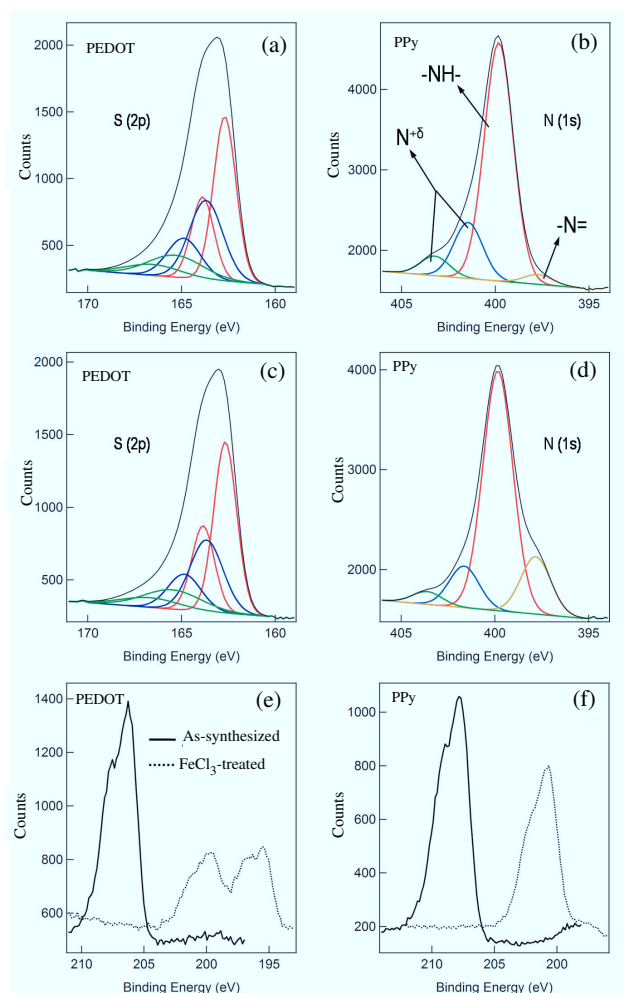


Figure C.2: (a) and (b) S2p and N1s XPS fitted spectra of as-synthesized PEDOT and PPy films, respectively. (c) and (d) S2p and N1s XPS fitted spectra of PEDOT and PPy films, respectively, after the $FeCl_3$ treatment. (e) and (f) Cl2p XPS spectra of as-synthesized $FeCl_3$ treated PEDOT and PPy films, respectively.

C.2 Towards Thermal Characterization of Single Nanowires

In the current economic and environmental contexts, many efforts are directed towards developing energy-harvesting applications. In this respect, thermoelectric phenomena, which involve the conversion between thermal and electrical energy, are expected to play an increasingly important role in meeting the energy challenge of the future [281, 282]. Indeed, thermoelectricity materials have attracted increased attention due to their prospective applications as power cogenerators, harvesting the vast amount of waste heat produced by combustion-based power generators [282]. Such materials utilize the Seebeck effect for power generation and the Peltier effect for cooling [283, 284]. The thermoelectricity and more precisely the associated thermoelectric effects (Seebeck, Peltier and Thomson effects) are also interesting in the point of view of more fundamental physic because these effects are linked to intrinsic² properties of materials and thus could be used to probe the properties of novel materials [286].

The Seebeck effect named after the German physicist Thomas Johann Seebeck (1770-1831), consists in the appearance of a voltage ΔV in an open loop (see Fig. C.3) formed by two different materials when a temperature difference ($T_1 - T_2$) is imposed to the junctions. Conversely, the Peltier effect is the fact that when current flows through a material a temperature gradient arises because the charged carriers exchange thermal energy [182]. The Seebeck coefficient or thermopower S of a materials can be defined as the thermoelectric voltage (TEV) change rate with respect to temperature T at a given temperature

$$S = \frac{dV}{dT}, \quad (\text{C.1})$$

Interestingly, this thermal/electric conversion is perform without moving parts or toxic gases, which make them unique among power generation and cooling methods. Presently, thermoelectrics find only limited use because of their poor efficiency. This efficiency is ranked by a dimensionless figure of merit, ZT , which is defined as

$$ZT = S^2 \sigma T / \kappa, \quad (\text{C.2})$$

where S is the thermopower or Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature.

²For instance, the Seebeck coefficient can also be defined as the amount of entropy per charge carrier [285].

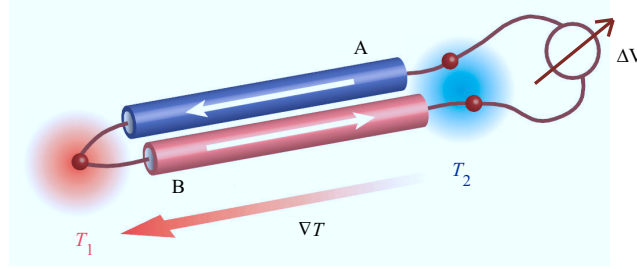


Figure C.3: Principle of the Seebeck effect. A voltage is created in the presence of a temperature difference between two different materials A and B. Adapted from reference [25].

Nowadays, commercially available thermoelectric devices have a ZT values of only about 1. To be competitive compared with conventional refrigerators and generators, one must develop materials with $ZT > 3$ [181]. Obviously to maximize ZT , S and σ should be as large as possible while κ must be small to reduce heat leakage and maintain a temperature difference [287]. However, from the Weidmann-Franz law, the ratio σ/κ is limited. Hopefully, low-dimensional materials and especially NWs offer the possibility of enhanced thermoelectric figure of merit compared with bulk materials [283].

While the definition of the Seebeck coefficient is relatively simple, its measurement is not trivial. The main challenge of the Seebeck coefficient measurement is to apply a temperature gradient to the sample and to measure it correctly which is not as simple as it seems. Indeed, compared to electric measurements, thermal measurements require special care. Therefore, in this work, microdevices adapted to the thermal characterization of NW like samples have been designed, fabricated and characterized. Furthermore, a vacuum chamber and a sample holder were designed especially for these microdevices to allow the thermal measurements to be performed under vacuum conditions ($p \approx 10^{-6}$ mbar) as a function of the temperature (2- 300 K) and the magnetic field. In the following section, we briefly review the fabrication of different types of devices designed for the measurement of the Seebeck coefficient of NW like samples. Each device configuration presents advantages and inconveniences that will be discussed briefly below.

C.2.1 Microdevices for Thermal Measurements

As show in the Fig. C.4, three types of devices were designed for the Seebeck coefficient measurement of single nanowire like materials and

batch fabricated using a wafer-stage microfabrication process. All the devices are equipped with at least two electrodes used for measuring the conductivity and the thermal voltage across the nanowire, and two thermometers defined close to each electrode to measure the temperature gradient. Often, two heaters are added to separate the temperature measurement leads from the heating leads.

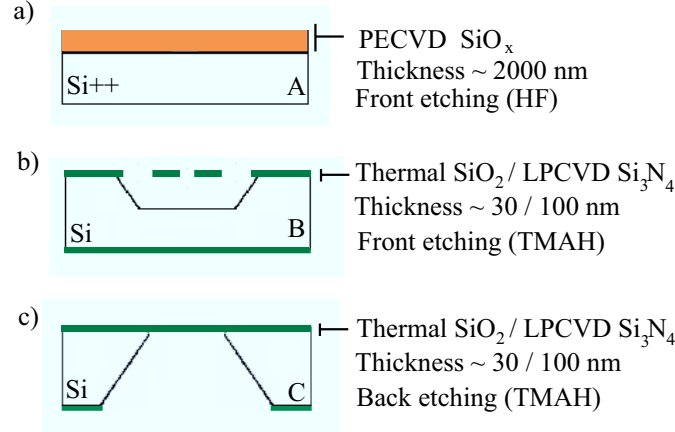


Figure C.4: Schematized view of the different types of devices fabricated for the thermal characterization of single NW-like materials.

While the devices of type A, more robust are based on a thick oxide layer SiO_x deposited by plasma enhanced chemical vapor deposition (PECVD) with an average thickness of $2 \mu\text{m}$, the other devices are based on nitride membranes which offer a better control over the heat fluxes. A CCD image of a typical device of type A is given in the Fig. C.5.(a). The advantages of these devices is their robustness and the possibility to use the substrate as a back gate. Similar devices were used recently for the characterization of SWCNT and single InSb NWs [288, 289, 290].

In principle, The NW integration can be performed by either of the techniques presented in the section 4.2, nevertheless, the best approach is the EBL technique which allow to define custom electrodes and gives the lowest thermal resistance between the sample and the substrate. Hochbaum *et al.* used a bottom-contact approach for the measurement of Si NWs and they reduce the thermal contact resistance, by depositing a Pt/C pads using the EBID or FIB techniques [291].

The types B and C are based on a LPCVD nitride membrane. In the type B, the membrane is structured to obtain two *islands* on top of which are defined separately a Pt/ti heater/thermometer and a set of electrodes similarly to the devices of the references [292, 293, 291]. Each island is

suspended and connected to the substrate by long ($L > 200 \mu\text{m}$) SiN/Pt leads presenting high thermal resistance. As a result, the heat fluxes are better controlled. This allows to perform the thermal conductivity measurement of the sample [284]. A SEM micrograph of a device of type B is given in the Fig. C.5.(b). These devices are very fragile which is an important issue for the NW deposition. Indeed, because of the mechanical properties of the stoichiometric nitride, the deposition of a single NW on top of electrodes is really challenging as most of the time, the deposition breaks the SiN/Pt leads. The devices of type C correspond to the microdevices described in the section 4.4.2 and will be described later.

C.2.2 Thermopower Measurements

Generally, the thermopower³ or thermoelectric power (TEP) measurement consists in applying a temperature gradient ΔT between two points of the sample. This temperature gradient induces a thermoelectric voltage (TEV) ΔV in the sample which is measured using appropriate electrodes. Finally, for small ΔT , the Seebeck coefficient is obtained as $S = \Delta V / \Delta T$. Nevertheless, this value is not the absolute Seebeck coefficient of the sample because of the contribution of the voltage probes which is always included in the measured value.

Practically, for all the devices presented in the previous section, the measurement of the Seebeck coefficient consists in passing a current through a heater which locally heats the substrate (the SiO_2 layer or the Si_3N_4 membrane), thus resulting in a temperature gradient along the sample. This temperature increase (ΔT) is estimated by the resistance change of thin metal lines contacted in a four-probe configuration and measured by the lock-in technique. Prior to the measurement, a calibration of the heating and the sensing thermometers was performed for each device and consists in recording the thermometer resistances as a function of the temperature.

For the device of type A, the heat generated with a heater or directly through one of the thermometers, initially propagates through the $2 \mu\text{m}$ thick SiO_2 layer, which has a relatively lower thermal conductivity ($\approx 0.5 \text{ W m}^{-1} \text{ K}^{-1}$) [288]. This results in a temperature gradient across the NW and the surface of the substrate to which it is thermally anchored (see the inset of the Fig. C.5).(b). The heat dissipates quickly, once it reaches the underlying silicon substrate, which has higher thermal conductivity ($\approx 100 \text{ W m}^{-1} \text{ K}^{-1}$).

³Thermopower is a misleading term since it is not related to the electric power but express the voltage induced in response to a temperature difference.

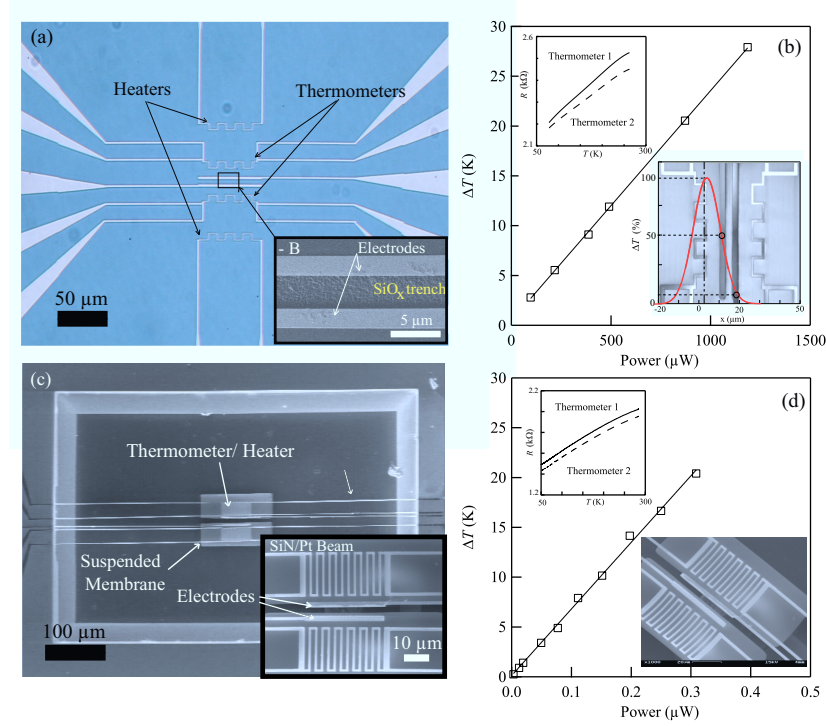


Figure C.5: CCD and SEM views of microdevices of type A (a) and B (c). (b-d) Temperature calibration as a function of the power for two devices of type A and B. The insets give the T dependent calibration of the resistance of each thermometer.

In the device of type B, thanks to the high thermal insulation of the two islands, the power required to apply a temperature gradient is more than 3 order of magnitude lower as shown in the inset of the Fig. C.5.(d). Nevertheless, the extreme fragility of these devices impeded their use for the characterization of single NWs as no device survived all the steps required for measurements (i.e. NW deposition and device handling and mounting on the measurement system).

The TEV measurements of 70 nm diameter Au and Co single NWs performed using devices of type A, are shown in Fig. C.6.(c) and (d) respectively. The two-probe ($I - V$) characteristics of the contacted Co NW are given for $T = 77$ and 300 K in the Fig. C.6.(c). The high resistance $R_{2C} \approx 8800 \Omega$ value deduced from the slope dV/dI is stemming mainly from the long voltage probes as each probe contributes roughly for more than 4350 k Ω as estimated from the metal resistivity obtained from the thermometer four-probe measurements. The good linearity

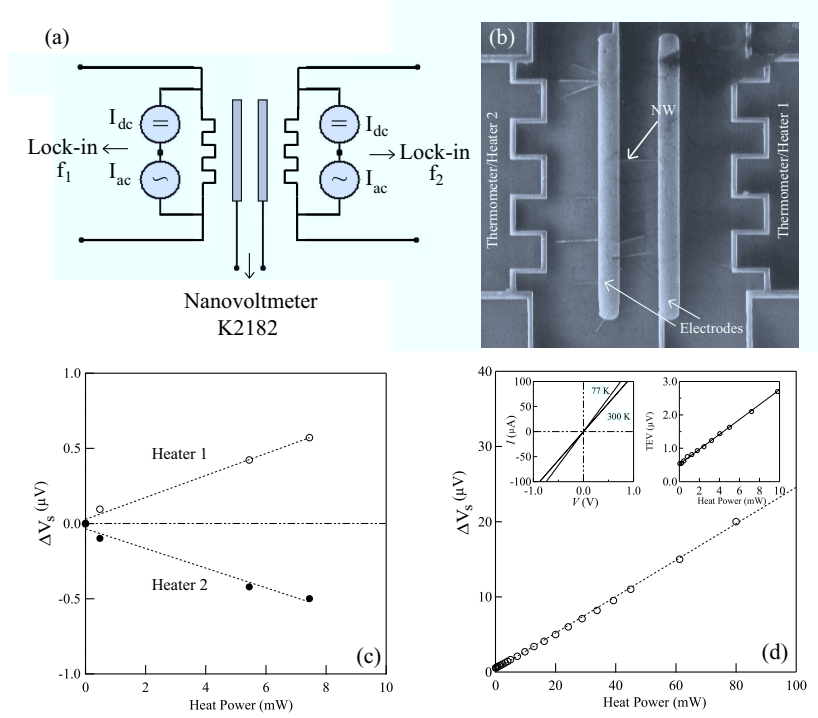


Figure C.6: (a) Seebeck measurement electrical configuration. (b) SEM micrograph of a single Au NW deposited by the dielectrophoretic method. (c-d) typical thermoelectric voltage response ΔV measured on devices shown in the panel (b), as a function of heating power for a Au (c) and a Co NW (d).

of the $(I - V)$ curves demonstrates that the charge transport is not dominated by charge injection at the electrodes/NW interfaces.

The thermometer calibration and the Seebeck measurements were carried out at room temperature under high vacuum conditions obtained with a diffusion pump system. The pressure is a crucial parameter that should be kept as low as possible to minimize the convective heat transfer. A pressure in the range of $2 - 4 \times 10^{-6}$ mbar was kept during all the measurements.

Figure C.5 demonstrates, the linearity of the observed TEV with respect to the applied power, indicating S is a constant in both cases. As we already mentioned, the measured TEV is really that of the NW/voltage probes couple since it contains a contribution from the thermoelectric power of the metal electrodes. However, in our case, the contribution of the electrodes is negligible as the Seebeck coefficient of Pt and Ti tend

to cancel each other [287]. As expected, for a good measurement, the TEV was proportional to the applied power and thus to the temperature gradient. Also, the sign of the observed TEV changed when the temperature gradient was reversed, as shown in the Fig. C.5.(c). Nevertheless, the deduced values for the Seebeck coefficients are much lower than values reported in the literature for Au and Co (2 and 30 $\mu V/K$). This discrepancy originates mainly from the difficulty of measuring precisely the local temperature at the closest points of nanowire/metal contacts especially with the devices of type A, where the thermometers and electrodes are 10 μm apart. Consequently the effective temperature gradient applied to the sample is much lower than ΔT which translates into a lower S value. To fix this issue, Hochbaum *et al.* performed a numerical simulation of the two dimensional heat conduction along the device NW, to estimate the effective temperature gradient along the nanowire [291].

Finally, the development of devices for the thermal characterization of single nanobjects led to devices of type C which combine the thermal features advantages of devices of type A and B with the possibilities of correlated characterization of the microdevices as detailed in this chapter. The contacting technique chosen for these devices is the EBL based top-contact approach as it allows for each sample a custom design of the electrodes and thermometers sets. The Fig. C.7 gives CCD and TEM micrographs of a typical sample (a single HNW (Au-PPy-Au)) ready for measurements. Because silicon nitride exhibit good thermal properties in a wide range of temperature (e.g. $\kappa = 30 \text{ Wm}^{-1}\text{K}^{-1}$) and thanks to the thickness of the membrane of the microdevice (typically 80 nm thick), the heat propagation allows a better temperature profile [225] along the sample. At the same time, the EBL resolution allows to decrease considerably the distance between the electrodes and the thermometers (less than 1 μm), which results in a better evaluation of the effective temperature gradient.

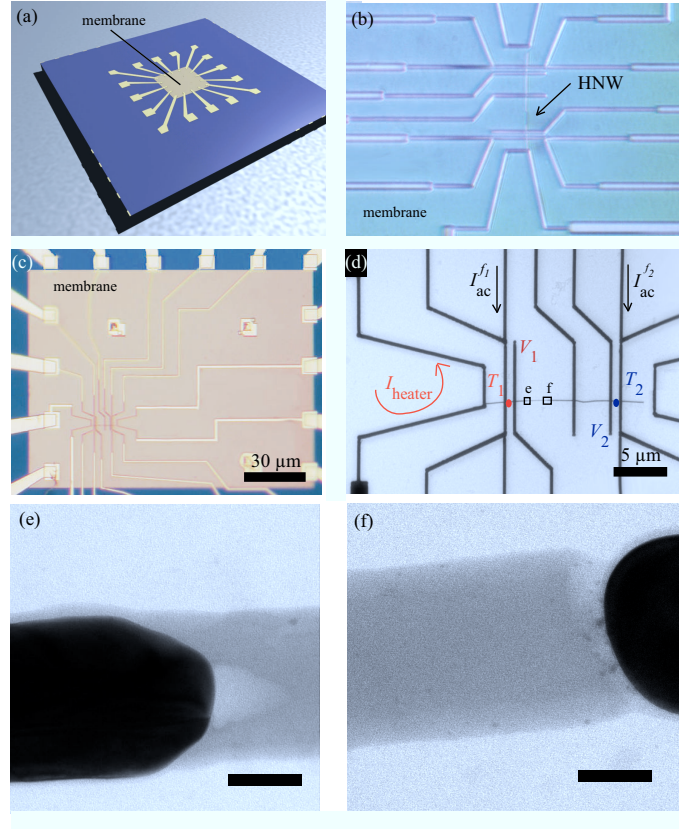


Figure C.7: (a) Schematic view of a device of type C. (b) CCD image HNW deposited on a microdevice and contacted with a set of electrodes and thermometers. (c) CCD image of the membrane after metal deposition. (d) TEM micrograph obtained after the measurements. (e-f) Zoom on the Metal/CP junction of the HNW. the scale bars are 50 nm.

Appendix D

Process Sheets

The Table below provides the detailed process sheet used to fabricate the single NWs devices. All of the fabrication steps, with the exception of those marked with asterisk are performed in a clean-room environment (implying the use of microelectronic grade chemicals and materials).

Step description	Products/Sub-steps	Parameters
Substrates	<i>Si</i> 3-inch wafers	<111>; 3-5 <i>mOhm/sq</i>
Standard cleaning	- H_2SO_4/H_2O_2 v:v=2:5 - H_2SO_4/H_2O_2 v:v=2:5 - HF 2% - rinser dryer	15 min boiling 5 min rinse water 15 min boiling 5 min rinse water 15 sec 5 min rinse water
Thermal oxidation	900°C, O_2 post-annealing N_2	120 nm dry quality oxide
Inspection	Ellipsometry	check thickness
Metalization	5 nm <i>Cr</i> 80-120 nm <i>Au</i>	deposition rates $\sim 1 \text{ \AA/s}$
Photolithography	- coating <i>AZ6612</i> thickness - bake	6600 rpm 1.1 μm 1 min at 110°C

	- exposure <i>i-line</i> mask - Development - rinser dryer	200 - 350 mJ/cm ² CommonMask - <i>AZ-MIF762</i> 1 min 1 min rinse water
Inspection	Optical microscope	check quality
<i>Au</i> wet-etch	- HNO_3/HCl v:v=1:3 <i>Aqua Regia</i> - <i>Acetone</i> - H_2SO_4/H_2O_2 v:v=2:5	1 - 3 min visual etch stop detection 5 min rinse water 10 min boiling remove photoresist remove <i>Ti</i> 5 - 10 sec 5 min rinse water
Inspection	Optical microscope	check quality
Dicing	- Protective coating bake - Dicing	3000 rpm 1 min at 110°C chip size 6 × 10 mm
Cleaning	<i>Acetone</i> <i>Acetone</i> <i>IPA</i> <i>N₂</i>	5 min boiling 1 min ultrasonic bath 5 min boiling rinse blown dry
Inspection	Optical microscope	check quality

Table D.1: Process sheet for the micro- and nano-fabrication of single nanowire devices.

Step description	Products/Sub-steps	Parameters
Substrates	<i>Si</i> 3-inch wafers	<100>; 20 <i>Ohm</i> /sq
Standard cleaning	- H_2SO_4/H_2O_2	15 min boiling

	v:v=2:5 - H_2SO_4/H_2O_2 v:v=2:5 - HF 2% - rinser dryer	5 min rinse water 15 min boiling 5 min rinse water 15 sec 5 min rinse water
Thermal oxidation	900 °C, O_2 post-annealing N_2	30 nm dry quality oxide
Tempress	Si_3N_4 deposit rate 8 nm/min SiH_4 39% - 500 sccm NH_3 68% 500 sccm	$T = 800^\circ C$
Inspection	Ellipsometry	check thickness
Photolithography alignment on flat	- coating <i>AZ6612</i> thickness bake - exposure <i>i-line</i> mask - Development - rinser dryer	6600 rpm 1.1 μm 1 min at 110°C 200 - 350 mJ/cm ² Sdev2009 Etching - <i>AZ-MIF762</i> 1 min 1 min rinse water
Inspection	Optical microscope	check quality
SiN_x RIE etching Electrotech 340 Metalization	SF6 30 mTorr 30 nm/min LCP/TCP = 069/022° $V_{DC} \approx 140 V$ $APC = 52.5^\circ$ 5 nm <i>Cr</i> 80 nm <i>Au</i> or <i>Pt</i>	$P = 30 W$ 50 nm/min $V_{AC} \approx 200 V$ deposition rates $\sim 1 \text{ \AA/s}$
Photolithography	- coating <i>AZ6612</i>	6600 rpm

	thickness bake - exposure <i>i-line</i> mask - Development - rinser dryer	1.1 μm 1 min at 110°C 200 - 350 mJ/cm ² Sdev2009 Metal - <i>AZ-MIF762</i> 1 min 1 min rinse water
Inspection	Optical microscope	check quality
<i>Au</i> wet-etch	- HNO_3/HCl v:v=1:3 <i>Aqua Regia</i> - <i>Acetone</i> - $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ v:v=2:5	1 - 3 min visual etch stop detection 5 min rinse water 10 min boiling remove photoresist remove <i>Ti</i> 5 - 10 sec 5 min rinse water
Inspection	Optical microscope	check quality
Cleaning	<i>Acetone</i> <i>Acetone</i> <i>IPA</i> <i>N₂</i>	5 min boiling 1 min ultrasonic bath 5 min boling rinse blown dry
TMAH etching	<i>TMAH</i> 10 % thickness 225 $\mu\text{m} \pm$ 25 μm	$T = 90^\circ \text{C}$ $\sim 0.8 \mu\text{m}/\text{min}$
Wafer cleaving		
Cleaning (Single device)	<i>H₂O DI</i> <i>IPA</i> <i>N₂</i>	10 min boiling rinse blown dry
<i>Hot Dropcast</i> Cleaning	<i>N₂</i> <i>Dichloromethane</i>	blown dry 10 min boiling

Resist spin coating	N_2 <i>Copo/PMMA</i> 950K 4.5%/4% in <i>chlorobenzene</i> thickness	blown dry 2000/2000 rpm/s; 1 min $\sim 1 \mu\text{m}$
EBL		magnification: $\times 200$ or 400 dose: $400 \mu\text{C}/\text{cm}^2$ $I_{beam} \sim 1 \text{ nA}$
Development	- <i>MIBK/IPA</i> v:v=1:3 - <i>IPA</i> - N_2	1 min 30 sec 30 sec rinse 5 min rinse water blown dry
Inspection	Optical microscope	check quality
Emitech	- O_2 ash 5 sccm	2 mbar; 20 W 45 "
Metalization	2 nm <i>Cr</i> 120 nm <i>Au</i> or <i>Pt</i>	deposition rates $\sim 1 \text{ \AA}/\text{s}$
PMMA striping	- <i>Acetone</i> - <i>IPA</i> - N_2	5 min boiling rinse blown dry
Inspection	Optical microscope	check quality

Table D.2: Process sheet for the fabrication of membrane-based micrdevices.

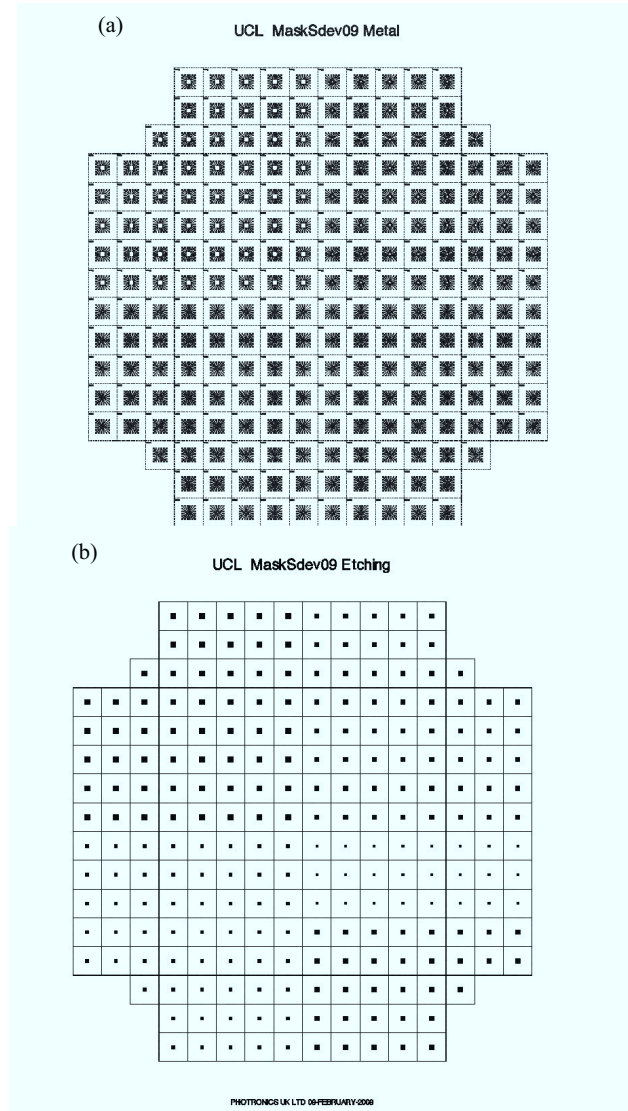


Figure D.1: Overview of the set of two optical lithography masks designed for the fabrication of membrane-based devices. (a) definition of the the metal layer and (b) the etching areas.

Bibliography

- [1] Jack Kilby. Nobel lecture. 2000.
- [2] T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai. A large-area, flexible pressure sensor matrix with organic field-effect transistors for artificial skin applications. *Proceedings of the National Academy of Sciences of the United States of America*, 101(27):9966–9970, 2004.
- [3] J. Jang. Conducting polymer nanomaterials and their applications. *Adv Polym Sci.*, 199:189–259, 2006.
- [4] Echem Nano Tech Services. *V3-Cell*. Bangalore, India.
- [5] M. Wan. A template-free method towards conducting polymer nanostructures. *Advanced Materials*, 20(15):2926–2932, 2008.
- [6] L. L. Zhang and M. Wan. Self-assembly of polyaniline - from nanotubes to hollow microspheres. *Advanced Functional Materials*, 13(10):815–820, 2003.
- [7] C. Debiemme-Chouvy. Template-free one-step electrochemical formation of polypyrrole nanowire arrays. *Electrochemistry communications*, 11:298–301, 2008.
- [8] S.Ramakrishna, K. Fujihara, W.-E. Teo, T. Yong, Z. Ma, and R. Ramaseshan. Electrospun nanofibers: solving global issues. *Materials Today*, 9(3):40 – 50, 2006.
- [9] J. Jang, M. Chang, and H. Yoon. Chemical sensors based on highly conductive PEDOT nanorods. *Advanced Materials*, 17(13):1616, 2005.
- [10] Y. Guo, Q. Tang, H. Liu, Y. Zhang, Y. Li, W. Hu, S. Wang, and D. Zhu. Light-controlled organic/inorganic p-n junction nanowires. *Journal of the American Chemical Society*, 130:9198, 2008.

- [11] J. Shen, Z. Chen, N. Wang, H. Yan, G. Shi, A. Jin, and C. Gu. Electrical properties of a single electrochemically template-synthesized polypyrrole nanowire. *Applied Physics Letters*, 88(25):253106, 2006.
- [12] J.-L. Duvail, Y. Long, S. Cuenot, Z. Chen, and C. Gu. Tuning electrical properties of conjugated polymer nanowires with the diameter. *Applied Physics Letters*, 90(10):102114, 2007.
- [13] A. Rahman and M. K. Sanyal. Bias dependent crossover from variable range hopping to power law characteristics in the resistivity of polymer nanowires. *Journal of Physics: Condensed Matter*, 22(17):175301, 2010.
- [14] J.-L. Duvail, P. Retho, V. Fernandez, G. Louarn, P. Molinie, and O. Chauvet. Effects of the confined synthesis on conjugated polymer transport properties. *The Journal of Physical Chemistry B*, 108(48):18552–18556, 2004.
- [15] Y.-Z. Long, Z. Chen, C. Gu, M. Wan, J.-L. Duvail, L. Zongwen, and S. P. Ringer. *Nanowires Science and Technology: A Review on Electronic Transport Properties of Individual Conducting Polymer Nanotubes and Nanowires*. Intech-Scyio, 2010.
- [16] Y. Cao, A. E. Kovalev, R. Xiao, J. Kim, T. S. Mayer, and T. E. Mallouk. Electrical transport and chemical sensing properties of individual conducting polymer nanowires. *Nano Letters*, 8(12):4653–4658, 2008.
- [17] A. B. Kaiser, J. G. Park, B. Kim, S. H. Lee, and Y. W. Park. Polypyrrole micro-line: current-voltage characteristics and comparison with other conducting polymers. *Current Applied Physics*, 4(5):497–500, 2004.
- [18] A. Rahman and M. K. Sanyal. Observation of charge density wave characteristics in conducting polymer nanowires: Possibility of wigner crystallization. *Physical Review B*, 76(4):045110, 2007.
- [19] T. A. Skotheim and J. R. Reynolds. *Handbook of Conducting Polymers: heory, Synthesis, Properties, and Characterization*. CRC press, New York, 3rd edition, 1998.
- [20] Z. Zhou, K. Xiao, R. Jin, D. Mandrus, J. Tao, D. B. Geohegan, and S. Pennycook. One-dimensional electron transport in cu-tetracyanoquinodimethane organic nanowires. *Applied Physics Letters*, 90(19):193115, 2007.

- [21] M. A. Bangar, C. M. Hangarter, B. Yoo, Y. Rheem, W. Chen, A. Mulchandani, and N. V. Myung. Magnetically assembled multisegmented nanowires and their applications. *Electroanalysis*, 21(1):61–67, 2009.
- [22] J. Huang, R. Fan, S. Connor, and P. Yang. One-step patterning of aligned nanowire arrays by programmed dip coating. *Angew. Chem. Intl. Ed.*, 46(14):2414–2417, 2007.
- [23] L. Reimer. *Scanning Electron Microscopy*. Springer, 2nd edition, 1998.
- [24] Y. K. Hong, D. H. Park, S. H. Park, S. K. Park, and J. Joo. Effects of electron-beam irradiation on conducting polypyrrole nanowires. *Applied Physics Letters*, 94(5):053111, 2009.
- [25] K. Uchida, S. Takahashi, K. Harii, J. Ieda, W. Koshibae, K. Ando, S. Maekawa, and E. Saitoh. Observation of the spin seebeck effect. *Nature*, 455(7214):778–781, 2008.
- [26] J. A. Bearden and A. F. Burr. Reevaluation of x-ray atomic energy levels. *Rev. Mod. Phys.*, 39(1):125–142, Jan 1967.
- [27] R. W. G. Wyckoff. *Crystal Structures*. John Wiley and Sons, New York, 1963.
- [28] K. E. Drexler. Molecular engineering: An approach to the development of general capabilities for molecular manipulation. *Proceedings of the National Academy of Sciences of the United States of America*, 78(9):5275–5278, 1981.
- [29] S. E. Thompson and S. Parthasarathy. Moore’s law: the future of si microelectronics. *Materials Today*, 9(6):20–25, 2006.
- [30] J.-P. Colinge, C.-W. Lee, A. Afzalian, N. D. Akhavan, R. Yan, I. Ferain, P. Razavi, B. O’Neill, A. Blake, M. White, A.-M. Kellerher, B. McCarthy, and R. Murphy. Nanowire transistors without junctions. *Nature Nanotechnology*, 5(3):225–229, 2010.
- [31] R. Capelli, S. Toffanin, G. Generali, H. Usta, A. Facchetti, and M. Muccini. Organic light-emitting transistors with an efficiency that outperforms the equivalent light-emitting diodes. *Nature Materials*, 9(6):496–503, 2010.
- [32] S. P. Anthony and S. M. Draper. Nano/microstructure fabrication of functional organic material: Polymorphic structure and

- tunable luminescence. *The Journal of Physical Chemistry C*, 114(27):11708–11716, 2010.
- [33] G. E. Moore. Cramming more components onto integrated circuits. *Electronics Magazine*, 18:309, 1965.
- [34] European plastic converter. The compelling facts about plastics 2009. 2009.
- [35] J. D. Yuen, R. Menon, N. E. Coates, E. B. Namdas, S. Cho, S. T. Hannahs, D. Moses, and A. J. Heeger. Nonlinear transport in semi-conducting polymers at high carrier densities. *Nature Materials*, 8(7):572–573, 2009.
- [36] T. Someya and T. Sekitani. Printed skin-like large-area flexible sensors and actuators. *Procedia Chemistry*, 1(1):9 – 12, 2009. Proceedings of the Eurosensors XXIII conference.
- [37] J. A. Rogers, T. Someya, and Y. Huang. Materials and Mechanics for Stretchable Electronics. *Science*, 327(5973):1603–1607, 2010.
- [38] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$. *J. Chem. Soc. Chem. Commun.*, 578–580, 1977.
- [39] Y. Cao, P. Smith, and A. J. Heeger. Mechanical and electrical properties of polyacetylene films oriented by tensile drawing. *Polymer*, 32(7):1210 – 1218, 1991.
- [40] H. Haberkorn, W. Heckman, G. Kohler, N. Narmaan, J. Schlag, P. Simak, N. Theophilou, and R. Voekel. Pa. *Eur. Polym. J.*, 24(497), 1988.
- [41] J. A. Merlo and C. D. Frisbie. Field effect transport and trapping in regioregular polythiophene nanofibers. *J. Phys. Chem. B*, 108(19169), 2004.
- [42] S. I. Cho and S. B. Lee. Fast electrochemistry of conductive polymer nanotubes: Synthesis, mechanism, and application. *Acc. Chem. Res.*, 41(699), 2008.
- [43] J. X. Huang, S. Virji, B. H. Weiller, and R. B. Kaner. Polyaniline nanofibers: Facile synthesis and chemical sensors. *J. Am. Chem. Soc.*, 125(314), 2003.

- [44] X. Y. Zhang, W. J. Goux, and S. K. Manohar. Synthesis of polyaniline nanofibers by *Nanofiber Seeding*. *J. Am. Chem. Soc.*, 126(4502), 2004.
- [45] R. L. Greene and G. B. Street and L. J. Suter. Superconductivity in polysulfur nitride (SN)_x. *Phys. Rev. Lett.*, 34(10):577–579, 1975.
- [46] A. G. MacDiarmid. Nobel lecture. 2000.
- [47] G. Hadziioannou and (Eds.) P.F. van Hutten. *Semiconducting Polymers: Chemistry, Physics and Engineering*. Springer-Verlag, Berlin, 2006.
- [48] S. Sadki, P. Schottland, N. Brodiec, and G. Sabouraud. The mechanisms of pyrrole electropolymerization. *Chem. Soc. Rev.*, 29:283, 2000.
- [49] V. Callegari. *PhD Thesis, Université catholique de Louvain*. UCL–Ecole Polytechnique de Louvain, Louvain-la-Neuve, 2009.
- [50] E. M. Genies, G. Bidan, and A. F. Diaz. Spectroelectrochemical study of polypyrrole films. *J. Electroanal. Chem.*, 149(101), 1983.
- [51] S. Asavapiriyant, G. K. Chandler, G. A. Gunawardena, and D. Pletcher. The electrodeposition of polypyrrole films from aqueous solutions. *Journal of Electroanalytical Chemistry*, 177:229, 1984.
- [52] C. O. Yoon, Reghu M., D. Moses, and A. J. Heeger. Transport near the metal-insulator transition: Ppy doped with PF₆. *Phys. Rev. B*, 49(16):10851–10863, Apr 1994.
- [53] K. Potje-Kamloth. Semiconductor junction gas sensors. *Chemical Reviews*, 108:367–399, 2008.
- [54] M. Ranger and M. Leclerc. Novel base-dopable poly(2,7-fluorenylene) derivatives. *Chem. Commun.*, pages 1597–1598, 1997.
- [55] J. L. Bredas and G. B. Street. Polarons, bipolarons, and solitons in conducting polymers. *Accounts of Chemical Research*, 18:309, 1985.
- [56] M. Reghu, S. V. Subramanyam, and S. Chatterjee. Contribution of polarons and bipolarons to low-temperature conductivity in doped polypyrrole. *Phys. Rev. B*, 43(5):4236–4243, 1991.

- [57] S. Braun, W. R. Salaneck, and M. Fahlman. Energy-level alignment at organic/metal and organic/organic interfaces. *Advanced Materials*, 21(14-15), 2009.
- [58] A. Facchetti. Semiconductors for organic transistors. *Materials Today*, 10(3):28 – 37, 2007.
- [59] H. D. Tran, D. Li, and R. B. Kaner. One-dimensional conducting polymer nanostructures: Bulk synthesis and applications. *Advanced Materials*, 21(1):1–13, 2009.
- [60] H. S. Nalwa, editor. *Polymeric Nanostructures and Their Applications*. American Scientific Publishers, 1nd edition, 2006.
- [61] S. Yunus, A. Attout, and P. Bertrand. Controlled aniline polymerization strategies for polyaniline micro- and nano self-assembling into practical electronic devices. *Langmuir*, 25(3):1851, 2009.
- [62] A. Vlad, C. A. Dutu, P. Guillet, P. Jedrasik, C.-A. Fustin, U. Sdervall, J.-F. Gohy, and S. Melinte. Highly ordered conjugated polymer nanoarchitectures with three-dimensional structural control. *Nano Letters*, 9(8):2838 –2843, 2009.
- [63] J.-L. Duvail, S. Dubois, S. Demoustier-Champagne, Y. Long, and L. Piraux. Physical properties of magnetic metallic nanowires and conjugated polymer nanowires and nanotubes. *International Journal of Nanotechnology*, 5(6):838–850, 2008.
- [64] S. J. Hurst, E. K. Payne, L. Qin, and C. A. Chad A. Mirkin. Multi-segmented one-dimensional nanorods prepared by hard-template synthetic methods. *Angew. Chem. Intl. Ed.*, 45(17):2672–2692, 2006.
- [65] N. Kovtyukhova, B. K. Kelley, and T. E. Mallouk. Coaxially gated in-wire thin-film transistors made by template assembly. *Journal of the American Chemical Society*, 126(40):12738, 2004.
- [66] J. M. Lorcy, F. Massuyeau, O. Moreau, P. Chauvet, J. Faulques, E. Wery, and J.-L. Duvail. Coaxial nickel/poly(p-phenylene vinylene) nanowires as luminescent building blocks manipulated magnetically. *Nanotechnology*, 20(40):405601, 2009.
- [67] C. R. Martin. Membrane-based synthesis of nanomaterials. *Chemistry of Materials*, 8(8):1739, 1996.

- [68] H. Yoon, M. Chang, and J. Jang. Formation of 1d PEDOT nano-materials in reverse microemulsions and their application to chemical sensors. *Advanced Functional Materials*, 17(3):1616, 2004.
- [69] R. M. Penner and C. R. Martin. Preparation and electrochemical characterization of ultramicroelectrode ensembles. *Analytical Chemistry*, 59(21):2625–2630, 1987.
- [70] V. Callegari, L. Gence, S. Melinte, and S. Demoustier-Champagne. Electrochemically template-grown multi-segmented gold-conducting polymer nanowires with tunable electronic behavior. *Chemistry of Materials*, 21(18):4241–4247, 2009.
- [71] Z. Hu, B. Muls, L. Gence, D. A. Serban, J. Hofkens, S. Melinte, B. Nysten, S. Demoustier-Champagne, and A. M. Jonas. High-throughput fabrication of organic nanowire devices with preferential internal alignment and improved performance. *Nano Letters*, 7(12):3639–3644, 2007.
- [72] N.-R. Chiou, C. Lu, J. Guan, L. J. Lee, and A. J. Epstein. Growth and alignment of polyaniline nanofibres with superhydrophobic, superhydrophilic and other properties. *Nature Nanotechnology*, 2(6):354–357, 2006.
- [73] Y. Long, L. Zhang, Z. Chen, K. Huang, Y. Yang, H. Xiao, M. Wan, A. Jin, and C. Gu. Electronic transport in single polyaniline and polypyrrole microtubes. *Phys. Rev. B*, 71(16):165412, Apr 2005.
- [74] N. J. Pinto, A. G. Macdiarmid, C. H. Mueller, N. Theofylaktos, D. C. Robinson, and F. A. Miranda. Electrospun polyaniline/polyethylene oxide nanofiber field-effect transistor. *Applied Physics Letters*, 83(20):4244–4246, 2003.
- [75] Z. Yangxin, M. Freitag, J. Hone, C. Staii, N. J. Pinto, and A. G. Macdiarmid. Fabrication and electrical characterization of polyaniline-based nanofibers with diameter below 30 nm. *Applied Physics Letters*, 83(18):3800–3802, 2003.
- [76] Z. Huang. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, 63(15):2223–2253, November 2003.
- [77] N. J. Pinto, K. V. Carrasquillo, C. M. Rodd, and R. Agarwal. Rectifying junctions of tin oxide and poly(3-hexylthiophene) nanofibers fabricated via electrospinning. *Applied Physics Letters*, 94(8):083504, 2009.

- [78] A. Camposeo, F. Di Benedetto, R. Stabile, A. A. R. Neves, R. Cingolani, and D. Pisignano. Laser emission from electrospun polymer nanofibers. *Small*, 5(5):562–566, 2009.
- [79] Z. L. Wang. *Nanowires and Nanobelts*. Springer, New York, 2005.
- [80] P.A. Serena and N. Garcia. *Nanowires*. Kluwer, Dordrecht, Nederland, 1997.
- [81] C. M. Lieber and Z. L. Wang. Functional nanowires. *MRS BULLETIN*, 32:99, 2007.
- [82] J. Wang. Biomolecule-functionalized nanowires: From nanosensors to nanocarriers. *ChemPhysChem*, 10(11):1748 – 1755, 2009.
- [83] S. Park, S.-W. Chung, and C. A. Mirkin. Hybrid organic-inorganic, rod-shaped nanoresistors and diodes. *Journal of the American Chemical Society*, 126:11772, 2004.
- [84] H.-J. Chung, H. H. Jung, Y.-S. Cho, S. Lee, J.-H. Ha, J. H. Choi, and Y. Kuk. Cobalt-polypyrrole-cobalt nanowire field-effect transistors. *Applied Physics Letters*, 86(21):213113, 2005.
- [85] A. K. Wanekaya, M. A. Bangar, M. Yun, W. Chen, N. V. Myung, and A. Mulchandani. Field-effect transistors based on single nanowires of conducting polymers. *The Journal of Physical Chemistry C*, 111(13):5218–5221, 2007.
- [86] H. Liu, J. Kameoka, D. A. Czaplewski, and H. G. Craighead. Polymeric nanowire chemical sensor. *Nano Letters*, 4(4):1530, 2008.
- [87] M. D. Shirsat, M. A. Bangar, M. A. Deshusses, N. V. Myung, and A. Mulchandani. Polyaniline nanowires-gold nanoparticles hybrid network based chemiresistive hydrogen sulfide sensor. *Applied Physics Letters*, 94(8):083502, 2009.
- [88] Y. Dan, Y. Cao, T. E. Mallouk, S. Evoy, and A. T. C. Johnson. Gas sensing properties of single conducting polymer nanowires and the effect of temperature. *Nanotechnology*, 20(43):434014, 2009.
- [89] K. Ramanathan, M. A. Bangar, M Yun, W. Chen, N. V. Myung, and A. Mulchandani. Bioaffinity sensing using biologically functionalized conducting-polymer nanowire. *Journal of the American Chemical Society*, 127(2):496–497, 2005.

- [90] C. D. Muller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, , O. Nuyken, H. Becker, and K. Meerholz. Multi-colour organic light-emitting displays by solution processing. *Nature*, 421(6925):829–833, 2003.
- [91] M. Ahlskog, Reghu Menon, A. J. Heeger, T. Noguchi, and T. Ohnishi. Metal-insulator transition in oriented poly(p-phenylenevinylene). *Phys. Rev. B*, 55(11):6777–6787, Mar 1997.
- [92] V. I. Kozub, A. N. Aleshin, D.-S. Suh, and Y. W. Park. Evidence of magnetoresistance for nanojunction-controlled transport in heavily doped polyacetylene. *Physical Review B (Condensed Matter and Materials Physics)*, 65(22):224204, 2002.
- [93] A. N. Aleshin, T. J. Kim, D. S. Suh, Y. W. Park, H. Kang, and W. Kang. Effects of pressure and magnetic field on the low-temperature conductivity of fecl_4^- -doped polyacetylene: The influence of scattering by low-energy excitations. *Physical Review B (Condensed Matter and Materials Physics)*, 63(23):235209, 2001.
- [94] A. N. Aleshin, V. I. Kozub, D.-S. Suh, and Y. W. Park. Low-temperature saturation of dephasing in heavily doped conjugated polymers. *Current Applied Physics*, 2(1):91 – 96, 2002.
- [95] J. C. Scott and G. G. Malliaras. Charge injection and recombination at the metal-organic interface. *Chemical Physics Letters*, 299(2):115–119, 1999.
- [96] M. G. Helander, Z. B. Wang, M. T. Greiner, J. Qiu, and Z. H. Lu. Experimental design for the determination of the injection barrier height at metal/organic interfaces using temperature dependent current-voltage measurements. *Review of Scientific Instruments*, 80(3):033901, 2009.
- [97] J. A. Freire and G. Voss. Master equation approach to charge injection and transport in organic insulators. *The Journal Of Chemical Physics*, 122(12):124705, 2005.
- [98] M. G. Helander, Z. B. Wang, J. Qiu, and Z. H. Lu. Band alignment at metal/organic and metal/oxide/organic interfaces. *Applied Physics Letters*, 93(19):193310, 2008.
- [99] F. Feller, C. Rothe, M. Tammer, D. Geschke, and A. P. Monkman. Temperature dependence of the space-charge distribution in injection limited conjugated polymer structures. *Journal of Applied Physics*, 91(11):9225–9231, 2002.

- [100] D. Braun. Electronic injection and conduction processes for polymer devices. *Journal of Polymer Science Part B: Polymer Physics*, 41(21):2622–2629, 2003.
- [101] S. H. Choi, B. Kim, and C. Daniel Frisbie. Electrical Resistance of Long Conjugated Molecular Wires. *Science*, 320(5882):1482–1486, 2008.
- [102] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler. Charge injection into light-emitting diodes: Theory and experiment. *Journal of Applied Physics*, 84(2):848–856, 1998.
- [103] S. M. Sze. *Physics of Semiconductor Devices*. Wiley, New York, 2nd edition, 1981.
- [104] H. Koezuka and S. S. Etoh. Schottky barrier type diode with an electrochemically prepared copolymer having pyrrole and n-methylpyrrole units. *Journal of Applied Physics*, 54(5):2511–2516, 1983.
- [105] C.-K. Yang, C.-M. Yang, H.-H. Liao, S.-F. Horng, and H.-F. Meng. Current injection and transport in polyfluorene. *Applied Physics Letters*, 91(9):093504, 2007.
- [106] G. D. J. Smit, S. Rogge, and T. M. Klapwijk. Scaling of nano-schottky-diodes. *Applied Physics Letters*, 81(20):3852–3854, 2002.
- [107] A. Miller and E. Abrahams. Impurity conduction at low concentrations. *Phys. Rev.*, 120(3):745–755, Nov 1960.
- [108] P. W. Anderson. Absence of diffusion in certain random lattices. *Phys. Rev.*, 109(5):1492–1505, 1958.
- [109] P. A. Lee and T. V. Ramakrishnan. Impurity conduction at low concentrations. *Rev. Mod. Phys.*, 57(2):287–337, April 1985.
- [110] A. Rose. Space-charge-limited currents in solids. *Phys. Rev.*, 97(6):1538–1544, Mar 1955.
- [111] P. Mark and W. Helfrich. Space-charge-limited currents in organic crystals. *Journal of Applied Physics*, 33(1):205–215, 1962.
- [112] P. W. M. Blom, R. M. Wolf, J. F. M. Cillessen, and M. P. C. M. Krijn. Ferroelectric schottky diode. *Phys. Rev. Lett.*, 73(15):2107–2110, Oct 1994.

- [113] M. M. Mandoc, B. de Boer, G. Paasch, and P. W. M. Blom. Trap-limited electron transport in disordered semiconducting polymers. *Phys. Rev. B*, 75(19):193202, May 2007.
- [114] J. Frenkel. On pre-breakdown phenomena in insulators and electronic semi-conductors. *Phys. Rev.*, 54(8):647–648, Oct 1938.
- [115] P. Sheng. Fluctuation-induced tunneling conduction in disordered materials. *Phys. Rev. B*, 21(6):2180–2195, 1980.
- [116] A. B. Kaiser and Y. W. Park. Conduction mechanisms in polyacetylene nanofibers. *Current Applied Physics*, 2(1):33 – 37, 2002.
- [117] J. G. Park, B. Kim, S. H. Lee, A. B. Kaiser, S. Roth, and Y. W. Park. Tunneling conduction in polyacetylene nanofiber. *Synthetic Metals*, 135-136:299–300, 2003.
- [118] G. T. Kim, J. Muster, V. Krstic, J. G. Park, Y. W. Park, S. Roth, and M. Burghard. Field-effect transistor made of individual v_2o_5 nanofibers. *Applied Physics Letters*, 76(14):1875–1877, 2000.
- [119] A. N. Aleshin. Quasi-one-dimensional transport in conducting polymer nanowires. *Physics of the Solid State*, 49(11):2015 – 2033, 2007.
- [120] A. N. Aleshin, H. J. Lee, Y. W. Park, and K. Akagi. One-dimensional transport in polymer nanofibers. *Physical Review Letters*, 93(19):196601, 2004.
- [121] A. B. Kaiser, S. A. Rogers, and Y. W. Park. Charge transport in conducting polymers: Polyacetylene nanofibres. *Molecular Crystals and Liquid Crystals*, 415:115–124, 2004.
- [122] N. F. Mott and E. A. Davis. *Electronic Processes in Non-Crystalline Materials*. Clarendon Press, Oxford, 1979.
- [123] S. R. Elliott. *Physics of amorphous materials, Second edition*. Longman Scientific and Technical, Harlow, UK, 1990.
- [124] A. J. Epstein, W.-P. Lee, and V.N. Prigodin. Low-dimensional variable range hopping in conducting polymers. *Synthetic Metals*, 117(1-3):9 – 13, 2001.
- [125] J. J. van Hapert. *PhD Thesis, Universiteit Utrecht*. Faculteit Natuur en Sterrenkunde, Utrecht, Netherlands, 2002.

- [126] B.I. Shklovskii and A.L. Efros. *Electronic Processes in Non-crystalline Materials*. Clarendon Press, Oxford, 1979.
- [127] B.I. Shklovskii and A.L. Efros. *Electronic Properties of Doped Semiconductors*. Springer, Berlin, 1984.
- [128] N. Apsley and H. Hughes. Temperature-and field-dependence of hopping conduction in disordered systems. *Philo. Mag.*, 30:963, 1974.
- [129] N. Apsley and H. Hughes. Temperature- and field-dependence of hopping conduction in disordered systems, ii. *Philo. Mag.*, 31:1327, 1975.
- [130] D. Shahar and Z. Ovadyahu. Dimensional crossover in the hopping regime induced by an electric field. *Phys. Rev. Lett.*, 64(19):2293, 2000.
- [131] Z. H. Xiong, Di Wu, Z. Valy Vardeny, and Jing Shi. Giant magnetoresistance in organic spin-valves. *Nature*, 427(6977):821–824, 2004.
- [132] S. Pramanik, C.-G. Stefanita, S. Patibandla, S. and Bandyopadhyay, K. Garre, N. Harth, and M. Cahay. Observation of extremely long spin relaxation times in an organic nanowire spin valve. *Nature Nanotechnology*, 2(4):216–219, 2007.
- [133] M. P. Delmo, S. Yamamoto, S. Kasai, T. Ono, and K. Kobayashi. Large positive magnetoresistive effect in silicon induced by the space-charge effect. *Nature*, 457(7233):1112–1115, 2009.
- [134] Ö. Mermer, G. Veeraraghavan, T. L. Francis, Y. Sheng, D. T. Nguyen, M. Wohlgenannt, A. Köhler, M. K. Al-Suti, and M. S. Khan. Large magnetoresistance in nonmagnetic π -conjugated semiconductor thin film devices. *Phys. Rev. B*, 72(20):205202, Nov 2005.
- [135] S. A. Bagnich, U. Niedermeier, C. Melzer, W. Sarfert, and H. von Seggern. Origin of magnetic field effect enhancement by electrical stress in organic light emitting diodes. *Journal of Applied Physics*, 105(12), 2009.
- [136] T. Sugawara and M. M. Matsushita. Anomalous room temperature magnetoresistance in organic semiconductors. *J. Mater. Chem.*, 19:1738–1753, 2009.

- [137] V. N. Prigodin, J. D. Bergeson, D. M. Lincoln, and A. J. Epstein. Anomalous room temperature magnetoresistance in organic semiconductors. *Synthetic Metals*, 156(9-10):757 – 761, 2006.
- [138] P. A. Bobbert, T. D. Nguyen, F. W. A. van Oost, B. Koopmans, and M. Wohlgenannt. Bipolaron mechanism for organic magnetoresistance. *Physical Review Letters*, 99(21):216801, 2007.
- [139] F. L. Bloom, M. Kemerink, W. Wagemans, and B. Koopmans. Sign inversion of magnetoresistance in space-charge limited organic devices. *Physical Review Letters*, 103(6):066601, 2009.
- [140] B. Z. Nguyen, V. L. Spivak and B. I. Shklovskii. Tunnel hopping in disordered systems. *JETP Lett.*, 41(42), 1985.
- [141] U. Sivan, O. Entin-Wohlman, and Y. Imry. Orbital magnetoconductance in the variable-range-hopping regime. *Phys. Rev. Lett.*, 60(15):1566–1569, Apr 1988.
- [142] Y. Long, K. Huang, J. Yuan, D. Han, L. Niu, Z. Chen, C. Gu, A. Jin, and J.-L. Duvail. Electrical conductivity of a single au/polyaniline microfiber. *Applied Physics Letters*, 88(16):162113, 2006.
- [143] T.-I. Su, C.-R. Wang, S.-T. Lin, and R. Rosenbaum. Magnetoresistance of $al_{70}pd_{22.5}re_{7.5}$ quasicrystals in the variable-range hopping regime. *Phys. Rev. B*, 66(5):054438, Aug 2002.
- [144] Y. Long, Z. Chen, J. Shen, Z. Zhang, L. Zhang, K. Huang, M. Wan, A. Jin, C. Gu, and J.-L. Duvail. Magnetoresistance studies of polymer nanotube/wire pellets and single polymer nanotubes/wires. *Nanotechnology*, 17(24):5903–5911, 2006.
- [145] L. Gence, S. Faniel, C. Gustin, S. Melinte, V. Bayot, V. Callegari, O. Reynes, and S. Demoustier-Champagne. Structural and electrical characterization of hybrid metal-polypyrrole nanowires. *Physical Review B (Condensed Matter and Materials Physics)*, 76(11):115415, 2007.
- [146] F. L. Bloom, W. Wagemans, and B. Koopmans. Temperature dependent sign change of the organic magnetoresistance effect. *Proceedings of the 52nd Annual Conference on Magnetism and Magnetic Materials*, 103(7):07F320, 2008.

- [147] A. N. Aleshin. Polymer nanofibers and nanotubes: Charge transport and device applications. *Advanced Materials*, 18(1):17–27, 2006.
- [148] T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds. *Handbook of Conducting Polymers*. Dekker, New York, 2nd edition, 1998.
- [149] Y. Long, J.-L. Duvail, Z. J. Chen, A. Z. Jin, and C. Z. Gu. Electrical properties of isolated poly(3,4-ethylenedioxythiophene) nanowires prepared by template synthesis. *Polymers for Advanced Technologies*, 20(6):541–544, 2009.
- [150] S. Maji, S. Mukhopadhyay, R. Gangopadhyay, and A. De. Smooth crossover from variable-range hopping with coulomb gap to nearest-neighbor interchain hopping in conducting polymers. *Physical Review B (Condensed Matter and Materials Physics)*, 75(7):073202, 2007.
- [151] R. V. Parthasarathy and C. R. Martin. Template-synthesized polyaniline microtubules. *Chemistry of Materials*, 6(10):1627–1632, 1994.
- [152] M. Granström and O. Inganäs. Electrically conductive polymer fibres with mesoscopic diameters: 1. studies of structure and electrical properties. *Polymer*, 36(15):2867 – 2872, 1995.
- [153] J. G. Park, S. H. Lee, B. Kim, and Y. W. Park. Electrical resistivity of polypyrrole nanotube measured by conductive scanning probe microscope: The role of contact force. *Applied Physics Letters*, 81(24):4625–4627, 2002.
- [154] A. N. Aleshin, H. J. Lee, S. H. Jhang, H. S. Kim, K. Akagi, and Y. W. Park. Coulomb-blockade transport in quasi-one-dimensional polymer nanofibers. *Physical Review B (Condensed Matter and Materials Physics)*, 72(15):153202, 2005.
- [155] H. J. Lee, Z. X. Jin, A. N. Aleshin, J. Y. Lee, M. J. Goh, K. Akagi, Y. S. Kim, D. W. Kim, and Y. W. Park. Dispersion and current-voltage characteristics of helical polyacetylene single fibers. *Journal of the American Chemical Society*, 126(51):16722–16723, 2004. PMID: 15612700.
- [156] N. Kang, J. S. Hu, W. J. Kong, L. Lu, D. L. Zhang, Z. W. Pan, and S. S. Xie. Consistent picture of strong electron correlation from magnetoresistance and tunneling conductance measurements

- in multiwall carbon nanotubes. *Phys. Rev. B*, 66(24):241403, Dec 2002.
- [157] A. B. Kaiser and Y. W. Park. Current-voltage characteristics of conducting polymers and carbon nanotubes. *Synthetic Metals*, 152(1-3):181 – 184, 2005. Proceedings of the International Conference on Science and Technology of Synthetic Metals.
- [158] A. I. Larkin and D. E. Khmel'nitskii. Activation conductivity in disordered systems with large localization length. *Sov. Phys. JETP*, 56(3):647–652, 1982.
- [159] A. N. Aleshin, J. Y. Lee, S. W. Chu, S. W. Lee, B. Kim, S. J. Ahn, and Y. W. Park. Hopping conduction in polydiacetylene single crystals. *Physical Review B (Condensed Matter and Materials Physics)*, 69(21):214203, 2004.
- [160] J. Voit. One-dimensional fermi liquids. *Reports on Progress in Physics*, 58(9):977, 1995.
- [161] H. J. Schulz. Wigner crystal in one dimension. *Phys. Rev. Lett.*, 71(12):1864–1867, Sep 1993.
- [162] H. Sirringhaus, M. Bird, T. Richards, and N. Zhao. Charge transport physics of conjugated polymer field-effect transistors. *Advanced Materials*, 22:1–6, 2010.
- [163] A. Bachtold, M. de Jonge, K. Grove-Rasmussen, P. L. McEuen, M. Buitelaar, and C. Schönenberger. Suppression of tunneling into multiwall carbon nanotubes. *Phys. Rev. Lett.*, 87(16):166801, Oct 2001.
- [164] M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen. Luttinger-liquid behaviour in carbon nanotubes. *Nature*, 397(6720):598–601, 1999.
- [165] Z. Yao, H. W. C. Postma, L. Balents, and C. Dekker. Carbon nanotube intramolecular junctions. *Nature*, 402(273), 1999.
- [166] L. Venkataraman, Y. S. Hong, and P. Kim. Electron transport in a multichannel one-dimensional conductor: Molybdenum selenide nanowires. *Phys. Rev. Lett.*, 96(7):076601, Feb 2006.
- [167] S. N. Artemenko and S. V. Remizov. Low-temperature conductivity of quasi-one-dimensional conductors: Luttinger liquid stabilized by impurities. *Phys. Rev. B*, 72(12):125118, 2005.

- [168] A. Rahman and M. K. Sanyal. Negative capacitance in wigner crystal forming polymer nanowires. *Applied Physics Letters*, 94(24):242102, 2009.
- [169] L. Piraux, S. Dubois, and A. Fert. Perpendicular giant magnetoresistance in magnetic multilayered nanowires. *J. Magn. Magn. Mater.*, 159(L287), 1996.
- [170] J. K. N. Mbindyo, T. E. Mallouk, J. B. Mattzela, I. Kratochvilova, B. Razavi, T. N. Jackson, and T. S. Mayer. Template synthesis of metal nanowires containing monolayer molecular junctions. *Journal of the American Chemical Society*, 124(15):4020–4026, 2002.
- [171] R. M. Hernandez, L. Richter, S. Semancik, S. Stranick, and T. E. Mallouk. Template fabrication of protein-functionalized gold-polypyrrole-gold segmented nanowires. *Chemistry of Materials*, 16(18):3431, 2004.
- [172] O. Reynes and S. Demoustier-Champagne. Template electrochemical growth of polypyrrole and gold-polypyrrole-gold nanowire arrays. *Journal of The Electrochemical Society*, 152(9):D130–D135, 2005.
- [173] L. Gence, V. Callegari, S. Faniel, A. Vlad, C. Dutu, L., S. Melinte, S. Demoustier-Champagne, and V. Bayot. Size related transport mechanisms in hybrid metal–polymer nanowires. *Physica Status Solidi (a)*, 205(6):1447–1450, 2008.
- [174] L. Gence, V. Callegari, S. Melinte, S. Demoustier-Champagne, Y. Long, A. Dinescu, and J.-L. Duvail. *Nanowires Science and Technology: Conjugated Polymer and Hybrid Polymer-Metal Single Nanowires: Correlated Characterization and Device Integration*. Intech-Scyio, 2010.
- [175] L. Dauginet-De Pra. *PhD Thesis, Université catholique de Louvain*. UCL, Louvain-la-Neuve, 2004.
- [176] A. Lahav, E. Weiss, Q. Xu, and G. M. Whitesides. Core-shell and segmented polymer-metal composite nanostructures. *Nano Letters*, 6(9):2166, 2006.
- [177] Z. Cai and C. R. Martin. Electronically conductive polymer fibers with mesoscopic diameters show enhanced electronic conductivities. *Journal of the American Chemical Society*, 111(11):4138 – 4139, 1989.

- [178] J. P. Spatz, B. Lorenz, K. Weishaupt, H. D. Hochheimer, V. Menon, R. Parthasarathy, C. R. Martin, J. Bechtold, and P.-H. Hor. Observation of crossover from three-to two-dimensional variable-range hopping in template-synthesized polypyrrole and polyaniline. *Phys. Rev. B*, 50(20):14888–14892, Nov 1994.
- [179] J. X. Huang and R. B. Kaner. A general chemical route to polyaniline nanofibers. *J. Am. Chem. Soc.*, 126(851), 2004.
- [180] J.-L. Duvail, P. Rétho, S. Garreau, G. Louarn, C. Godon, and S. Demoustier-Champagne. Charge carrier transport in organic semiconductors. *Synthetic Metals*, 131:123, 2002.
- [181] J. P. Heremans, C. M. Thrush, D. T. Morelli, and M.-C. Wu. Thermoelectric power of bismuth nanocomposites. *Phys. Rev. Lett.*, 88(21):216801, 2002.
- [182] J. P. Heremans, C. M. Thrush, D. T. Morelli, and M.-C. Wu. Resistance, magnetoresistance, and thermopower of zinc nanowire composites. *Phys. Rev. Lett.*, 91(7):076804, 2003.
- [183] L. Gravier, S. Serrano-Guisan, F. Reuse, and J.-Ph. Ansermet. Spin-dependent peltier effect of perpendicular currents in multilayered nanowires. *Phys. Rev. B*, 73(5):052410, Feb 2006.
- [184] N. Chtanko, M. E. Toimil Molares, T. Cornelius, D. Dobrev, and R. Neumann. Etched single-ion-track templates for single nanowire synthesis. *The Journal of Physical Chemistry B*, 108(28):9950, 2004.
- [185] N. Karl. Charge carrier transport in organic semiconductors. *Synthetic Metals*, 133-134:649 – 657, 2003.
- [186] G. Juska, K. Arlauskas, R. Österbacka, and H. Stubb. Time-of-flight measurements in thin films of regioregular poly(3-hexyl thiophene). *Synthetic Metals*, 109(1-3):173–176, 2000.
- [187] D. V. Lang. Deep-level transient spectroscopy: A new method to characterize traps in semiconductors. *Journal of Applied Physics*, 45(7):3023–3032, 1974.
- [188] A. J. Campbell, D. D. C. Bradley, E. Werner, and W. Brütting. Deep level transient spectroscopy (dlts) of a poly(p-phenylene vinylene) schottky diode. *Synthetic Metals*, 111-112:273 – 276, 2000.

- [189] O. Gaudin, R. B. Jackman, T.-P. Nguyen, and P. Le Rendu. Determination of traps in poly(p-phenylene vinylene) light emitting diodes by charge-based deep level transient spectroscopy. *Journal of Applied Physics*, 90(8):4196, 2001.
- [190] C. Gustin. *PhD Thesis, Université catholique de Louvain*. UCL–Ecole Polytechnique de Louvain, Louvain-la-Neuve, 2005.
- [191] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, and C. D. Frisbie. Comparison of electronic transport measurements on organic molecules. *Advanced Materials*, 15(22):1881–1890, 2003.
- [192] B. Bufon, J. Vollmer, T. Heinzl, P. Espindola, H. John, and J. Heinze. Relationship between chain length, disorder, and resistivity in polypyrrole films. *The Journal of Physical Chemistry B*, 109(41):19191–19199, 2005.
- [193] J. Aguilar-Hernández and K. Potje-Kamloth. Optical and electrical characterization of a conducting polypyrrole composite prepared by in situ electropolymerization. *Phys. Chem. Chem. Phys.*, 1:1735–1742, 1999.
- [194] J. Joo, J. K. Lee, J. S. Baeck, K. H. Kim, E. J. Oh, and J. Epstein. Electrical, magnetic, and structural properties of chemically and electrochemically synthesized polypyrroles. *Synthetic Metals*, 117(1-3):45 – 51, 2001.
- [195] I. N. Hulea, H. B. Brom, A. K. Mukherjee, and R. Menon. Doping, density of states, and conductivity in polypyrrole and poly(p-phenylene vinylene). *Phys. Rev. B*, 72(5):054208, Aug 2005.
- [196] K. D. Bozdag, N.-R. Chiou, V. N. Prigodin, and A. J. Epstein. Magnetic field, temperature and electric field dependence of magneto-transport for polyaniline nanofiber networks. *Synthetic Metals*, In Press, Corrected Proof, 2009.
- [197] C. L. Choy and D. Greig. The low temperature thermal conductivity of isotropic and oriented polymers. *Journal of Physics C: Solid State Physics*, 10(2):169–179, 1977.
- [198] B. L. Altshuler, V. E. Kravtsov, I. V. Lerner, and I. L. Aleiner. Jumps in current-voltage characteristics in disordered films. *Phys. Rev. Lett.*, 102(17):176803, Apr 2009.
- [199] C. R. Martin. Nanomaterials: A Membrane-based synthetic approach. *Science*, 266(5193):1961–1966, 1994.

- [200] C. R. Martin. Template synthesis of electronically conductive polymer nanostructures. *Accounts of Chemical Research*, 28(2):61–68, 1995.
- [201] I. Orgzall, B. Lorenz, S. T. Ting, P.-H Hor, V. Menon, Ch. R. Martin, and H. D. Hochheimer. Thermopower and high-pressure electrical conductivity measurements of template synthesized polypyrrole. *Phys. Rev. B*, 54(23):16654–16658, Dec 1996.
- [202] H. Ma and U. Schollwöck. Effect of electron-electron interactions on the charge carrier transitions in trans-polyacetylene. *The Journal of Physical Chemistry A*, 114(17):5439–5444, 2010.
- [203] R. Menon, C. O. Yoon, D. Moses, A. J. Heeger, and Y. Cao. Transport in polyaniline near the critical regime of the metal-insulator transition. *Phys. Rev. B*, 48(24):17685–17694, Dec 1993.
- [204] Z. Cai, J. Lei, W. Liang, V. Menon, and C. R. Martin. Molecular and supermolecular origins of enhanced electric conductivity in template-synthesized polyheterocyclic fibrils. 1. supermolecular effects. *Chemistry of Materials*, 3(5):960–967, 1991.
- [205] C. L. Kane and M. P. A. Fisher. Transport in a one-channel luttinger liquid. *Phys. Rev. Lett.*, 68(8):1220–1223, Feb 1992.
- [206] A. Troisi. Polymers as one-dimensional metals. *Nature Materials*, 8:538, 2009.
- [207] C. Tanase, P. W. M. Blom, M. Mulder, and D. M. de Leeuw. Enhanced hole transport in poly(p-phenylene vinylene) planar metal-polymer-metal devices. *Journal of Applied Physics*, 99(10):103702, 2006.
- [208] W. Lee, G. Du, S. M. Long, A. J. Epstein, S. Shimizu, T. Saitoh, and M. Uzawa. Charge transport properties of fully-sulfonated polyaniline. *Synthetic Metals*, 84(1-3):807 – 808, 1997.
- [209] S. K. Saha. Room-temperature single-electron tunneling in conducting polypyrrole nanotube. *Applied Physics Letters*, 81(19):3645–3647, 2002.
- [210] A. S. Rodin and M. M. Fogler. Apparent power-law behavior of conductance in disordered quasi-one-dimensional systems. *Phys. Rev. Lett.*, 105(10):106801, Sep 2010.

- [211] J. H. Worne, J. E. Anthony, and D. Natelson. Transport in organic semiconductors in large electric fields: From thermal activation to field emission. *Applied Physics Letters*, 96(5):053308, 2010.
- [212] S. Michotte, S. Mátéfi-Tempfli, and L. Piraux. Current–voltage characteristics of pb and sn granular superconducting nanowires. *Applied Physics Letters*, 82(23):4119–4121, 2003.
- [213] S. V. N. T. Kuchibhatla, A. S. Karakoti, D. Bera, and S. Seal. One dimensional nanostructured materials. *Progress in Materials Science*, 52(5):699 –913, 2007.
- [214] M. C. P. Wang and B. D. Gates. Directed assembly of nanowires. *Materials Today*, 12(5):34 – 43, 2009.
- [215] A. Vlad. *PhD Thesis, Université catholique de Louvain*. UCL –Ecole Polytechnique de Louvain, Louvain-la-Neuve, 2009.
- [216] M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis, and H. A. Atwater. Enhanced absorption and carrier collection in si wire arrays for photovoltaic applications. *Nature Materials*, 9:239–244, 2010.
- [217] C. Thelander, P. Agarwal, S. Brongersma, J. Eymery, L. F. Feiner, A. Forche, M. Scheffler, W. Riess, B. J. Ohlsson, U. Gösele, and L. Samuelson. Nanowire–based one–dimensional electronics. *Materials Today*, 9(10):28–35, 2006.
- [218] C. S. Lao, J. Liu, P. Gao, L. Zhang, D. Davidovic, R. Tummala, and Z. L. Wang. Zno nanobelt/nanowire schottky diodes formed by dielectrophoresis alignment across au electrodes. *Nano Letters*, 6(2):263 – 266, 2006.
- [219] W. Ahmed, E. S. Kooij, A. van Silfhout, and B. Poelsema. Quantitative analysis of gold nanorod alignment after electric field–assisted deposition. *Nano Letters*, 9(11):3786–3794, 2009.
- [220] W. M. Arnold. Particle patterning using fluidics and electric fields. *IEEE Trans. Dielectr. Electr. Insul.*, 15:144–151, 2008.
- [221] M. Sagnes, J.-M. Broto, B. Raquet, T. Ondarçuhu, C. Laurent, E. Flahaut, C. Vieu, and F. Carcenac. Alignment and nano–connections of isolated carbon nanotubes. *Microelectronic Engineering*, 67–68:683 – 689, 2003. Proceedings of the 28th International Conference on Micro– and Nano–Engineering.

- [222] Z. Hu, M. D. Fischbein, and M. Drndic. Local charge transport in two-dimensional pbse nanocrystal arrays studied by electrostatic force microscopy. *Nano Letters*, 5(7):1463–1468, 2005.
- [223] Z. Hu, M. D. Fischbein, C. Querner, and M. Drndic. Electric-field-driven accumulation and alignment of cdse and cdte nanorods in nanoscale devices. *Nano Letters*, 6(11):2585–2591, 2006.
- [224] O. Vazquez-Mena, G. Villanueva, V. Savu, K. Sidler, M. A. F. van den Boogaart, and J. Brugger. Metallic nanowires by full wafer stencil lithography. *Nano Letters*, 8(11):3675–3682, 2008.
- [225] A. Reguer, F. Bedu, S. Nitsche, D. Chaudanson, B. Detaillieur, and H. Dallaporta. Probing the local temperature by in situ electron microscopy on a heated si₃n₄ membrane. *Ultramicroscopy*, 110(1):61 – 66, 2009.
- [226] Y. Huang, X. F. Duan, Q. Q. Wei, and C. M. Lieber. Directed assembly of one-dimensional nanostructures into functional networks. *Science*, 291(5504):630–633, 2001.
- [227] J. J. Boote and S. D. Evans. Dielectrophoretic manipulation and electrical characterization of gold nanowires. *Nanotechnology*, 16:1500–1505, 2005.
- [228] A. Jamshidi, P. J. Pauzauskie, P. J. Schuck, A. T. Ohta, P.-Y. Chiou, J. Chou, P. Yang, and M. C. Wu. Dynamic manipulation and separation of individual semiconducting and metallic nanowires. *Nature PHOTONICS*, 2(2):85–89, 2008.
- [229] L. Tong, V. D. Miljkovic, and M. Kall. Alignment, Rotation, and Spinning of Single Plasmonic Nanoparticles and Nanowires Using Polarization Dependent Optical Forces. *NANO LETTERS*, 10(1):268–273, 2010.
- [230] L. Vila. *PhD Thesis, Université catholique de Louvain*. UCL, Louvain-la-Neuve, 2004.
- [231] MicroChem. *NANO PMMA and Copolymer*. MicroChem Corp., 2001.
- [232] S. Roche, E. Akkermans, O. Chauvet, F. Hekking, J.-P. Issi, R. Martel, G. Montambaux, and P. Poncharal. Transport properties. *Lecture notes in physics*, 677:35–437, 2006.

- [233] Y.-F. Lin and W.-B. Jian. The impact of nanocontact on nanowire based nanoelectronics. *Nano Letters*, 8(10):3146 – 3150, 2008.
- [234] E. Stern, G. Cheng, M. P. Young, and M. A. Reed. Specific contact resistivity of nanowire devices. *Applied Physics Letters*, 88(5):053106, 2006.
- [235] C. Vanoni, T. A. Jung, and S. Tsujino. Temperature dependent charge-injection at the metal-organic semiconductor interface and density of states in pristine and doped pentacene. *Applied Physics Letters*, 94(25):253306, 2009.
- [236] D. R. Ciarlo. Silicon nitride membranes for biomedical applications. *Biomedical Microdevices*, 4(1):63–68, 2002.
- [237] L. Gence. *Activity report: Raith E-line Demonstration October 2008*. EPL, UCL, Louvain-la-Neuve, 2008.
- [238] O. Tabata, R. Asah, H. Funabashi, K. Shimaoka, and S. Sugiyama. Anisotropic etching of silicon in tmah solutions. *Sensors and Actuators A*, 34:51, 1992.
- [239] D. C. Bell, Y. Wu, C. J. Barrelet, Gradecak, J. Xiang, B. P. Timko, and C. M. Lieber. Imaging and analysis of nanowires. *Microscopy Research and Technique*, 64(5-6):373–389, 2004.
- [240] B. Hackens, F. Martins, T. Ouisse, H. Sellier, S. Bollaert, X. Wal-lart, A. Cappy, J. Chevrier, V. Bayot, and S. Huant. Imaging and controlling electron transport inside a quantum ring. *NATURE PHYSICS*, 2(12):826–830, 2006.
- [241] S. Cuenot, S. Demoustier-Champagne, and B. Nysten. Elastic modulus of polypyrrole nanotubes. *Phys. Rev. Lett.*, 85(8):1690–1693, Aug 2000.
- [242] A. Volodin, M. Ahlskog, E. Seynaeve, C. Van Haesendonck, A. Fonseca, and J. B. Nagy. Imaging the elastic properties of coiled carbon nanotubes with atomic force microscopy. *Phys. Rev. Lett.*, 84(15):3342–3345, Apr 2000.
- [243] D. E. Newbury and D. B. Williams. The electron microscope: the materials characterization tool of the millennium. *Acta Materialia*, 48(1):323–346, 2000.
- [244] E. L. Hall. *Analytical Electron Microscopy*. VCH Publishers, New York, 1992.

- [245] J. I. Goldstein, D. B. Williams, and G. Cliff. *Principles of Analytical Electron Microscopy*. Plenum Press, New York, 2nd edition, 1989.
- [246] J. L. Lábár. Consistent indexing of a (set of) single crystal saed pattern(s) with the processdiffraction program. *Ultramicroscopy*, 103(3):237 – 249, 2005.
- [247] S. Frabboni, G. C. Gazzadi, L. Felisari, and A. Spessot. Fabrication by electron beam induced deposition and transmission electron microscopic characterization of sub-10-nm freestanding pt nanowires. *Applied Physics Letters*, 88(21):213116, 2006.
- [248] O.N. Uryupin, M. V. Vedernikov, A. A. Shabaldin, Y. V. Ivanov, Y. A. Kumzerov, and A. V. Fokin. Thermoelectric properties of insb nanowires over a wide temperature range. *Journal of Electronic Materials*, 38:990, 2009.
- [249] C. L. Kane and M. P. A. Fisher. Thermal transport in a luttinger liquid. *Phys. Rev. Lett.*, 76(17):3192–3195, Apr 1996.
- [250] S. G. Im, K. K. Gleason, and E. A. Olivetti. Doping level and work function control in oxidative chemical vapor deposited poly (3,4-ethylenedioxythiophene). *Applied Physics Letters*, 90(15):152112, 2007.
- [251] F. Zhang, A. Petr, H. Peisert, M. Knupfer, and L. Dunsch. Electrochemical variation of the energy level of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). *The Journal of Physical Chemistry B*, 108(45):17301–17305, 2004.
- [252] A. Saheb, M. Josowicz, and J. Janata. Chemically sensitive field-effect transistor with polyaniline-ionic liquid composite gate. *Analytical Chemistry*, 80(11):4214–4219, 2008.
- [253] J. D. Fowler, S. Virji, R. B. Kaner, and B. H. Weiller. Hydrogen detection by polyaniline nanofibers on gold and platinum electrodes. *The Journal of Physical Chemistry C*, 113(16):6444–6449, 2009.
- [254] S.-T. Yau, C. Zhang, P. C. Innis, and P.C. Innis. Asymmetry and rectification in the tunnel current of a nanometer-sized metal-conjugated polymer-metal junction. *Journal of Chemical Physics*, 112(15), 2000.

- [255] C. Y. Nam, D. Tham, and J. E. Fischer. Disorder effects in focused-ion-beam-deposited pt contacts on gan nanowires. *Nano Letters*, 10(5):2029 – 2033, 2005.
- [256] Y. Yang, Q. Liao, J. Qi, Y. Zhang, L. Tang, and N. Ye. Ptir/zno nanowire/pentacene hybrid back-to-back double diodes. *Applied Physics Letters*, 93(13):133101, 2008.
- [257] S. A. Wilson and *et al.* New materials for micro-scale sensors and actuators: An engineering review. *Materials Science and Engineering: R: Reports*, 56(1–6):1 – 129, 2007.
- [258] A. S. Lee, S. F. Peteu, J. V. Ly, A. G. Requicha, M. E. Thompson, and C. Zhou. Actuation of polypyrrole nanowires. *Nanotechnology*, 19(16):165501, 2008.
- [259] L. Rotkina, J.-F. Lin, and J. P. Bird. Nonlinear current-voltage characteristics of pt nanowires and nanowire transistors fabricated by electron-beam deposition. *Applied Physics Letters*, 83(21):4426–4428, 2003.
- [260] H. W. P. Koops, A. Kaya, and M. Weber. Fabrication and characterization of platinum nanocrystalline material grown by electron-beam induced deposition. *The 38th International symposium on electron, ion, and photon beams*, 13(6):2400–2403, 1995.
- [261] A. Fernández-Pacheco, J. M. De Teresa, R. Córdoba, and M. R. Ibarra. Metal-insulator transition in pt-C nanowires grown by focused-ion-beam-induced deposition. *Phys. Rev. B*, 79(17):174204, May 2009.
- [262] W. F. van Dorp and C. W. Hagen. A critical literature review of focused electron beam induced deposition. *Journal of Applied Physics*, 104(8):081301, 2008.
- [263] Raith GmbH. *Operation Manual, Gas Injection System*. Raith GmbH, 2nd edition, 2005.
- [264] A. Botman, M. Hesselberth, and J.J.L. Mulders. Improving the conductivity of platinum-containing nano-structures created by electron-beam-induced deposition. *Microelectronic Engineering*, 85(5–6):1139 – 1142, 2008.
- [265] A. Botman. *Towards high purity nanostructures from electron beam induced deposition of platinum, PHD Thesis*. Technische Universiteit Delft, Delft, 2009.

- [266] M. Weber, M. Rudolph, J. Kretz, and H. W. P. Koops. Electron-beam induced deposition for fabrication of vacuum field emitter devices. *7th International Vacuum Microelectronics Conference*, 13(2):461–464, 1995.
- [267] L. Rotkina, S. Oh, J. N. Eckstein, and S. V. Rotkin. Logarithmic behavior of the conductivity of electron-beam deposited granular $pt^?c$ nanowires. *Phys. Rev. B*, 72(23):233407, Dec 2005.
- [268] K. Yoshino, S. Hayashi, G. Ishii, and Y. Inuishi. Electrical transport in electron beam irradiated polyacetylene. *Solid State Communications*, 46(5):405 – 408, 1983.
- [269] S. Bhadra and D. Khastgir. Degradation and stability of polyaniline on exposure to electron beam irradiation (structure–property relationship). *Polymer Degradation and Stability*, 92(10):1824–1832, 2007.
- [270] H. A. Pohl. *Dielectrophoresis*. Wiley, New York, 1nd edition, 1981.
- [271] L. Zheng, J. P. Brody, and P. J. Burke. Electronic manipulation of dna, proteins, and nanoparticles for potential circuit assembly. *Biosensors and Bioelectronics*, 20(3):606–619, 2004.
- [272] H.-Y. Lee and J Voldman. Optimizing micromixer design for enhancing dielectrophoretic microconcentrator performance. *Analytical Chemistry*, 79(5):1833–1839, 2007.
- [273] P. A. Smith, C. D. Nordquist, T. N. Jackson, T. S. Mayer, B. R. Martin, J. Mbindyo, and T. E. Mallouk. Electric-field assisted assembly and alignment of metallic nanowires. *Applied Physics Letters*, 77(9):1399–1401, 2000.
- [274] L. Dong, J. Bush, V. Chirayos, R. Solanki, J. Jiao, Y. Ono, J. F. Conley, and B. D. Ulrich. Dielectrophoretic manipulation and electrical characterization of gold nanowires. *Nanotechnology*, 16:1500–1505, 2005.
- [275] A. D. Wissner-Gross. Dielectrophoretic reconfiguration of nanowire interconnects. *Nanotechnology*, 17(19):4986–4990, 2006.
- [276] M. E. Toimil Molares, E. M. Höhberger, C. Schaefflein, R. H. Blick, R. Neumann, and C. Trautmann. Electrical characterization of electrochemically grown single copper nanowires. *Applied Physics Letters*, 82(13):2139–2141, 2003.

- [277] E. T. Kang, K. G. Neoh, Y. K. Ong, K. L. Tan, and B. T. G. Tan. X-ray photoelectron spectroscopic studies of polypyrrole synthesized with oxidative Fe(III) salts. *Macromolecules*, 24:2822, 1991.
- [278] P. Pflüger and G. B. Street. Chemical, electronic, and structural properties of conducting heterocyclic polymers: A view by xps. *J. Chem. Phys.*, 80:544, 1984.
- [279] S. Ghosh, G. A. Bowmaker, R. P. Cooney, and J. M. Seakins. Infrared and Raman spectroscopic studies of the electrochemical oxidative degradation of polypyrrole. *Synthetic Metals*, 95(1):63 – 67, 1998.
- [280] M. Hasik, A. Bernasik, A. Drelinkiewicz, K. Kowalski, E. Wenda, and J. Camra. XPS studies of nitrogen-containing conjugated polymers-palladium systems. *Surface Science*, 507–510:916 – 921, 2002.
- [281] A. Majumdar. MATERIALS SCIENCE: Enhanced: Thermoelectricity in Semiconductor Nanostructures. *Science*, 303(5659):777–778, 2004.
- [282] A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, W. A. Yu, J.-K. Goddard III, and J. R. Heath. Silicon nanowires as efficient thermoelectric materials. *Nature*, 451(7175):168–171, 2008.
- [283] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J.-P. Fleurial, and P. Gogna. New directions for low-dimensional thermoelectric materials. *Advanced Materials*, 19(8):1043–1053, 2007.
- [284] A. I. Hochbaum and P. Yang. Semiconductor nanowires for energy conversion. *Chemical Reviews*, 110(1):527–546, 2010.
- [285] P. M. Chaikin and G. Beni. Thermopower in the correlated hopping regime. *Phys. Rev. B*, 13(2):647–651, Jan 1976.
- [286] P. Wei, W. Bao, Y. Pu, C. N. Lau, and J. Shi. Anomalous thermoelectric transport of Dirac particles in graphene. *Phys. Rev. Lett.*, 102(16):166808, Apr 2009.
- [287] A. Boukai, K. Xu, and J. R. Heath. Size-dependent transport and thermoelectric properties of individual polycrystalline bismuth nanowires. *Advanced Materials*, 18(7):864–869, 2006.

- [288] J. P. Small. Thermopower measurement of individual single walled carbon nanotubes. *Microscale Thermophysical Engineering*, 8(1):1–5, 2004.
- [289] F. Zhou, J. H. Seol, A. L. Moore, L. Shi, Q. L. Ye, and R. Scheffler. One-dimensional electron transport and thermopower in an individual insb nanowire. *Journal of Physics: Condensed Matter*, 18(42):9651, 2006.
- [290] W. Liang, A. I. Hochbaum, M. Fardy, O. Rabin, M. Zhang, and P. Yang. Field-effect modulation of seebeck coefficient in single pbse nanowires. *Nano Letters*, 9(4):1689–1693, 2009.
- [291] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang. Enhanced thermoelectric performance of rough silicon nanowires. *Nature*, 451(7175):163–167, 2008.
- [292] L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, and A. Majumdar. Measuring thermal and thermoelectric properties of one-dimensional nanostructures using a microfabricated device. *Journal of Heat Transfer*, 125(5):881–888, 2003.
- [293] L. Shi, C. Yu, and J. Zhou. Thermal characterization and sensor applications of one-dimensional nanostructures employing micro-electromechanical systems. *The Journal of Physical Chemistry B*, 109(47):22102–22111, 2005.