# UNIVERSITY OF LJUBLJANA FACULTY OF MATHEMATICS AND PHYSICS DEPARTMENT OF PHYSICS

Marko Uplaznik

Transport properties of electrons in  $Mo_6S_xI_{9-x}$  nanowire integrated chips

Doctoral thesis

ADVISER: prof. dr. Dragan Dragoljub Mihailović

Ljubljana, 2009

# UNIVERZA V LJUBLJANI FAKULTETA ZA MATEMATIKO IN FIZIKO ODDELEK ZA FIZIKO

Marko Uplaznik

Transportne lastnosti elektronov v integriranih čipih z nanožicami ${\rm Mo}_6 {\rm S_x I_{9-x}}$ 

Doktorska disertacija

MENTOR: prof. dr. Dragan Dragoljub Mihailović

Ljubljana, 2009

#### Abstract

Basic property determination of novel nanomaterials is one of the main fields in nanotechnology. The research includes along with the goal experiment also the material preparation, design and manufacture of measurement circuits, the integration of nanoparticles in the chips and the analysis of results. In this doctoral dissertation we report on the electron transport properties of  $Mo_6S_xI_{9-x}$  nanowires. The synthesized material was dispersed in acetone using ultrasound and was later replaced with isopropanol due to dielectrophoretical integration of single bundles in measurement chips, that were annealed before the measurement at 700°C in vacuum, improving electrical connection between the bundle and the contacts. The circuit that was produced with electron beam lithography included a several 100 nm narrow gap, that was bridged by bundles integrating them into the circuit. The measured variables were the current versus voltage characteristics at different temperatures from room temperature till 18 K. The result analysis of four thin bundles was based on three main theoretical transport predictions: the Luttinger liquid, environmental Coulomb blockade and variable range hopping. Two bundles showed Luttinger liquid and variable range hopping, whereas the other two combined the hopping mechanism with the effects of environmental Coulomb blockade. We confirmed that the bundles are composed of single nanowires strands but included also high disorder and even insulated islands that act as quantum dots. For thicker bundles we observed the effect of cycling two times, where the conductivity changed for each temperature scan. We suggest an explanation of the phenomenon through Fermi glass theory by assuming the transformation of localized states to non-localized ones in such a way that the mobility edge passes the Fermi energy and thus fundamentally alters the transport mechanisms in the system.

PACS: 73.63.Nm, 73.40.Cg

Keywords: inorganic nanowires, electron transport properties, disordered nanowires, temperature annealing, variable range hopping, environmental Coulomb blockade, Luttinger liquid, nanowire dispersion

#### Povzetek

Določevanje osnovnih lastnosti nanomaterialov je eno temeljnih področij nanotehnologije. Raziskave poleg ciljnih eksperimentov vključujejo pripravo razpršin materiala, oblikovanje in izdelavo merlinih vezij, integracijo nanodelcev v čipe in analizo rezultatov. V tej doktorski disertaciji poročamo o meritvah elektronskih lastnosti nanosvežnjev  $Mo_6S_xI_{9-x}$ . Sintetiziran material smo z ultrazvokom razpršili v acetonu in ga kasneje nadomestili z izopropanolom zaradi dielektroforetične integracije posameznih svežnjev v merilne čipe, ki smo jih pred meritvijo popuščali v vakuumu na temperaturi 700°C, s čimer smo izboljšali električno povezavo med kontakti in svežnjem. Vezje, ki smo ga izdelali s pomočjo elektronske nanolitografije, je v osnovi vsebovalo ozko režo širine nekaj 100 nm, ki so jo svežnji premostili ter se tako integrirali v vezje. Merilne opazljivke so bile karakteristike toka skozi merilni čip v odvisnosti od napetosti, merjene pri različnih temperaturah od sobne do 18 K. Analiza rezultatov meritev štirih tankih svežnjev je temeljila na teoretičnih napovedih glavnih transportnih mehanizmov: Luttingerjeve tekočine, impedančne Coulombove blokade in preskakovanja spremenljivega dosega. Pri dveh svežnjih smo pokazili na soobstoj Luttingerjeve tekočine in preskakovanja, pri preostalih dveh pa smo poleg preskakovanja sklepali še na impedančno Coulombovo blokado. Tako smo potrdili, da so svežnji sestavljeni iz posameznih nanožic, vendar pa so prepredeni z nehomogenostmi in celo električno izoliranimi strukturnimi otočki, ki delujejo kot kvantne pike. Pri debelejših svežnjih smo v dveh primerih opazili še efekt cikliranja, kjer se prevodnost spreminja ob vsakem temperaturnem ciklu. Pojav razložimo s teorijo Fermijevega stekla, kjer predvidevamo prehajanje lokaliziranih v nelokaliziranana stanja ob spreminjanju strukture med meritvijo tako, da rob mobilnosti prečka Fermijevo energijo, s čimer se fundamentalno spremenijo transportni mehanizmi v sistemu.

Stvarni vrstilec (PACS): 73.63.Nm, 73.40.Cg

Ključne besede: anorganske nanožice, elektronski transport, nehomogene nanožice, temperaturno popuščanje, preskakovanje spremenljivega dosega, impedančna Coulombova blokada, Luttingerjeva tekočina, razpršina nanožic

#### Acknowledgements - Zahvale

This dissertation couldn't be made without the devoted team of my colleagues and fellow researches. Non of the experiments would be possible without the material that was synthesized and processed by Damjan Vengust and Aleš Mrzel. The basis for the measurements was developed by Roman Yusupov, supported by priceless experience of Primož Kušar and Tomaž Mertelj. Many fundamental steps of nanowire handling and integration were established and developed by Boštjan Berčič. His work on thicker bundles and nanobundle networks was considered exemplary and enabled the difficult transition towards thinner nanobundles. The team was supervised by my mentor, professor Mihailović, that guided the research through fruitful debates and with his persistence and patience facilitated reaching our goals. A thanks goes also to all other members of the department for complex matter, that followed me on my research path from the beginning till the end. Special thanks goes to Jure Strle that often sacrificed his time for theoretical debates, calculations and remarks on my work.

Posebna hvala gre mojim kolegom, ki so me podpirali in vzpodbujali se posebej ob težjih trenutkih. Hvala Andreju Vrečkotu, Matjažu Zemljiču, Lukatu Ravniku, Mirkotu Kokoletu, Ireni Dolenc, Blažu Zupančiču in starejšim kolegom Danijelu Vrbaniču ter Poloni Umek, ki sta z razmevanjem delila svoje bogate izkušnje. K uspešnem zaključku dela sta prispevala tudi moja stara prijatelja Miha Nemevšek in Andrej Pukšič, ki sta vedno verjela vame. Zahvala pa gre tudi moji družini in stricu Stankotu, ki me je usmerjal na moji akademski poti.

Mostly I would like to thank Mihaela Ploscaru, that morally supported and helped me in the research. Multumesc pentru tot, Burticiţa mea!

# Contents

<b>2</b>	The	eoretica	al overview of one-dimensional electron transport	15		
	2.1	Basic	consequences of strong 1D confinement	15		
		2.1.1	Quantum wells - quantum dots	15		
		2.1.2	Long range (dis)order in 1D structures	18		
	2.2	Ballist	tic transport in 1D - Landauer formula	20		
	2.3	Fabry-	Perot segmentation	27		
		2.3.1	One and two scattering places	28		
		2.3.2	Three and $n$ scattering places $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	28		
	2.4	Electro	on transport in quantum dots	34		
		2.4.1	Coulomb blockade oscillations	34		
		2.4.2	Environmental Coulomb blockade theory	43		
	2.5	Variab	le range hopping	49		
	2.6	Luttin	ger liquid	56		
	-	_				
3	San	Sample preparation and measurements				
	3.1	E-bear	m lithography	61		
		3.1.1	Substrate and e-resist spinning	64		
		3.1.2	E-beam writing and developing	65		
		3.1.3	Sputtering and lift-off	68		
	3.2	MoSIx	Nanowires	70		
		3.2.1	The synthesis and the chemical structure of			
			MoSIx nanowires	71		
	3.3	$3.3$ Dielectrophoretical attachment of single bundles over a narrow gap $\therefore$				
		3.3.1	Theoretical considerations	78		
		3.3.2	The attachment procedure	80		
	3.4	Measu	rements	88		
		3.4.1	Measurement setup	88		
		3.4.2	The process of temperature annealing	89		
		3.4.3	Measured samples	98		

4	Results and discussion       10         4.1       The thin bundles       10         4.1.1       The "S" curves       10         4.1.2       The "J" curves       10         4.2       The thick bundles       10         4.2.1       The cycling effect       11		
5	Conclusion		
	Razširjeni povzetek v slovenščini	127	
6	Jvod	128	
7	Ceoretične napovedi       I         .1 Kvantne pike in (impedančna) Coulombova blokada	<b>130</b> 130 136 138	
8	Nanožice MoSIx in izvedba eksperimenta       14         8.1       Nanožice MoSIx       1         8.2       Priprava razpršin in izdelava merilnih čipov       1         8.3       Meritev       1		
9	Rezultati       .1       Tanki svežnji	147 147 149 150 154	
10	Zaključek	158	

# Chapter 1

# Introduction

Nanotechnology appears to be a novel promising route in many fields of scientific research, in medicine, electronics, physics, biochemistry,... and is expected to find new applications in the areas of information industry, diagnostics, even cancer treatment. What makes this new approach exciting and demanding are the scales and dimensions of objects involved in order to explore new possibilities and phenomena that arise when the macroworld collides with the micro- even nanoworld. These systems are often called mesoscopic and are considered to be one of the unexplored areas of science that utilizes highly developed technology and precise instruments, since the minute objects, that behave in practically the same way as molecules, need to be handled with the same precision as macro objects. This is the core of the nanotechnology: the structures are precisely designed on the atomic level and are intended to be controlled perfectly in terms of position and function. Such high expectations make nanotechnology a multidisciplinary science that includes particularly (bio)chemistry, physics, electronics that have to be combined in order to reach the set goals. The field already has a huge success in designing and controllably manufacturing different compounds and novel materials such as nanoparticles, nanowires, nanorods, nanohorns, ..., that are characterized under modern microscopy (transmission and scanning electron microscopy (TEM, SEM), atomic force microscopy (AFM), scanning tunneling microscopy (STM) and spectroscopic techniques (X-ray diffraction (XRD), X-ray absorption fine structure (XSAFS), Raman spectroscopy, UV-VIS spectroscopy,...). The integration of the compounds into the circuits was also demonstrated and many basic properties were explored, but the transition into high scale production hasn't yet been established. Mostly the materials are used as additives and coatings, but functional mechanical or electronic devices are still in the phase of research. Promising materials for such devices are the nanowires and nanotubes that exhibit novel physical properties on the basis of quantum mechanics and can be at the same time handled with sufficient accuracy to integrate them into measurement chips that are produced using the e-beam lithography [1] with sufficiently high resolution in the nanometer range. Exemplary work on carbon nanotubes [2, 3, 4] confirms the onedimensional behavior of narrow wires through the presence of Luttinger liquid [5, 6]. Other low dimensional phenomena such as environmental Coulomb blockade have also been observed, confirming theoretical predictions for such systems [7, 8, 9]. In inorganic nanowires (niobium and molybdenum

selenide) similar Luttinger liquid behavior was measured along with charge density wave formation and variable range hopping transport [10, 11]. Such behavior is predicted in the theory of Fermi glasses developed by Mott and Anderson [12] and is closely related to the disorder in the systems. Research involving the inorganic compound based on molybdenum, sulfur and iodine with a general formula  $Mo_6S_xI_{9-x}$  under the signature MoSIx [13, 14] was mainly concentrated on bulk samples in form of pressed pellets and included optical properties [15, 16, 17, 18], sound propagation studies [19] and electrical transport properties of nanowire sheets [20] or networks [21, 22], where also variable range hopping has been observed. Other studies involved sample preparation techniques and solubility properties in various solvents [23, 24] proving an intrinsic compatibility with a variety of chemicals, including water. The transport of individual, thick bundles (above 50 nm in diameter) has also been explored and again variable range hopping was observed [1, 25] whereas thinner bundle were studied on their self-assembling properties with different (bio)materials, setting the route to biochemistry [26]. In our work we attempted to measure basic electronic properties of single and thin MoSIx bundles, which proved to be quite a challenge. Our research included, apart form the material synthesis, all technological steps that lead to the final experiment. We were confronted with the majority of problems that also other researchers face: sample preparation, circuit production, single bundle integration and finally the transport measurement.

In this thesis we begin with physical phenomena in one dimension and introduce the theories from the experimental point of view. After the basic description of our nanowires and dispersion preparation we turn our attention to the circuit production, discussing the process and challenges of the e-beam lithography, followed by dielectrophoretical bundle integration into a circuit, forming the measurement chip. Before describing the measurements, we report on the thermal annealing procedure and in the end we conclude with the analysis of results and general discussion.

# Chapter 2

# Theoretical overview of one-dimensional electron transport

One-dimensional systems are especially interesting for theoretical considerations since strong particle confinement lies in the area of the quantum mechanics thus having new physical properties which are often quite unexpected compared to the well explored bulk material properties. Our field of interest is electron current transport through such systems from theoretical and from experimental point of view by the exploration of single nanobundle measurement chips.

In this chapter we first discuss the general properties of strong electron confinement in quantum mechanical terms, followed by some main transport theories that could be applied to a real measured system. We consider some 1D systems in terms of impurity and non-homogeneity content that have profound impact on electron travel along the system, especially if the confinement isn't as strong and allows transport along other dimensions. We tried to present the issues so that the underlying physics comes upfront, sometimes even with basic mathematical treatments that lead to commonly familiar result.

# 2.1 Basic consequences of strong 1D confinement

Before we begin with the overview of some theoretical models let us depict the fundamental consequences in 1D structures that arise solely due to the strong spatial confinement of fermions. They are driven by quantum mechanical effects that become significant at low temperatures and in confined dimensions.

# 2.1.1 Quantum wells - quantum dots

Let us consider an independent and isolated system, where the electrons are trapped. We describe it as a quantum well with harmonic, step-like or other potential barrier shape. In every case, the calculated energy states become less dense due to the shrinkage of space. Let us take a look into basic properties on the example of 1D quantum harmonic oscillator [27] [28](Fig. 2.1), that describes a deep quantum well with a harmonic (quadratic)

potential:

$$V = \frac{1}{2}m\omega^2 x^2, \tag{2.1}$$

where  $\omega$  denotes an equivalent to classical angular frequency in terms of  $(K/m)^{1/2}$  with K being the elastic constant of classical analogy with a mass on a spring, m mass and x the position of the particle inside the well.



Figure 2.1: The energy levels of a 1D harmonic oscillator (left) and eigenstate probabilities of the first four energy levels (right); the colors denote the same n in both diagrams.

To determine the wave functions and hence the probability for a particle to be found at the specific point in the oscillator, we need to solve the Schrödinger equation that includes also the energy levels for each wave function:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\,\psi,$$
(2.2)

where  $\psi$  denotes wave function and E its energy level. The solution of the problem is a family of eigenfunctions with proper boundary conditions  $(\psi(x \to -\infty) = 0 \text{ and } \psi(x \to \infty) = 0)$ , each with its eigenenergy. Here we only write the result:

$$\psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} \left(2^n n!\right)^{-\frac{1}{2}} H_n\left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}x\right],\tag{2.3}$$

where n denotes the index of each wave function and  $H_n$  the Hermite polynomials of order n. The eigenenergies are equally spaced and follow the expression:

$$E_n = \hbar\omega(n + \frac{1}{2}). \tag{2.4}$$

If we are interested in three dimensional confinement, as is often the case in nanotechnology, the described 1D solutions can be easily expanded to include new dimensions, if the quantum states in each dimension remain uncoupled and the potential is isotropic, by adding new quantum numbers for each new dimension. For the harmonic oscillator in 3D we have three quantum numbers:  $n_x$ ,  $n_y$  and  $n_z$ . The solutions in this case have the same basic form as for the 1D:

$$E_{n_x, n_y, n_z} = \hbar \omega (n_x + n_y + n_z + \frac{3}{2}).$$
(2.5)

Even though the spacing between the levels remains constant, the number of states with same energy grows quadratically with the energy, since more degenerate eigenstates are possible. The eigenstates are a product of 1D states for each dimension:

$$\psi_{n_x,n_y,n_z} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} e^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)} \left(2^{n_x+n_y+n_z}n_x!n_y!n_z!\right)^{-\frac{1}{2}} \cdot H_{n_x} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}x\right] H_{n_y} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}y\right] H_{n_z} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}z\right]. \quad (2.6)$$

For the infinitely deep 1D square well [27] between 0 and  $x_0$  we similarly get a family of eigenfunctions with eigenenergies but with the difference that now the energy levels are not equally spaced any more, but grow quadratically with the index of the wave function Fig. 2.2 [27][28]:

$$\psi_{n} = \left(\frac{2}{x_{0}}\right)^{\frac{1}{2}} \sin(\frac{n\pi x}{x_{0}}),$$

$$E_{n} = \frac{n^{2}\pi^{2}\hbar^{2}}{2mx_{0}^{2}}.$$
(2.7)

As with the harmonic oscillator we generalize by introducing a quantum number for each new (additional) dimension. The total energy is a sum over all dimensions and the corresponding wave functions become the product of the wave functions for each dimension:

$$\psi_{n_x,n_y,n_z} = \left(\frac{2}{x_0}\right)^{\frac{1}{2}} \left(\frac{2}{y_0}\right)^{\frac{1}{2}} \left(\frac{2}{z_0}\right)^{\frac{1}{2}} \sin\left(\frac{n_x\pi x}{x_0}\right) \sin\left(\frac{n_y\pi y}{y_0}\right) \sin\left(\frac{n_z\pi z}{z_0}\right),$$
  

$$E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{x_0^2} + \frac{n_y^2}{y_0^2} + \frac{n_z^2}{z_0^2}\right).$$
(2.8)

As we will see later, this quantization and energy steps between states above typical thermal energy kT lead to interesting transport phenomena in a very unexpected way.



Figure 2.2: The energy levels in infinitely deep 1D square well (left) and eigenstate probabilities for the first four energy levels (right); the colors match in both diagrams.

## 2.1.2 Long range (dis)order in 1D structures

The mechanisms of electron scattering in an arbitrary electron guide are diverse. Along with the common scattering on the lattice disorder, stoichiometric discrepancies and on impurities, more exotic phonon and magnon interactions with the electrons are present. For low temperatures the phonon scattering is negligible, however, as we briefly show in this subsection, the magnon population remains present even at absolute zero temperature. The last claim follows from the more fundamental Mermin-Wagner theorem <sup>1</sup>. If we cite the abstract of their publication [29]:

"It is rigorously proven that at any nonzero temperature, a one- or twodimensional isotropic spin-S Heisenberg model with finite range exchange interaction can be neither ferromagnetic nor antiferromagnetic. The method of proof is capable of excluding a variety of types of ordering in one and two dimensions."

That report deals rigorously with the theorem, while here we just illustrate the physical base for this phenomenon [30]. We will show that at a given non-zero temperature the magnon excitations destroy the magnetic order in one (or two) dimension.

We start with writing the magnetization at some temperature as the difference between the magnetization at absolute zero (M(T = 0)) and the thermally excited magnon magnetization  $\Delta M(T)$ :

$$M(T) = M(T = 0) - \Delta M(T).$$
 (2.9)

The reduction in magnetization is proportional to the number of excited states, obtained by the integration of the product between the density of states g(E) and the

<sup>&</sup>lt;sup>1</sup>Also known as Mermin-Wagner-Hohenberg theorem or Coleman theorem.

probability for the state occupation according to the Bose-Einstein statistics:

$$\Delta M(T) \sim \int_0^\infty g(E) \left[ \frac{1}{e^{\frac{E}{k_B T}} - 1} \right] dE.$$
(2.10)

The density of states is obtained by calculating the volume element for each state in k space. Naturally the result depends strongly on the dimensionality of the system. Let us consider the general case for a d dimensional system and the energy dispersion  $E \propto |\mathbf{k}|^n$ . For the limiting case of infinite system size the number of states on an interval  $(\mathbf{k}, \mathbf{k} + d\mathbf{k})$  or (E, E + dE) is quotient of the volume of the shell in d-dimensional k space and the volume for one single state :

$$N = g(\mathbf{k})d\mathbf{k} = g(E)dE = \frac{V_{\text{shell}}}{V_{\text{single state}}}.$$
(2.11)

We are interested only in exponent dependencies of k or E so we write the result only qualitatively:

$$g(E)dE \propto |\mathbf{k}|^{d-1}d\mathbf{k}.$$
(2.12)

From the dispersion relation we get the differentials:

$$E \propto |\mathbf{k}|^n \Longrightarrow \frac{d\mathbf{k}}{dE} \propto |\mathbf{k}|^{(1-n)}$$
 (2.13)

which enable us to write the expression for g(E) from (2.12):

$$g(E) \propto |\mathbf{k}|^{d-1} \frac{d\mathbf{k}}{dE} = |\mathbf{k}|^{\frac{d-n}{n}}.$$
(2.14)

Let us now explore the case of ferromagnetic coupling with quadratic dispersion relation (n = 2). For better illustration we gather the expressions for different dimensions in the table 2.1.

dimension	g(E)
1	$\propto E^{-\frac{1}{2}}$
2	const
3	$\propto E^{\frac{1}{2}}$
d	$\propto E^{\frac{d-2}{2}}$

Table 2.1: The density of states g(E) for different system dimensions.

Taking a closer look at the target integral 2.10 we notice that for finite dimensions the upper value  $(E \to \infty)$  limits the integral till zero, leaving us to explore the behavior at

E = 0. Now we expand the Bose-Einstein function around zero<sup>2</sup> and rewrite the integral to:

$$\Delta M(T) \sim kT \int_0^\infty g(E) \left[ \frac{1}{e^{\frac{E}{kT}} - 1} \right] \doteq (kT)^2 \int_0^\infty g(E) \frac{1}{E}.$$
 (2.15)

Due to the power law connection between the density of states g(E) and the energy E the value of the last integral at E = 0 depends strongly on dimensionality of the system. Placing the expressions from the table 2.1 into (2.15) we find divergent behavior for d = 1 and d = 2 at vanishing E. Let us write the whole magnetization once more:

$$M(T) = M(T = 0) - \text{const } T \int_0^\infty g(E) \frac{1}{E}.$$
 (2.16)

The consequence of the divergence is the destruction of the magnetization order in the system M(T = 0) for even the slightest non-zero temperatures thus prohibiting long range order in one- and two dimensional spin arrays. Practically that would mean that an electron traveling in strongly confined 1D system would encounter (at least) many magnons on its way resulting in scattering and thus preventing undisturbed transport. This result already gives the taste of unexpected phenomena in a system, especially a realistic one since even in perfect structures and strong confinement the traveling electron encounters scattering.

# 2.2 Ballistic transport in 1D - Landauer formula

One of the basic models for transport through a 1D system is a direct, unscattered travel of an electron from one side of the system to the other. This transport is called *ballistic* since the electron passes the whole length of a 1D structure without being obstructed by any kind of mechanism, hence like a bullet. This model applies for the most ideal system of perfectly uniform and impurity free nanowires.

Let us describe the system as a 1D wire of length L between two bulk electrodes (Fig. 2.3). We can also say that we have confinement in two dimensions, y an z whereas x remains unconstricted.

As presented in the previous section the states in the system get separated in both confined dimensions y and z according to the given potential and the geometry of the wire, whereas in the x direction the electron states suffer no restrictions, thus being described as plane waves with the continuum of energy levels. If we deal with the problem similarly as presented for the case of the harmonic oscillator or the potential well, we solve the Schrödinger equation for the y and z direction and separately for the x direction. Since we have in mind only basic consequences for the transport we treat the confinement potential as a general function V(y, z). Writing the equation:

$$-\frac{\hbar^2}{2m} \left(\frac{d^2\varphi_n(y,z)}{dy^2} + \frac{d^2\varphi_n(y,z)}{dz^2}\right) + V(y,z)\,\varphi_n(y,z)(n) = \epsilon_n\,\varphi_n(y,z)\,,\qquad(2.17)$$

$$^{2}e^{x} - 1 \approx x + \ldots + \sigma(x^{2})$$



Figure 2.3: The transport channel with the transmission  $\tau[E]$  between two reservoirs with chemical potentials  $\mu_{\rm L}$  and  $\mu_{\rm R}$  a) and an artistic rendering of a nanowire/nanotube suspended between two major gold reservoirs. The inside of the tube shows schematically the positional probability of an electron for the case of cylindric potential well; the solutions for this quantum system are the sombrero-shaped Bessel functions - here we show the first three states (I, II and III on the image).

where index n denotes some excitation state,  $\varphi_n(y, z)$  the adequate eigen function for the confinement in y and z and  $\epsilon_n$  the energy of the state. Combining this result with the plane waves in x direction we can write the whole wave function  $\psi_{k_x,n}$  as:

$$\psi_{k_x,n} = \frac{e^{ik_xx}}{\sqrt{L}} \,\varphi_n(y,z). \tag{2.18}$$

The total energy  $E_{n,k_x}$  is the sum of the energies of the plane wave and the solution for the confined dimensions y and z:

$$E_{n,k_x} = \epsilon_n + \frac{\hbar^2 k_x^2}{2m}.$$
(2.19)

As we learned from dealing with harmonic potential and the 1D potential well the energy levels in transversal, confined direction become separated. Together with the continuum of plane wave energies the system consists of subbands of continuous states that begin with the discrete values of  $\epsilon_n$  and overlap in steps as the energy rises; naturally also the subbands carry the adequate index n. A scheme of subband structure is depicted in Fig. 2.4a).

Having introduced the electronic levels into our system we deal now also with the electric current. As schematically depicted on figure 2.3a we consider two contact reservoirs with chemical potentials  $\mu_{\rm L}$  and  $\mu_{\rm R}$  connected to our finite 1D system of length L. Starting with the definition of the current density j inside a subband n for an interval dk around a specific k and having in mind also discrete energy distribution due to the finite length L we can write for zero temperature and the transmission set to 1:

$$j_{n,k} = e \ \rho \ v(k) = \frac{2e}{L} \ v(k),$$
 (2.20)

where the linear density of states  $\rho$  includes also the two possibilities for the spin of the electrons. For finite number of electrons and a finite temperature we need to add the probability factor for the electron to occupy the level with the energy E(k) in the form of the Fermi function  $f(E - \mu)$ . We get:

$$j_{n,k} = \frac{2e}{L} v_n(k) f(E - \mu_{\rm L}).$$
 (2.21)

To get full current for one subband we make a sum over k and since we are interested in the right direction of the current we take only k > 0. Since for 1D systems the current density j and the current I are interchangeable we write:

$$I_n^{\to} = \frac{2e}{L} \sum_{k>0} v_n(k) f(E - \mu_L), \qquad (2.22)$$

where the arrow over  $I_n$  points in the direction of current from left to right. In the continuous limit (the length if the channel is large compared to its width) we can write an integral instead of the summation:

$$I_n^{\rightarrow} = \frac{2e}{\mathcal{L}} \int_0^\infty v_n(k) f(E - \mu_{\mathcal{L}}) d\tilde{n}, \qquad (2.23)$$

and by including the general expression for the k:

$$k = \frac{2\pi}{L}\tilde{n} \implies d\tilde{n} = \frac{L}{2\pi}dk \tag{2.24}$$

we can rewrite the (2.23) into:

$$I_n^{\rightarrow} = \frac{e}{\pi} \int_0^\infty v_n(k) f(E - \mu_{\rm L}) dk, \qquad (2.25)$$

which is then rewritten again via:

$$E = \frac{\hbar^2 k^2}{2m}, \ v_n(k) = \frac{\hbar k}{m} \Longrightarrow dk = \frac{dE}{\hbar v_n(k)}$$
(2.26)

in the integral over the energy for the entire subband, starting at the beginning of the subband  $\epsilon_n$ :

$$I_n^{\rightarrow} = \frac{2e}{h} \int_{\epsilon_n}^{\infty} f(E - \mu_{\rm L}) dE.$$
(2.27)



Figure 2.4: a) A scheme of subbands for a system with equally spaced subbands ( $\hbar\omega$ ) and b) a diagram of  $\chi(E)$  function for a system with equally spaced energy levels - red curve (e.g. harmonic oscillator Eq. (2.4)) and for nonconstant spacing - blue curve (e.g. potential well Eq. (2.7)).

Before we add all the contributions from each subband let us define a function  $\chi(E)$  that denotes the sum of Heaviside step functions  $H(E - \epsilon_n)$ :

$$\chi(E) = \sum_{n} H(E - \epsilon_n).$$
(2.28)

The step-like nature of  $\chi(E)$  is depicted on 2.4b).

Now we summarize the (2.27) over all subbands and get the overall current from left to right electrode:

$$I^{\rightarrow} = \sum_{n} I_{n}^{\rightarrow} = \sum_{n} \frac{2e}{h} \int_{\epsilon_{n}}^{\infty} f(E - \mu_{\rm L}) dE, \qquad (2.29)$$

which is simplified by summarizing over the subbands inside of the integral and stretching the integral from  $-\infty$  to  $\infty$  by limiting the subbands with the Heaviside function  $H(E - \epsilon_n)$ . The result now reads as:

$$I^{\rightarrow} = \frac{2e}{h} \int_{-\infty}^{\infty} \sum_{n} H(E - \epsilon_n) f(E - \mu_{\rm L}) dE = \frac{2e}{h} \int_{-\infty}^{\infty} f(E - \mu_{\rm L}) \chi(E) dE.$$
(2.30)

Naturally we write the same expression for the current from right to left but this time with chemical potential  $\mu_{\rm R}$ :

$$I^{\leftarrow} = \frac{2e}{h} \int_{-\infty}^{\infty} f(E - \mu_{\rm R}) \chi(E) dE, \qquad (2.31)$$

which gives the total current through the constriction as the difference between the left and right current:

$$I = I^{\to} - I^{\leftarrow} = \frac{2e}{h} \int_{-\infty}^{\infty} [f(E - \mu_{\rm L}) - f(E - \mu_{\rm R})]\chi(E)dE.$$
(2.32)

To get the basic idea, let us, along with the transmission set to unity, pin also the temperature to 0. In this case the Fermi function is a step function and the function  $\chi(E)$  is an integer  $\chi$  on the interval  $[\mu_{\rm R}, \mu_{\rm L}]$ . Now the Eq. (2.32) simplifies to:

$$I = \frac{2e}{h}\chi(\mu_{\rm L} - \mu_{\rm R}) = \frac{2e^2}{h}\chi\frac{\mu_{\rm L} - \mu_{\rm R}}{e} = \frac{2e^2}{h}\chi V,$$
(2.33)

from where we read the conductivity G as:

$$G = \frac{2e^2}{h}\chi,\tag{2.34}$$

since V denotes the voltage  $\frac{\mu_{\rm L}-\mu_{\rm R}}{e}$ . This is the fundamental result of this system. We learned that in the best case scenario, when the electron on its path doesn't encounter any kind of scattering, the conductance is limited by the quantum of conductance:

$$G_0 = \frac{2e^2}{h} = 7.75 \cdot 10^{-5} \,\mathrm{S} \qquad \text{or} \qquad \mathbf{R}_0 = 12.897 \,\mathrm{k}\Omega$$
 (2.35)

and takes the values of the multiples of  $G_0$ .

If the transmission isn't perfect, set to unity, then we introduce a multiplying parameter  $\tau \in (0, 1)$  that lowers the current in Eq. (2.32), transforming the conductance in Eq. (2.33) to

$$G = \frac{2e^2}{h}\chi\tau.$$
 (2.36)

This result carries the name the Landauer formula<sup>3</sup>.

Adding the transmission  $\tau(E)$ , that can be in general dependent on the energy of electrons, to the total current expression (2.32) we get the most general description of the electron transport through the system:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} [f(E - \mu_{\rm L}) - f(E - \mu_{\rm R})] \chi(E) \tau(E) dE.$$
 (2.37)

This expression can be simplified if we are interested in zero voltage limit conductance so that the difference between the chemical potentials of both electrodes remains small and we can write Taylor expansion of both Fermi functions. Let us set the values to:

$$\mu_{\rm L} = \mu + \delta \mu \text{ and } \mu_{\rm R} = \mu. \tag{2.38}$$

The expansion follows:

$$f(E - \mu_{\rm L}) - f(E - \mu_{\rm R}) = f(E - (\mu + \delta\mu)) - f(E - \mu) \approx -\delta\mu \frac{\partial f(E, \mu)}{\partial E}, \qquad (2.39)$$

<sup>&</sup>lt;sup>3</sup>Rolf Landauer; (1927 - 1999), an IBM physicist of German origin.

which transforms the Eq. (2.37) to:

$$I = \frac{2e^2}{h} \left[ \int_{-\infty}^{\infty} -\frac{\partial f(E,\mu)}{\partial E} \chi(E) \tau(E) dE \right] \frac{\delta\mu}{e}, \qquad (2.40)$$

directly giving us the final result for conductance:

$$G(\mu) = \frac{2e^2}{h} \int_{-\infty}^{\infty} -\frac{\partial f(E,\mu)}{\partial E} \chi(E)\tau(E)dE.$$
(2.41)

If we describe in words: the conductance for low voltage  $\delta \mu/e$  is the contribution of the subbands that overlap with the derivative of the Fermi function  $\frac{-\partial f(E,\mu)}{\partial E}$ . As the energy increases, the derivative travels towards higher subbands following the  $\chi(E)$  dependance as depicted on Fig. 2.4b. The derivative of the Fermi function is known also as the *broadening function*.

For a concrete example let us take the harmonic oscillator in 2D with equally spaced energy levels (Eq. (2.5)) and with the  $\chi(E)$  function. For ballistic transport the transmission is set to unity and the oscillator parameter  $\hbar\omega$  is set to 0.1 eV.

To clarify the numeric calculation we consider the definition of  $\chi(E)$  from the Eq. (2.28). By putting it into the Eq. 2.41 and placing the sum over all subbands before the integral we lift the lower integration limit to  $\epsilon_n$ :

$$G(\mu) = \frac{2e^2}{h} \sum_{n} \int_{-\infty}^{\infty} -\frac{\partial f(E,\mu)}{\partial E} H(E-\epsilon_n) dE = \frac{2e^2}{h} \sum_{n} \int_{\epsilon_n}^{\infty} -\frac{\partial f(E,\mu)}{\partial E} dE.$$
(2.42)

Now we can easily integrate and by evaluating the values at the limits we get:

$$G(\mu) = \frac{2e^2}{h} \sum_{n} -f(E-\mu) \Big|_{\epsilon_n}^{\infty} = \frac{2e^2}{h} \sum_{n} f(\epsilon_n - \mu).$$
(2.43)

We can say that the Fermi function travels from one band to the next one with the contribution to the sum of all passed subbands and those that cross the function. If we draw the conductance we get the very well known staircase (Fig. 2.6a)) with the step size  $\frac{2e^2}{h}$ . For higher temperatures the edges are smeared out but the distances between the levels remain the same as for low temperatures. Considering the expression Eq. (2.43), this result is the direct consequence of the subband energy level structure and the step shape of the Fermi function. With the increasing voltage ( $\mu$ ) the step crosses more and more subbands thus enabling them to contribute to the conductance (Fig. 2.5a). Due to the spacing between the subbands in comparison to the the width of Fermi function edge the conductance for the energies inside of the subband remains constant and only changes on the transition between the subbands.

As mentioned before, the expression (2.42) gives the same staircase only that in this case the broadening function  $-\frac{\partial f(E,\mu)}{\partial E}$  picks only narrow portions of the  $\chi(E)$  function to contribute significantly to the integral (Fig. 2.5b). In fact only those steps are integrated, around which the broadening function is centered thus making the steps smooth if the broadening function stands close to the edges, so that both neighboring steps get included



Figure 2.5: A graphical depiction of the numerical summarization/integration of the expressions (2.41) - b) and (2.43) - a) (in both cases transmission  $\tau$  was set to unity). It can be seen, that the broadening function (centered at  $\mu = 0.32 \ eV$ ) for higher temperatures  $(300 \ K)$  on the diagram b) overlaps significantly with the neighboring subbands whereas for the lower ones  $(100 \ K)$  the whole hump remains confined inside of one subband, except at the edges. The alternative summarization of Fermi function a) shows the intersection of the step with different subbands; the colored vertical lines represent the contribution to the overall sum (violet for 300 K and green for 100 K). Here the contribution to the step, and of minor cross sections of the function's hump. Again for high temperatures the frontal subbands participation rises whereas for the lower ones the whole step drops practically inside of one subband.



Figure 2.6: The temperature diagrams of conductance staircase a) for equidistant electron levels ( $\hbar\omega = 0.1 eV$ ) calculated according to Eq. (2.43) and of the broadening function b) with  $\mu = 0$ , thus centered at zero. For low temperatures the function gets close to Dirac delta function. The legend in the upper right corner holds for both graphs.

in the integral. The broadening functions for some temperatures are presented in Fig. 2.6b); note that for low temperatures the function gets close to the Dirac delta function.

Our brief demonstration of the 1D conductance gave an unfamiliar result. The conductance is limited! In bulk material theory and practical applications not only allow huge conductances like in superconductive materials. That is truly a remarkable twist in the story of transport measurements for small, confined but otherwise perfect current guides.

# 2.3 Fabry-Perot segmentation

Perhaps that first phenomenon that comes in mind when thinking about non-uniform systems is segmented structure with barriers separating portions consecutively. This situation is equivalent to light passing through a series of semi-mirrors with finite reflectivity and transmittivity also known as the Fabry-Perot transmitter. Using the same terminology we can adopt the idea and predict a series of tunneling barriers with tunneling probability<sup>4</sup> T standing for the light transmitivity. The situation is schematically shown in Fig. 2.7 where the incident electron stream encounters a sequence of barriers before reaching the other end. This model completely ignores quantum mechanical effects (except for allowing the electrons to tunnel through a barrier) in term of spin, wavefunctions, Pauli principle, interference, ... and focuses on the total transmitivity  $T_{\rm all}$  through such a system. Even though we are fully aware of the model's inadequacy we demonstrate that also relatively modest inhomogeneity can cause even in this model the transmitivity to drop fast at a small number of barriers despite considerable barrier transmitivity.



Figure 2.7: The particle stream from left encounters a sequence of n barriers with transmitivity T and reflectivity R. The fraction of the incident beam that passes through is denoted as  $T_{all}$  and depends on the number of barriers and the transmitivity of a single barrier.

We discuss the situation with an incident current of particles from left  $\overrightarrow{I}$  encounters *n* barriers with transmitivity *T* and reflectivity R = 1 - T. The goal is to obtain the

<sup>&</sup>lt;sup>4</sup>The notations for T and R in this section shouldn't be mistaken for temperature and resistance.

overall fraction  $T_{all}$  of the incident beam that passes through, formally written as:

$$\vec{I}_{\rm R} = T_{\rm all} \vec{I}_{\rm L}.$$
(2.44)

For introduction we solve the problem for one and two barriers followed by a general solution for n number of barriers.

### 2.3.1 One and two scattering places

In the case of one scattering place the result is trivial since the electrons don't return back. The transmitivity T is simply its nominal value.

For two barriers we need to take into account also the possibility of scattering many times before finally penetrating the second barrier. The contribution to the overall transmitivity can be divided into orders of scattering where we count the number of backscattering before leaving the system. First scattering order would then be just passing through without backscattering;  $TT = T^2$ . In the second order an electron scatters back at the second barrier and in order to reach again the end of the system it must scatter backwards again at the first barrier. We write this as  $TRRT = T^2R^2$ . If we itemize first four scattering orders:

- 1.  $T^2$
- 2.  $T^2 R^2$
- 3.  $T^2 R^4$
- 4.  $T^2 R^6$ 
  - ÷

We recognize the pattern, enabling us to summarize over all orders:

$$T_{\text{all}} = T^2 + T^2 R^2 + T^2 R^4 + T^2 R^6 + \dots$$
 (2.45)

$$= T^{2}(1 + R^{2} + R^{4} + R^{6} + \dots)$$
(2.46)

$$= T^2 \sum_{i=1}^{\infty} R^{2i} = \frac{T^2}{1 - R^2}$$
(2.47)

$$-\frac{T}{T}$$
(2.48)

$$= \frac{1}{2-T}$$
. (2.48)

# 2.3.2 Three and *n* scattering places

The counting of different scattering orders gets more complicated for three barrier system. In order to determine the contribution of each order we use the notation which will help us to count properly all possibilities. We follow the electron as it passes the barriers and write the product for each event. Of course now the electron can travel also backwards from the right segment to the left one which enriches the possibilities considerably. Not to loose the clarity we count the passing of the middle barrier that results as hopping between the segments and thus introduce *the hopping order*. For each scattering order we get similarly then for two barriers a table of possibilities. The hopping of order 1 gives the direct traveling from one segment to the other and prohibits the hopping between them but allows scattering inside of each segment: We can write the sum for this hopping

1. order - $T^3$	2. order - $T^3 R^2$	3. order - $T^3 R^4$	4. order - $T^3 R^6$
TTT	TRRTT	TTRRRRT	TTRRRRRT
	TTRRT	TRRTRRT	TRRTRRRRT
		TRRRRTT	TRRRRTRRT
			TRRRRRTT

Table 2.2: The first four scattering orders for hopping order 1 in two segment (3 barrier) system.

order:

$$T_{\text{hop1}} = T^{3}(1 + 2R^{2} + 3R^{4} + 4R^{6} + \dots)$$
(2.49)

$$= T^3 R^{-2} \sum_{i=1}^{n} i R^{2i}$$
 (2.50)

We summarize using a standard trick of summation and rename  $R^2 = x$ :

$$S = \sum_{i=1}^{\infty} ix^i \tag{2.51}$$

$$Sx + x + x^{2} + x^{3} + x^{4} + \dots = S$$
(2.52)

$$Sx + \frac{1}{1-x} - 1 = S \tag{2.53}$$

$$S = \frac{x}{(1-x)^2}.$$
 (2.54)

The summation then reads:

$$T_{\rm hop1} = \frac{T^3}{(1-R^2)^2}.$$
 (2.55)

Similarly we write the possibilities for the second hopping order where we allow one transition between the segments; strictly speaking there are additional two passes of middle barrier of the electron since it has to return in order to leave the system in the correct direction.

1. order - $T^5 R^2$	2. order - $T^5 R^4$	3. order - $T^5 R^6$	4. order - $T^5 R^8$
TTRTRTT	TTRTRTRT	TTRTRTRRRRT	TTRTRTRRRRRRT
	TTRTRRRTT	TTRTRRRTRRT	TTRTRRRRRRR
	TTRRRTRTT	TTRRRTRTRRT	TTRRRTRTRRRRT
	TRRTRTRTT	TRRTRTRTRT	TRRTRTRTRRRRT
		TTRTRRRRTT	TTRTRRRRRTRRT
		TTRRRTRRRTT	TTRRRTRRTRRT
		TRRTRTRRRTT	TRRTRTRRRRTRRT
		TTRRRRRTRTT	TTRTRRRRRRTT
		TRRTRRRTRTT	TTRRRTRRRRTT
		TRRRRTRTRTT	TRRTRTRRRRRTT
			TTRTRRRRRRTT
			TTRRRTRRRRTT
			TRRTRTRRRRRTT
			TTRRRRRTRRRTT
			TRRTRRRTRRRTT
			TRRRRTRTRRRTT
			TTRRRRRRTRTT
			TRRTRRRRRTRTT
			TRRRRTRRTRTT
			TRRRRRRTRTRTT

Let us write the contributions for first several orders:

Table 2.3: The first four scattering orders for hopping order 2 in two segment (3 barrier) system.

Before we can write the sum over all scattering orders:

$$T_{\rm hop2} = T^5 R^2 (1 + 4R^2 + 10R^4 + 20R^6 \dots)$$
(2.56)

we need to determine the coefficients for each scattering order. We notice that they follow a general rule:

$$1, 4, 10, 20 \dots = \binom{3}{3}, \binom{4}{3}, \binom{5}{3}, \binom{6}{3} \dots$$
(2.57)

We can even test this rule. If we examine the sequences of Ts and Rs we observe that each possibility starts and ends with a T (not surprisingly since the electron enters and leaves the system with tunneling through the barrier) and that they can be divided into strings of two characters that follow combinations and have some restrictions. What shuffles in each sequence is: n = (scattering order - 1) number of RR, one T and two sets of RT. There is one constriction: T and both RTs can only be in sequence<sup>5</sup> TRTRTwith possibility of the RRs in between. To get the number of sequences we take non repetitional permutations of the number of all shuffling strings (number of RRs plus one T plus two  $RTs \longrightarrow n - 1 + 1 + 2 = n + 2$ ), divide it with the factors for non repetitional permutation for those strings that are repeating and finally divide also by three due to the sequence condition for T and both RTs. The general coefficient reads as assumed in (2.57):

$$\frac{(n+2)!}{3\ 2!\ (n+2-3)!} = \binom{n+2}{3}.$$
(2.58)

The sum over all orders can be now written in a compact form:

$$T_{\rm hop2} = T^5 \sum_{n=1}^{\infty} \binom{n+2}{3} R^{2n}.$$
 (2.59)

We deal with the summation similarly as before  $(R^2 = x)$  (2.51):

$$S = \sum_{i=1}^{\infty} {\binom{i+2}{3}} x^i \tag{2.60}$$

$$S = x + 4x^{2} + 10x^{3} + 20x^{4} + 35x^{5} + \dots \quad (2.61)$$

$$Sx + x + 3x^{2} + 6x^{3} + 10x^{4} + \dots = S.$$
(2.62)

We get the new series which we summarize separately:

$$M = x + 3x^2 + 6x^3 + 10x^4 + \dots$$
 (2.63)

$$Mx + x + 2x^{2} + 3x^{3} + 4x^{4} + \dots = M$$
(2.64)

$$Mx + \frac{x}{(1-x)^2} = M (2.65)$$

$$M = \frac{x}{(1-x)^3}.$$
 (2.66)

The sum S (2.60) is then:

$$S = \frac{x}{(1-x)^4},$$
(2.67)

and thus the  $T_{\text{hop2}}$  from (2.59) and (2.67):

$$T_{\rm hop2} = T^5 \frac{R^2}{(1-R^2)^4}.$$
 (2.68)

We can estimate also other hopping order contributions and write the full sum over all hopping orders:

$$T_{\text{All}} = T^3 \frac{1}{(1-R^2)^2} + T^5 \frac{R^2}{(1-R^2)^4} + T^7 \frac{R^4}{(1-R^2)^6} + \dots$$
(2.69)

$$T_{\text{All}} = \frac{T^3}{(1-R^2)^2} \sum_{n=0}^{\infty} \left(\frac{R}{1+R}\right)^{2n}.$$
(2.70)

<sup>&</sup>lt;sup>5</sup>Any other possibility allows the electron to leave the system prematurely.

The expression is geometrical series and can be summarized to:

$$T_{\rm All} = \frac{T}{3 - 2T}.$$
 (2.71)

For the general case of n scattering barriers we have to look one last time at the series of transmissions for calculated systems:

$$T_1 = T = \frac{T}{1 - 0T}$$
(2.72)

$$T_2 = \frac{I}{2 - 1T}$$
(2.73)

$$T_3 = \frac{1}{3 - 2T} \tag{2.74}$$

$$T_n = \frac{T}{n - (n - 1)T}.$$
 (2.76)

This derivation used a brute force approach giving us the possibility to perform the summation over possible scattering and even hopping order. Another much simpler approach uses the derivation with the help of transformational matrices that describe the transition of the current over barriers.

Similarly than before we start with one barrier with the transmittance T and reflectivity R = 1 - T, but this time we take the general case of currents incoming and reflecting on both sides of the barrier:

$$\overrightarrow{I_{\rm R}} = T\overrightarrow{I_{\rm L}} + R\overleftarrow{I_{\rm R}}$$
(2.77)

$$\dot{I}_{\rm L} = RI_{\rm L} + T\dot{I}_{\rm R}. \qquad (2.78)$$

To get the transformational matrix we write the current on each side as vectors with components denoting the left and right direction:

$$\begin{bmatrix} \overrightarrow{I_{\rm R}} \\ \overleftarrow{I_{\rm R}} \end{bmatrix} = \frac{1}{T} \begin{bmatrix} T - R & R \\ -R & 1 \end{bmatrix} \begin{bmatrix} \overrightarrow{I_{\rm L}} \\ \overleftarrow{I_{\rm L}} \end{bmatrix}.$$
(2.79)

Since in our case the electrons come only from left  $\overrightarrow{I_{L}}$ , we set the current from right  $\overleftarrow{I_{R}}$  to zero. In order to get the total transmittance we write the transformation (2.79) inversely. The determinant of the transformational matrix is 1 and the inverse is written simply by switching the elements on the diagonal and changing the sign of the off diagonal elements:

$$\begin{bmatrix} \overrightarrow{I_{\rm L}} \\ \overleftarrow{I_{\rm L}} \end{bmatrix} = \frac{1}{T} \begin{bmatrix} 1 & -R \\ R & T-R \end{bmatrix} \begin{bmatrix} \overrightarrow{I_{\rm R}} \\ 0 \end{bmatrix}.$$
(2.80)

Now we write the reverse transformation of  $\overrightarrow{I}_{R}$  to  $\overrightarrow{I}_{L}$  and extract the incoming current:

$$\overrightarrow{I_{\rm R}} = T \overrightarrow{I_{\rm L}},\tag{2.81}$$

which is of course obvious solution.

For two barriers we simply multiply their transformational matrices. After simplifying using the connection between R and T we get new transformational matrix:

$$\frac{1}{T} \begin{bmatrix} T-R & R \\ -R & 1 \end{bmatrix} \frac{1}{T} \begin{bmatrix} T-R & R \\ -R & 1 \end{bmatrix} = \frac{1}{T} \begin{bmatrix} T-2R & 2R \\ -2R & 1+R \end{bmatrix}$$
(2.82)

and writing it in the inverse form as in (2.80):

$$\begin{bmatrix} \overrightarrow{I_{\rm L}} \\ \overleftarrow{I_{\rm L}} \end{bmatrix} = \frac{1}{T} \begin{bmatrix} 1+R & -2R \\ 2R & T-2R \end{bmatrix} \begin{bmatrix} \overrightarrow{I_{\rm R}} \\ 0 \end{bmatrix}.$$
(2.83)

Now the overall transmittance gets the form:

$$\overrightarrow{I_R} = \frac{T}{1+R}\overrightarrow{I_L} = \frac{T}{2-T}\overrightarrow{I_L},\tag{2.84}$$

which we already know from previous derivation (2.48).

We can already see the multiplying pattern in the new transformational matrix. We notice that simply R is subtracted or added to each matrix element. For the case of n barriers the matrix takes form:

$$\begin{bmatrix} \overrightarrow{I_{R}} \\ \overrightarrow{I_{R}} \end{bmatrix} = \frac{1}{T} \begin{bmatrix} T - nR & nR \\ -nR & 1 + (n-1)R \end{bmatrix} \begin{bmatrix} \overrightarrow{I_{L}} \\ \overleftarrow{I_{L}} \end{bmatrix}.$$
 (2.85)

and from its inverse we finally get the familiar total transmitivity (2.76):

$$\overrightarrow{I}_{\rm R} = \frac{T}{n - (n-1)T} \overrightarrow{I}_{\rm L} \quad \Rightarrow \quad T_{\rm all} = \frac{T}{n - (n-1)T}.$$
(2.86)

To obtain the quantitative nature of such system we tested the total transmitivity on the single barrier transmitivity at some fixed n (for long wires the n can easily be 10) revealing rather strong decrease (for  $T = 0.91 T_{all}$  is 0.5 from Fig. 2.8a) suggesting that in such sequence of segments the electrons will need to struggle to pass, even if the tunneling through individual barriers isn't strongly suppressed. Moreover also the number of segments reduces the total transmitivity for some fixed T. It turns out that for T = 0.95 the total fraction of electrons that travel through falls to ~ 60% (Fig. 2.8b).



Figure 2.8: a) The transmitivity  $T_{\rm all}$  decreases rapidly with decreasing T (n = 10). b) The transmitivity  $T_{\rm all}$  decreases also for increasing n; the T was set to 0.95.

Since this model ignores the basic quantum mechanical nature of electrons it becomes potentially useful if the measured systems are big enough to treat electrons as free projectiles without any interaction between each other. This demonstration shows that even though the ballistic transport governs the segments the barriers could decrease the conductance of a systems profoundly. Thus at this point we can already expect that the transport depends strongly on the system's structure or actually on the inhomogeneities throughout the system even at low non-uniformities. In the following subsections we discuss several possibilities of non-uniform structures with the emphasis on the transport properties through it.

# 2.4 Electron transport in quantum dots

Another interesting possibility for transport through confined structures is the case of a small island (quantum dot) weakly bound to the surrounding reservoirs. We introduced the basic description of such a dot in terms of quantum eigenstates in one of the previous sections 2.1.1 and here we deal with the transport through such a system coupled to external source, drain and the gate electrode. In general the island can be viewed locally or globally when connected to an external power source. In the first case the system is treated without the interaction to the rest of the world whereas in the latter one the charging energy rebalance is provided by external power supply widening the transport rules. In the first part of this section we discuss the basic Coulomb blockade phenomenon, followed by the environmental influence on the system's transport behavior.

# 2.4.1 Coulomb blockade oscillations

Now we discuss basic transport properties through a quantum dot, separated by a thin layer of insulator from the bulk reservoirs, weakly coupled via tunneling and unspoiled in terms of the state separation on the dot itself. This model can be applied in the case of thin nanowires, weakly connected to the guides (Fig. 2.9a) or in the case of special wire segmentation (2.9b), where an insulated region is formed during the synthesis growth, due to random constrictions and structural inhomogeneities in the middle of the compound.



Figure 2.9: a) A nanowire is weakly coupled to the reservoirs so that the electrons can hop on and off the wire-island only via tunneling. b) An insulated island can be formed in the middle of the wire due to physical constrictions (the bottom scheme) or due to structural inhomogeneities (the top scheme) creating a quantum dot.

Theoretically we describe the system as a series of source reservoir, an island with discrete ladder states (quantum dot with the typical energy gaps  $\Delta E$  between the states) and drain reservoir ([8] chapter 5). To investigate this assembly a gate electrode is introduced in order to influence the states on the dot (Fig. 2.11). For basic exploration we confine ourselves to the low temperature regime, where the thermic energy doesn't excite the electrons on the quantum dots to higher levels, thus  $\Delta E \gg k_B T$ , where  $\Delta E$  denotes level spacing of the dot state ladder. Our interest lies in the transport properties, more specifically in the different conducting and non-conducting regimes. A simplified view,



Figure 2.10: A quantum dot is connected to source and drain reservoirs. A gate electrode is placed in the vicinity to influence the position of the states in the dot.

that ignores the charging effects<sup>6</sup>, suggests that the transport through the system exhibits resonant behavior - the transport is possible only when a level in the dot's ladder aligns with the Fermi level of the source reservoir, controlled by source voltage. This simplified view depicted in Fig. 2.11 introduces the basic idea since real experiments become hard to illustrate as we show later. Continuously lifting the source voltage (gate voltage re-

<sup>&</sup>lt;sup>6</sup>Also spin and electron interactions are disregarded.



Figure 2.11: The source voltage is altered with constant gate voltage. a) The  $E_{FS}$  of the source lies between quantum dot states with the level spacing  $\Delta$  - the transport is prohibited. b) The  $E_{FS}$  is aligned to an empty state in the dot allowing an electron to tunnel on the dot and finally of it to the drain reservoir - transport is enabled. c) The current increases in steps as the voltage increases, enabling higher levels to conduct.



Figure 2.12: Zero bias conductance is monitored as gate voltage is altered. a) The  $E_{FS}$  of the source lies between quantum dot states - the transport is prohibited. b) The  $E_{FS}$  is aligned to an empty state in the dot, allowing an electron to tunnel on the dot and of it to the drain reservoir - transport is enabled. c) The current vs. voltage conductance peaks. Transport is allowed when empty dot states align with the Fermi energy.

mains constant), while disregarding the charging, the current would follow a step-like curve (known also as the Coulomb staircase) increasing according to the single level conductance with Landauer quantum (see section 2.2) disregarding the spin  $G_0 = \frac{e^2}{h} = 3.875 \cdot 10^{-5}$  S, when higher unoccupied levels start to conduct (Fig. 2.11c). Another way to observe such a system is to monitor zero bias conductance G as the gate voltage changes (Fig. 2.12).
Here the states in the ladder pass the Fermi level of the reservoir only conducting at discrete points when they perfectly align. Current vs. gate voltage plot shows conductance peaks when a dot level aligns to Fermi energy (Fig. 2.12c). This simplified model should be understood as the underlying idea for the transport conditions under different investigation approaches. In this spirit we first introduce charging energy, which is actually the driving force of quantum dot conductivity phenomena, and in the end we conclude with the treatment of realistic measurement conditions that reveal the more complex nature of quantum dot transport.

One way to determine the positions of the peaks, when charging energy is included, is through the equilibrium properties of electrons on the quantum dot in respect to the reservoirs. The grand canonical distribution gives us the probability to find N electrons on the quantum dot in equilibrium with the reservoirs:

$$P(N) \propto \exp(-\frac{1}{k_B T} [F(N) - NE_F]), \qquad (2.87)$$

where F(N) denotes free energy, T the temperature and N the number of electrons on the dot. The transport will be governed by the N that maximizes the probability. In fact, since our interest lies in the close-to-zero temperature regime, only one N gives non-zero P(N), namely the one that minimizes the thermodynamic potential  $\Omega(N) = F(N) - NE_F$ . When speaking about the transport it can be shown [7] that  $G \to 0$  when  $T \to 0$ . Moreover the transport is possible only when P(N) and P(N + 1) are non-zero for the same N. With other words, the dot is found in the thermodynamic equilibrium with respect to the reservoirs for N and N + 1 at the same time, thus allowing an electron to tunnel on (N + 1) and again off the dot (N) creating current through the system via dot occupancy  $N \to N + 1 \to N \to \dots$ . Formally speaking we have coexistence of two global minima<sup>7</sup> in the thermodynamic potential  $\Omega(N)$  for N and N + 1 from where we get the condition relation for both free energies at N and N + 1:

$$\Omega(N+1) = \Omega(N) \rightarrow F(N+1) - F(N) = E_F.$$
(2.88)

This convenient relation for conductance peaks demands the determination of the free energy for the system. We can write it as a sum of charging energy U(N) and single electron levels  $E_p$ :

$$F(N) = U(N) + \sum_{p=1}^{N} E_p,$$
(2.89)

where the charge imbalance between the reservoirs and the dot is taken into account macroscopically through the potential difference between the dot and the reservoir including the contribution of nearby charges and particularly of the gate electrode. The dot is capacitively coupled to the reservoirs and the gate electrodes with the macroscopic capacitance<sup>8</sup> C. The potential difference for charge Q reads classically as a sum of charge

 $<sup>^{7}\</sup>mathrm{In}$  general there could be also more minima, but we confine ourselves to the most probable case of two minima.

<sup>&</sup>lt;sup>8</sup>We assume that the capacitance remains constant in respect to N.

difference potential and the external field (gate electrode):

$$\phi(Q) = \frac{Q}{C} + \phi_{\text{ext}}.$$
(2.90)

U(N) is now the integral of the potential (2.90) over the charge<sup>9</sup>:

$$U(N) = \int_0^{-Ne} \phi(Q') dQ' = \frac{(Ne)^2}{2C} - Ne\phi_{\text{ext}}.$$
 (2.91)

Inserting (2.89) in (2.88) and relabeling N by N - 1 we get:

$$E_N + U(N) - U(N-1) = E_F, (2.92)$$

that gives with (2.91) the final condition for conductance peaks:

$$E_N + \left(N - \frac{1}{2}\right)\frac{e^2}{C} = E_F + e\phi_{ext}.$$
 (2.93)

One way of analyzing this condition is to take the bare ladder with N-1 electrons and count the charging energy of one electron tunneling onto the dot with the lowest free state at  $E_N$ . We write this as:

$$E_N + \frac{e^2}{2C} = E_F + e\phi_{\text{ext}}(N-1), \qquad (2.94)$$

again with N referring to the lowest unoccupied level. In other words: the lowest unoccupied state has to be positioned one half of the charging energy below the  $E_F$  level (Fig. 2.13a). As the electron jumps onto the dot, the equality now includes the newly occupied state at  $E_N$ . The number of electron is now of course  $N - 1 \rightarrow N$  yielding:

$$E_N - \frac{e^2}{2C} = E_F + e\phi_{\text{ext}}(N),$$
 (2.95)

now with N referring to the highest occupied state. In words: the highest occupied level has to be placed one half of the charging energy above the  $E_F$  level (Fig. 2.13b). Afterwards the electron tunnels from the dot and the situation resets to initial configuration (Fig. 2.13c). Let us summarize the tunneling of an electron through the dot in a compact form: an electron tunnels onto the unoccupied state of the dot that is positioned  $e^2/2C$ below the  $E_F$ , adds the charging energy  $(e^2/C)$  to the dot and thus lifts the newly occupied level to  $e^2/2C$  above the  $E_F$  before finally tunneling to the other side resetting the potentials to initial situation.

<sup>&</sup>lt;sup>9</sup> In literature a continuous "externally induced charge"  $Q_{\text{ext}} \equiv C\phi_{\text{ext}}$  is often defined next to quantized Q as a purely theoretical description. Now the potential reads:  $U(N) = \frac{(Ne - Q_{\text{ext}})^2}{2C} + \text{constant.}$ 



Figure 2.13: a) In order for an electron to tunnel onto the dot the lowest unoccupied state has to be  $e^2/2C$  below the  $E_F$  surface. b) Electron adds the charging energy  $e^2/C$  and the newly occupied level is now  $e^2/2C$  above the  $E_F$  surface. c) The final electron tunneling into the drain resets the system into initial situation.

The left side of (2.93) can be understood also as renormalized energy levels  $E_N^*$  with lifted spin degeneracy by the charging energy  $e^2/C$  that is added to level spacing  $\Delta^* = \Delta E + e^2/C$ ; the redefined levels are depicted on Fig. 2.14. In this sense we can also implement the charging into the simplified picture from Fig. 2.11 or Fig. 2.12, setting the period  $\Delta/e$  to e/C.



Figure 2.14: a) Bare quantum dot ladder is b) renormalized when charging energy is included. The scheme depicts the case where  $e^2/C \approx 2\langle \Delta E \rangle$ , where  $\langle \rangle$  denotes the average.

In experiments the dot is capacitively coupled in form of junctions to source, drain and gate electrode and requires additional treatment [9]. Fig. 2.15 depicts such a system with  $V_1$  being the voltage across the source junction  $(C_1)$ ,  $V_2$  across the drain junction and  $V_g$   $(C_2)$  the voltage on the gate, measured from drain electrode potential. For the moment we observe the case without the gate electrode and treat the system classically, comparing the Helmholtz free energy (the difference between the total energy and the work done by power sources) for electron tunneling through the junctions with rate  $n_1$ and  $n_2$  trough the first and second junction respectively. Basic electronics gives us the



Figure 2.15: Double junction circuit with gate. The electrons are allowed to tunnel through capacitors from source and towards drain, whereas the gate voltage induces continuous additional charge on the island.

charge on the junctions<sup>10</sup>:

$$q_1 = C_1 V_1, \ q_2 = C_2 V_2, \ q = q_2 - q_1 + q_0 = -ne + q_0,$$
 (2.96)

where the  $n = n_1 - n_2$  denotes the net number of electrons and  $q_0$  the background charge<sup>11</sup> on the island. Using the voltage drop equality:

$$V_S = V_1 + V_2, (2.97)$$

together with (2.96) we get:

$$V_1 = \frac{C_2 V_S + ne - q_0}{C_{\Sigma}}, \qquad V_2 = \frac{C_1 V_S - ne + q_0}{C_{\Sigma}}, \qquad \text{where} \qquad C_{\Sigma} = C_1 + C_2. \quad (2.98)$$

If we now consider  $n_1$  electrons to tunnel through the first junction on the island we observe according to (2.98) the voltage  $V_1$  increase by  $n_1 e/C_{\Sigma}$  consequently resulting as a voltage drop on  $V_2$  for  $-n_1 e/C_{\Sigma}$  due to (2.97) that has to be provided from the external power. Similar result is obtained for  $n_2$  electron tunneling through the second junction on the island and the external work  $W_{1,2}$  for both cases reads as:

$$W_1 = \frac{n_1 e V_S C_2}{C_{\Sigma}}$$
 and  $W_2 = \frac{n_2 e V_S C_1}{C_{\Sigma}}$ . (2.99)

Total energy is of course the sum of the capacitor energies in both junctions:

$$E_C = \frac{1}{2}C_1V_1^2 + \frac{1}{2}C_2V_2^2 = \frac{C_1C_2V_S^2 + (ne - q_0)^2}{2C_{\Sigma}}.$$
 (2.100)

<sup>&</sup>lt;sup>10</sup>The electron charge becomes  $e \to -e_0$  and e > 0.

<sup>&</sup>lt;sup>11</sup>The background charge is induced by stray capacitances and always present impurities on the island.

The free energy is a difference between (2.100) and (2.99):

$$F(n_1, n_2) = E_C - W = \frac{1}{C_{\Sigma}} \left( \frac{1}{2} \left( C_1 C_2 V_S^2 + (ne - q_0)^2 \right) - eV_S (C_1 n_2 + C_2 n_1) \right). \quad (2.101)$$

To get the conditions for an electron to tunnel onto the island and off it, we write the difference in free energies:

$$\Delta F^{\pm} = F(n_1 \pm 1, n_2) - F(n_1, n_2) = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \mp (C_2 V_S + ne - q_0) \right), \qquad (2.102)$$

$$\Delta F^{\pm} = F(n_1, n_2 \pm 1) - F(n_1, n_2) = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \mp (C_1 V_S - ne + q_0) \right).$$
(2.103)

The transport  $n_1 + 1$  and  $n_2 - 1$  from source to drain is possible if the difference in free energy falls below zero. For the case of n = 0 and  $q_0 = 0$  we get:

$$V_S > \frac{e}{2C_2}$$
 from (2.102) and  $V_S < -\frac{e}{2C_1}$  from (2.103). (2.104)

For symmetric junctions  $C_1 = C_2$  the condition reads in the compact form  $|V_S| > e/C_{\Sigma}$ .

If we want to include the gate, the (background) charge on the island has to be modified since the gate electrode additionally polarizes the dot:

$$q = -ne + q_0 + C_g(V_g - V_2)$$
 or  $q_0 \to q_0 + C_g(V_g - V_2).$  (2.105)

This addition transforms the voltages over the junctions from (2.98) into:

$$V_1 = \frac{(C_2 + C_g)V_S - C_gV_g + ne - q_0}{C_{\Sigma}}, \ V_2 = \frac{C_1V_S + C_gV_g - ne + q_0}{C_{\Sigma}},$$
(2.106)

where  $C_{\Sigma} = C_1 + C_2 + C_g$ . The energy differences from (2.102) and (2.103) become also gate voltage dependent and take the form:

$$\Delta F^{\pm} = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \mp \left( (C_2 + C_g) V_S - C_g V_g + ne - q_0 \right) \right), \qquad (2.107)$$

$$\Delta F^{\pm} = \frac{e}{C_{\Sigma}} \left( \frac{e}{2} \mp (C_1 V_S + C_g V_g - ne + q_0) \right).$$
(2.108)

The conductance conditions are the same as before and include lowering of the free energy and thus negative values of (2.107) and (2.108) to enable transport. We get a functional dependance for  $V_S$  and  $V_g$  in form of boundary lines with different slopes for tunneling through the first junction onto and through the second junction off the island. It reads:

$$V_S > \frac{C_g}{C_2 + C_g} V_g + \frac{e}{2(C_2 + C_g)} - \frac{ne}{C_2 + C_g}, \qquad (2.109)$$

$$V_S < -\frac{C_g}{C_1}V_g - \frac{e}{2(C_1)} + \frac{ne}{C_1}.$$
 (2.110)

This family of curves is usually depicted on  $V_S - V_g$  plot also known as the *Coulomb* diamonds. A scheme is shown on Fig. 2.16 for the case where  $C_1 = 30\% C_{\Sigma}$ . The white



Figure 2.16: A  $V_S$  vs. Vg plot for the family of the conduction conditions from (2.109) and (2.110). The white parallelograms denote the non-conducting regimes with corresponding number of electrons on the dot n, whereas their shaded complement stands for the conducting conditions. Two slopes  $k_1$  and  $k_2$  describe the linear boundaries of each n for tunneling onto the island through the first and off it through the second junction respectively, with coincidental zeros for same family with given n positioned at  $-e/2C_g + ne/C_g$ .

parallelograms are the regions where the transport gets suppressed, each off them carrying n electrons onto the dot ascending in integers from left to right. The shaded areas stand for the conductance regime according to (2.109) and (2.110). Also the zero-bias oscillations are present with the period  $e/C_g$  along with the other characteristic points (intersections A, B, T) and both slopes  $k_1$  and  $k_2$  from (2.109) and (2.110) respectively.

This rich result gives first clues that the transport in minute and disordered systems may yield a rich palette of possibilities, resulting as voltage regions of suppressed conduction. An isolated island can thus produce regions in parametric space that prohibits electrons to pass, which has to be taken into account when experiments for familiar systems are attempted. Unfortunately the story doesn't end here when real measurements are performed since one has to take into account also the realistic measurement equipment that places the measured system into an *environment* that affects the transport as well. In the following subsection we discuss this problem in detail.

#### 2.4.2 Environmental Coulomb blockade theory

In the previous subsection we discussed the transport properties from the transport blockade point of view. Even though obtaining the rich Coulomb diamond behavior demanded taking into account the environmental influence more closely, the dynamics of charge equilibrium reestablishment through the capacitive junctions still remained hidden. The treatment of the ultrasmall junction dynamics coupled to an external power circuit with finite impedance is know under the name *Environmental Coulomb blockade theory*. The theory's formalism is rather tedious and in most cases the final results aren't analytically solvable, often leaving the field for further theoretical exploration. For this reason only the basic steps are introduced, omitting the detailed derivations and giving only the core results.

An ultrasmall junction under investigation is composed of metal-insulator-metal series with finite tunneling rates  $\overrightarrow{\Gamma}$  and  $\overleftarrow{\Gamma}$  across it as depicted on Fig. 2.17a ([8] chapter 2). Such an element is embedded into an electric circuit with the impedance  $Z_{\omega}$  and a power source V (Fig. 2.17b).



Figure 2.17: a) Schematic drawing of a metal tunnel junction. The arrows indicate forward and backward tunneling through the barrier. b) An ultrasmall tunnel junction with capacitance C and tunneling resistance  $R_T$  coupled to a voltage source V via the external impedance  $Z_{\omega}$ .

The current vs. voltage characteristic is obtained as a difference between the charge tunnel rates in the opposite directions:

$$I(V) = e(\overrightarrow{\Gamma}(V) - \overleftarrow{\Gamma}(V)).$$
(2.111)

The Hamiltonian for the whole system includes the quasi particles in electrodes, the environmental part and the tunneling Hamiltonian:

$$H = \tilde{H}_{\rm qp} + H_{\rm env} + \tilde{H}_T. \tag{2.112}$$

The  $\tilde{H}_{qp}$  and the  $\tilde{H}_{T}$  include more convenient variables for phase difference  $\varphi$  and charge Q in the treatment:

$$\widetilde{\varphi}(t) = \varphi(t) - \frac{e}{\hbar}Vt \qquad (2.113)$$

and

$$\widetilde{Q} = Q - CV. \tag{2.114}$$

We can write them in form:

$$\widetilde{H}_{qp} = \sum_{k\sigma} (\epsilon_k + eV) c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{q\sigma} \epsilon_q c^{\dagger}_{q\sigma} c_{q\sigma} \qquad (2.115)$$

$$\widetilde{H}_{\rm T} = \sum_{kq\sigma} T_{kq} c_{q\sigma}^{\dagger} c_{k\sigma} e^{-\imath \widetilde{\varphi}} + H.c., \qquad (2.116)$$

where k and q denote the wave vectors with spin  $\sigma$  on the left and right electrode. In the (2.115) the sums correspond to the electrons over the energies  $\epsilon_k$  and  $\epsilon_q$  for the left and right one, respectively. In the (2.116) the term describes the annihilation of the electron with the wave vector k and spin  $\sigma$  in left and the creation of the electron with wave vector q and same spin on the right one. The  $T_{kq\sigma}$  denotes the matrix element for such left-to-right tunneling event.

If the tunneling resistance  $R_T$  is large compared to the natural resistance scale in terms of resistance quanta  $R_Q = h/e^2$  then the states in the electrodes mix weakly and the term  $\tilde{H}_T$  can be taken as a perturbation. Moreover if we assume that the charge equilibrium is established before tunneling (the time between two tunneling processes in larger than the charge relaxation) the tunneling rate from (2.111) can be obtained through the Fermi golden rule:

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | \tilde{H}_T | i \rangle \right|^2 \delta(E_i - E_f)$$
(2.117)

for tunneling from the initial state  $|i\rangle$  to final state  $|f\rangle$ . To obtain the matrix element they are written as a product of quasiparticle state and a charge state that becomes coupled to the environment (they are called the reservoir states):  $|i\rangle = |E\rangle|R\rangle$  and  $|f\rangle = |E'\rangle|R'\rangle$ . Now the factors in tunneling Hamiltonian act separately on quasiparticle space and on defined reservoir states and the matrix element reads:

$$\langle f|\widetilde{H}_T|i\rangle = \langle E'|H_T^{qp}|E\rangle\langle R'|e^{-i\widetilde{\varphi}}|R\rangle + \langle E'|H_T^{qp\dagger}|E\rangle\langle R'|e^{i\widetilde{\varphi}}|R\rangle, \qquad (2.118)$$

with:

$$\widetilde{H}_T^{qp\dagger} = \sum_{kq\sigma} T_{kq} c_{q\sigma}^{\dagger} c_{k\sigma}.$$
(2.119)

The total tunneling rate is a sum over all initial states weighted with the probability to find this states and over all final states. The expression to be evaluated now reads:

$$\vec{\Gamma}(V) = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} dE dE' \sum_{R,R'} |\langle E'|H_T^{qp}|E\rangle|^2 |\langle R'|e^{-i\tilde{\varphi}}|R\rangle|^2 \times P_{\beta}(E)P_{\beta}(R)\delta(E+eV+E_R-E'-E_R'). \quad (2.120)$$

Further derivation analyzes this expression in detail, finally presenting it in the form:

$$\overrightarrow{\Gamma}(V) = \frac{1}{e^2 R_T} \int_{-\infty}^{\infty} dE \frac{E}{1 - e^{-\beta E}} P(eV - E), \qquad (2.121)$$

where  $R_T$  gathers all the constants and denotes the tunneling resistance. The P(E) may be interpreted as the probability to exchange the energy between the tunneling electron and the environmental modes that can become excited in the resonances. Basically the tunneling electron excites environmental modes, that form according to the impedance and this is the core mechanism of environmental influence on the transport. Formally the P(E) is the Fourier transform of the phase-phase correlation function J(t):

$$P(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{J(t) + \frac{i}{\hbar}Et},$$
(2.122)

that is formally defined as:

$$J(t) = \langle [\widetilde{\varphi}(t) - \widetilde{\varphi}(0)] \widetilde{\varphi}(0) \rangle \tag{2.123}$$

and depends on the environmental impedance according to:

$$J(t) = 2 \int_{\infty}^{0} \frac{d\omega}{\omega} \frac{\operatorname{Re}Z_{t}(\omega)}{R_{Q}} \left\{ \operatorname{coth}\left(\frac{1}{2}\beta\hbar\omega\right) \left[\cos(\omega t) - 1\right] - \imath\sin(\omega t) \right\},$$
(2.124)

with the total impedance  $Z_t(\omega)$  calculated for the general case from the scheme 2.17b:

$$Z_t(\omega) = \frac{1}{\iota\omega C + Z^{-1}(\omega)}.$$
(2.125)

Now the current vs. voltage from (2.111) reforms into the key expression to determine the environmental impact on the transport properties:

$$I(V) = \frac{1}{eR_T} \left( 1 - e^{-\beta eV} \right) \int_{-\infty}^{\infty} dE \frac{E}{1 - e^{-\beta eV}} P(eV - E).$$
(2.126)

Several relations and functional properties help to utilize the results from (2.126) for different environmental cases:

$$\overleftarrow{\Gamma}(V) = \overrightarrow{\Gamma}(-V), \qquad (2.127)$$

$$P(-E) = e^{-\beta E} P(E), \qquad (2.128)$$

$$EP(E) = 2 \int_0^E dE' \frac{\operatorname{Re}\left[Z_t\left(\frac{E-E'}{\hbar}\right)\right]}{R_Q} P(E') \quad \text{for zero temperature.} \quad (2.129)$$

As mentioned in the introduction to this subsection the results often come in a nonanalytical form making it heavy to implement for realistic data comparison. Some special and limiting cases are soluble and we present some of them here, whereas for the others we present only qualitative description of numerically obtained hypothetical behavior for some sets of parameters. Low impedance environment In this case of vanishing impedance, where the impedance is effectively set to  $Z(\omega) = 0$  (the impedance is much lower than the conductance quantum  $R_Q$ ), formally speaking J(t) also vanishes yielding  $P(E) = \delta(E)$ . There is no mode excitement and the tunneling process remains elastic. The external voltage source keeps the voltage across the junction fixed at any time, immediately transferring the electron through the circuit after tunneling to restore the charge in the junction capacitor. Therefore the only work done is the eV that solely appears in the rate expression (2.121):

$$\overrightarrow{\Gamma}(V) = \frac{1}{e^2 R_T} \frac{eV}{1 - e^{-\beta eV}},$$
(2.130)

giving the current vs. voltage characteristic through (2.127) in Ohmic law form of voltagebiased tunnel junction:

$$I(V) = \frac{V}{R_T}.$$
(2.131)

In consequence the Coulomb gap can not be reached even at highest voltages.

**High impedance environment** In contrast to low impedance, high impedance environment allows the electron to easily excite the modes. It turns out that the spectral density is peaked at  $\omega = 0$ , making Ohmic damping, i.e.  $Z(\omega) = R$ , most suitable to consider this limit. The total impedance is given by  $R/(1 + (\omega RC)^2)$ , but takes the form  $(\pi/C)\delta(\omega)$  for the limit  $\omega \to 0$ . The correlation function J(t) gets the form:

$$J(t) = -\frac{\pi}{CR_Q} \left( \imath t + \frac{1}{\hbar\beta} t^2 \right), \qquad (2.132)$$

that gives P(E) from (2.122):

$$P(E) = \frac{1}{\sqrt{4\pi E_C kT}} e^{-\frac{(E-E_C)^2}{4E_C kT}},$$
(2.133)

where  $E_C$  denotes the transfer energy to the environment. In the low temperature limit  $kT \ll E_C$  the (2.133) simplifies to:

$$P(E) = \delta(E - E_C) \tag{2.134}$$

and the current vs. voltage characteristic can be obtained:

$$I(V) = \frac{eV - E_C}{eR_T} \chi(eV - E_C),$$
(2.135)

where  $\chi(E)$  is the step unit function. Since according to (2.134) a tunneling electron always transfers the energy  $E_C$  to the environment, tunneling becomes possible only if the energy eV at disposal exceeds  $E_C$ . Here we observe the Coulomb gap that corresponds to the charging energy similarly as in the isolated island case only that here the charging energy of the junction coupled to the environment causes the suppression of the transport. **Ohmic impedance** The case of finite and frequency-independent impedance  $Z_{\omega} = R$  is often understood under the term of environmental Coulomb blockade theory, since their results, even though in general analytically non-solvable, become in limiting terms most applicable when compared to measured data. We restrict ourselves to the case of zero temperature and consider the limits of low and high energies in P(E). For that we utilize the relation from (2.129) that is valid for zero temperature. To evaluate the integral the ratio between the real part of total impedance and the resistance quantum  $R_Q$  has to be obtained:

$$\frac{\operatorname{Re}Z_t}{R_Q} = \frac{1}{R_Q} \operatorname{Re}\left[\frac{1}{\imath\omega C + 1/R}\right] = \frac{1}{g} \frac{1}{1 + (\omega/\omega_R)^2},$$
(2.136)

where the dimensionless parameter g and the frequency  $\omega_R$  stand for:

$$g = \frac{R_Q}{R} \tag{2.137}$$

$$\omega_R = \frac{1}{RC} = \frac{g}{\pi} \frac{E_C}{\hbar}.$$
 (2.138)

The P(E) is obtained using the differential equation that arises after the derivation of (2.129):

$$\frac{dP(E)}{dE} = \left(\frac{2}{g} - 1\right)\frac{P(E)}{E},\tag{2.139}$$

with the solution:

$$P(E) \propto E^{\frac{2}{g}-1}$$
 (2.140)

for small positive energies. For negative energies P(E) vanishes since we consider the case of zero temperature. With a more detailed analysis of J(t) and P(E) one may determine also the normalization constant, completing the (2.140):

$$P(E) = \frac{e^{-2\gamma/g}}{\Gamma(2/g)} \frac{1}{E} \left[\frac{\pi}{g} \frac{E}{E_C}\right]^{\frac{2}{g}}, \qquad (2.141)$$

where  $\gamma$  denotes Euler constant<sup>12</sup>. To finally calculate the I(V) dependance the expression (2.126) gets simplified for zero temperature and assuming V > 0 into:

$$I(V) = \frac{1}{eR_T} \int_0^{eV} dE(eV - E)P(E), \qquad (2.142)$$

before inserting the (2.141) that yields:

$$I(V) = \frac{e^{-2\gamma/g}}{\Gamma(2+2/g)} \frac{V}{R_T} \left[ \frac{\pi}{g} \frac{e|V|}{E_C} \right]^{\frac{2}{g}} \quad \text{at} \quad T = 0 \quad \text{K} \quad \text{and} \quad V \to 0.$$
(2.143)

Now also the experimentally obtainable *zero-bias anomaly* of the conductance at low temperatures can be expressed:

$$\sigma(\text{low T, low V}) = \left(\frac{2}{g} + 1\right) \frac{e^{-2\gamma/g}}{\Gamma(2 + 2/g)} \frac{1}{R_T} \left[\frac{\pi}{g} \frac{e|V|}{E_C}\right]^{\frac{2}{g}}.$$
 (2.144)

 $^{12}\gamma = 0.577\ldots$ 

This is one of the main results of environmental Coulomb blockade theory and importantly remains valid in terms of power law behavior (the prefactor depends on the high-frequency behavior of the impedance) even for general environments as long as the zero-frequency impedance Z(0) stays finite (e.g.  $Z = \sqrt{L/C}$ ). The power exponent changes accordingly into:

$$\frac{2}{g} = \frac{2Z(0)}{R_Q}.$$
(2.145)

For high energies the P(E) in general behaves according to:

$$P(E) = \frac{2}{E} \frac{\operatorname{Re}Z_t(E/\hbar)}{R_Q},$$
(2.146)

that gives with (2.136):

$$P(E) = \frac{2g}{\pi^2} \frac{E_C^2}{E^3} \text{ for } E \to \infty.$$
(2.147)

Inserting it into (2.142) gives the current vs. voltage:

$$I(V) = \frac{1}{R_T} \left[ V - \frac{e}{2C} + \frac{g}{\pi^2} \frac{e^2}{4C^2} \frac{1}{V} \right] \quad \text{for} \quad V \to \infty.$$
 (2.148)

As expected for higher voltages the behavior approaches Ohm's law, with the shift in



Figure 2.18: Zero-temperature a) current-voltage characteristics for the Ohmic model and b) the derivative dI/dV that approaches the constant value  $1/R_T$  for high voltages at  $g = \infty, 20, 2, 0.2$  and 0 from top to bottom.

charging energy. The numerical investigation from Fig. 2.18 depicts the situations for different values of parameter g (or resistance R). The curves show the transition from low- to high impedance environment demonstrating that quantum fluctuations destroy the Coulomb blockade. As a criterion for the occurrence of the Coulomb blockade one may require that for vanishing voltages the curvature for the current-voltage characteristic goes to zero or current derivative as a function of voltage that starts at some initial value

(close to zero for low g values) and approaches a constant value for high voltages (Fig. 2.18b). One can see the parameter g as a function of temperature since the environmental resistance could be connected to the coupling between the system and the current leads. In this case the Fig. 2.18 could indicate behavior for different temperatures, but with addition, that the high voltage slopes (and the asymptotic values for the derivative) could also change with temperature since the  $R_T$  gets affected as well.

# 2.5 Variable range hopping

Until now systems with rather specific scattering sites have been introduced that resulted in specific transport characteristics based on the nature of electron interaction with the scattering entity (barriers from 2.3, quantum dot from 2.4). A more general approach [12] on the other hand deals with a non-crystalline system as a whole, treating imperfections as possible electron traps acting as localization places overlooking its local nature (whether its an impurity, local defect, and alien island, a lattice deformation). If we take a look at the possibilities regarding scattering we get three scenarios observing the uncertainty  $\Delta k$ compared to k:

- 1.  $\Delta k/k \ll 1$  scattering is weak and surfaces of constant energy are spherical (e.g. liquid metals).
- 2.  $\Delta k/k \sim 1$  scattering is strong and k is not a good quantum number for describing eigenstates and the concept of Fermi surface (for metals) is no longer valid.
- 3. Yet stronger interaction yields a localized wavefunction  $\psi_E$  at some given energy E.

We are particularly interested in the last case where strong scattering suppresses the electron transport. Here the wavefunction  $\psi_E$  with quantized energy is confined to a small region of space, falling off exponentially with distance<sup>13</sup> as  $\exp(-\alpha R)$ . What is surprising is that even though one can have a finite and continuous density of states N(E), all states are localized, although there can be strong overlap between the wavefunctions of neighboring states. Moreover if the states are filled up to a limiting Fermi energy in the range where states are localized, the conductivity ( $\sigma(E)$ ) vanishes as the temperature tends to zero. This is very different from the crystals where the insulating behavior occurs when the Fermi energy lies in the region with vanishing N(E). In other words the non-crystalline materials can become insulators even with the finite value of  $N(E_F)$ . The materials that exhibit such a property are called *Fermi glasses*. The statement of complete suppression conductivity at zero temperature can be manifested in vanishing of the total wavefunction contribution to conductivity at given E obtained as configurational average:

$$\langle \sigma_E \rangle.$$
 (2.149)

In fact this criterium is used as satisfactory condition of localization for wavefunctions of energy E. To get  $\sigma_E$ , commonly an electromagnetic wave  $F \cos \omega t$  is used to get  $\sigma_E(\omega)$  and

 $<sup>^{13}</sup>$ This localization is known as the Anderson localization. For consistency with the literature we use the symbol R for the distance.

then by limiting the  $\omega$  towards zero the  $\sigma_E(0)$  can be deduced. The approach is convenient because we can grab the problem with Fermi golden rule and write for some  $\psi_E(x, y, z)$ in a volume  $\Omega$  the probability per unit of time that an electron makes a transition for a state with energy E to any of the states with energy  $E + \hbar \omega$ :

$$\frac{1}{4}e^2F^2\frac{2\pi}{\hbar}|\chi_{E+\hbar,E}|^2_{\text{avg}}\Omega N(E+\hbar\omega).$$
(2.150)

The matrix elements are averaged over all states with the energy near  $E' = E + \hbar \omega$  and are obtained by:

$$\chi_{E+\hbar\omega,E} = \int \psi_{E'}^* x(\psi_E) d^3x. \qquad (2.151)$$

By redefining the matrix element from (2.151) to

$$\chi_{E+\hbar\omega,E} = \frac{\hbar}{m\omega} \int \psi_{E+\hbar\omega}^* \frac{\partial}{\partial x} (\psi_E) d^3 x = \frac{\hbar}{m\omega} D_{E+\hbar,E}$$
(2.152)

and by defining the conductivity  $\sigma_E(\omega)$  so that  $\sigma_E(\omega)\frac{1}{2}F^2$  is the mean rate loss of energy per unit volume we integrate the conductivity over all energies multiplied by the number of occupied states per unit volume in the energy range dE and taking into account the probability of (un)occupied states for up- and downward jumps along with the spin factor 2, we get the expression:

$$\sigma_E(\omega) = \frac{2\pi e^2 \hbar^2 \Omega}{m^2 \omega} \int [f(E)\{1 - f(E + \hbar\omega)\} - f(E + \hbar\omega)\{1 - f(E)\}] |D|^2_{\text{avg}} N(E) N(E + \hbar\omega) dE. \qquad (2.153)$$

After limiting the expression at zero temperature for  $\omega \to 0$  the final result known also as Kubo-Greenwood formula arises:

$$\sigma_E(0) = \frac{2\pi e^2 \hbar^3 \Omega}{m^2} |D_E|^2_{\text{avg}} \{N(E)\}^2, \qquad (2.154)$$

with

$$D_E = \int \psi_{E'}^* \frac{\partial}{\partial x} (\psi_E) d^3x \quad (E = E').$$
(2.155)

Again the avg represents an average over all states E and all states E' such that E = E', so that at T = 0 the conductivity  $\sigma(0)$  is given by:

$$\sigma(0) = \{\sigma(0)\}_{E=E_F}.$$
(2.156)

This fundamental result is the base for other theories but it will not be the core of our discussion. Nevertheless the formula yields zero conductivity for the localized states since all the functions  $D_E$  vanish because  $\int \psi_{E'}^* \frac{\partial}{\partial x} (\psi_E) d^3 x$  is zero and the overlap between two localized functions  $\psi_1, \psi_2$  with the same energy is impossible. The reason for that is immediate separation of hypothetical overlapping states in the two linear combinations of the form  $A_1\psi_1 + A_2\psi_2$  and  $B_1\psi_1 + B_2\psi_2$ .



Figure 2.19: a) Potential wells for a crystalline lattice with corresponding energy band of width B. b) Crystalline lattice is randomly altered within  $V_0$  to create a non-crystalline lattice - Anderson lattice.

The localized states are usually described in the Anderson model where crystalline potential wells separated by a with band-width B (Fig. 2.19a) are randomly modified within the spread of energies  $V_0$  to create a non-uniform potential (Fig. 2.19b).

Using the tight-binding approximation, many studies have been made to observe the transition between crystalline and non-crystalline structure in terms of functions becoming localized. The Anderson criterion uses the ratio  $V_0/B$  as the limit that makes the states localized together with the coordination number z that is connected to<sup>14</sup> B. We can say that this parameter describes the non-crystallinity of the system transforming a crystal into a random lattice. First calculations proposed the value 5.5 for the coordination 6 but further calculations tend to lower this value. What is important from our point of view is the result for one-dimensional systems that predicts all states to be localized. The more general case deals with situations in which the states are non-localized in one range of energies and localized in another. We also believe that this is most likely the case for a realistic system such as our own, quasi-onedimensional objects. Also the theoreticians explored the phenomenon first proving that the localized and non-localized states (when the Anderson criterion is not satisfied) cannot coexist for a given configuration, in fact they proved the existence of the critical energy  $E_C$  that separates non-localized and localized states (Fig. 2.20a). They discovered that localized states are gathered near the extremities of the energy band without any discontinuity in N(E) nor in any of its derivations.  $E_C$  is also known as the *mobility edge*. The position of this edge regarding the Anderson ratio was of great interest since the band structure and the basic properties depend on it. A schematic depiction in Fig. 2.20b shows that  $E_C$  lies (measured from the middle of the band) on the limit of the band for  $V_0 = 0$  - perfect crystalline structure, then the band broadens and the edge moves outwards, reaches its peak and finally falls in the middle of the band after overpassing the Anderson criterion (in this case  $V_0/B = 2$ ) entering fully

<sup>&</sup>lt;sup>14</sup>In tight binding approximation B = 2zI where I denotes the transfer integral.

localized case of non-crystalline lattice.



Figure 2.20: a) Density of states in the Anderson model where the non-localized states are in the center of the band, separated by  $E_C$  and  $E'_C$  from the localized ones near the band extremities. b) The plot of  $E_C$  against  $V_0/B$  measured from the middle of band.

If the Fermi energy  $E_F$  lies within localized states the system resembles a semiconductor or better, a doped semiconductor where a gap is formed between the filled states (valence band for pure semiconductor or states of impurities) and the conductive continuum band. The conductivity can now be written in the same form as for the semiconductor by replacing the  $E_g$  with the  $E_C - E_F$ :

$$\sigma(0) = \sigma_{\min} e^{\frac{E_C - E_F}{kT}},\tag{2.157}$$

with  $\sigma_{\min}$  denoting the the conductivity of continuum band. This form of conduction is predominant at higher temperatures or when  $E_F$  lies close to  $E_C$ . Moreover if in the system of Fermi glass type the Fermi energy at zero temperature can move from below to above  $E_C$  (e.g. the change in composition/disorder of the system) there should be a sharp change in the DC conductivity from zero to a finite value as schematically depicted on Fig. 2.21a. Such a change is called an *Anderson transition*. Another theoretical investigation involves the temperature dependance of resistivity as a function of Anderson ratio  $V_0/B$ . Not surprisingly when the  $E_F$  upon the  $V_0/B$  change passes the  $E_C$  into the localized states the gap opens and conductivity follows the law from (2.157)<sup>15</sup> as schematically depicted on Fig. 2.21b.

The second conductivity mechanism is called *thermally activated hopping conduction* and includes electrons close to the  $E_F$ . As illustrated on Fig. 2.22 the conduction rate is determined by the hopping of an electron from the state A below the  $E_F$  to one above B. The probability p per unit of time that this occurs is determined by three factors:

a) the Boltzman factor  $e^{-W/kT}$ , where W denotes the difference between the two states,

<sup>&</sup>lt;sup>15</sup>Here the pre-factor is taken to be constant towards temperature.



Figure 2.21: a)The D.C. conductivity  $\sigma_E$  as a function of E. b) The plot of resistivity  $\rho$  against T for values of  $V_0/B$  increasing from curves 1 to 4, evoking the conduction of the Fermi glass by energy excitations above  $E_C$ . Curve 2 shows the value of  $\rho$  for  $E_F$  at  $E_C$  so that  $1/\rho = \sigma_{\min}$ .

- b) a factor  $\nu_{\rm ph}$  depending on the phonon spectrum,
- c) a factor  $e^{-2\alpha R}$  containing the overlap of wavefunctions<sup>16</sup>,

giving the expression:

$$p = \nu_{\rm ph} e^{-2\alpha R - \frac{W}{kT}}.$$
 (2.158)

In the external field F and at finite temperature T the current j can be obtained by multiplying the hopping probability with the number of electrons at Fermi energy  $2N(E_F)kT$ followed by charge e, hopping distance R and finally taking into account the possibility of hopping in two directions regarding the field:

$$j = 2eRkTN(E_F)\nu_{\rm ph}e^{-2\alpha R}e^{-\frac{W\pm eRF}{kT}} = 2eRkTN(E_F)\nu_{\rm ph}e^{-2\alpha R-\frac{W}{kT}}\sinh\left(-\frac{eRF}{kT}\right).$$
(2.159)

This is the most general result that is valid also for higher fields and temperatures. In weaker fields,  $eRF \ll kT$  the expression can be approximated and the conductivity gets the form:

$$\sigma = \frac{j}{F} = 2e^2 R^2 N(E_F) \nu_{\rm ph} e^{-2\alpha R - \frac{W}{kT}}.$$
(2.160)

For low temperatures the hopping distance R increases and the conductivity expression reforms. We need to calculate the maximum hopping probability knowing the activation energy W for the states in the range R (for 3D):

$$W = \frac{3}{4\pi R^3 N(E_F)},$$
(2.161)

<sup>&</sup>lt;sup>16</sup>This is called "nearest neighbor" or "Miller - Abrahams" hopping.



Figure 2.22: The mechanism of hopping conduction. Two hops are shown from an occupied state A to B and from B to C.

and taking into account the average hopping distance  $\overline{R}$ :

$$\overline{R} = \frac{\int^{R} r^{3} dr}{\int^{R} r^{2} dr} = \frac{3R}{4}.$$
(2.162)

The hopping probability (2.158) using  $\overline{R}$  instead of R has maximum when<sup>17</sup>:

$$\frac{3}{2}\alpha = \frac{9}{4\pi R^4 N(E_F)kT},$$
(2.163)

giving the optimum value for R:

$$R = \frac{3^{1/4}}{\{2\pi\alpha N(E_F)kT\}^{1/4}}.$$
(2.164)

Now the probability (2.158) reads as:

$$p = \nu_{\rm ph} e^{-\frac{B}{T^{1/4}}},\tag{2.165}$$

where B equals:

$$B = B_0 \left\{ \frac{\alpha^3}{kN(E_F)} \right\}^{1/4} \text{ and } B_0 = 2 \left( \frac{3}{2\pi} \right)^{1/4}.$$
 (2.166)

The conductivity (2.160) is therefore:

$$\sigma = 2e^2 \bar{R}^2 N(E_F) \nu_{\rm ph} e^{-\frac{B}{T^{1/4}}} = \frac{9}{8} e^2 R^2 N(E_F) \nu_{\rm ph} e^{-\frac{B}{T^{1/4}}}.$$
 (2.167)

Other treatments give similar results with the difference of numerical pre-factor  $B_0$  that can vary upon the method used.

<sup>&</sup>lt;sup>17</sup>Assuming that  $\nu_{\rm ph}$  varies little with R and T.

The same derivation can be performed also for two and one dimension, revealing the same behavior as (2.167) thus following general law, in theory often written in form:

$$\sigma = A e^{-\frac{B}{T^{\lambda}}},\tag{2.168}$$

with adequate constants A, B and exponent  $\lambda$  for each dimension. We gather the results in table 2.4. Perhaps a more convenient form of (2.168) from an experimental point of

dimension	$A[e^2 R^2 N(E_F)\nu_{\rm ph}]$	В	$B_0$	$T_0$	λ
1	$\frac{1}{2}$	$B_0 \left\{ \frac{\alpha}{kN(E_F)} \right\}^{1/2}$	$\sqrt{2}$	$\frac{2\alpha}{kN(E_F)}$	$\frac{1}{2}$
2	$\frac{8}{3}$	$B_0 \left\{ \frac{\alpha^2}{kN(E_F)} \right\}^{1/3}$	$\left(\frac{3}{\pi}\right)^{1/3}$	$\frac{3\alpha^2}{\pi k N(E_F)}$	$\frac{1}{3}$
3	$\frac{9}{8}$	$B_0 \left\{ \frac{\alpha^3}{kN(E_F)} \right\}^{1/4}$	$2\left(\frac{3}{2\pi}\right)^{1/4}$	$\frac{24\alpha^3}{\pi k N(E_F)}$	$\frac{1}{4}$

Table 2.4: The constants of (2.168) and (2.169) for 1D, 2D and 3D.

view would be:

$$\sigma = A e^{-\left(\frac{T_0}{T}\right)^{\lambda}},\tag{2.169}$$

with  $T_0$  also in the table 2.4.

More recent work observing closely [31] the impurity distances and the effects of strongly anisotropic screening of the Coulomb potential yields yet richer possibilities for conductivity. The same general conductivity temperature dependance has been proposed but with additional possibilities taking into account also different cases of the density of states that arise due to 3D Coulomb interactions. The main result has the same form as (2.169):

$$\sigma = \sigma_0 e^{-\left(\frac{T_{\text{VRH}}}{T}\right)^{\lambda}} \quad \text{and} \quad \lambda = \frac{\mu+1}{\mu+d+1}, \tag{2.170}$$

where  $\mu$  denotes the power-law exponent in the density of states  $N(E) \propto E^{\mu}$  and d the hopping dimension. The values are gathered in table 2.5.

dimension	N(E) = constant	$N(E) \propto  E $	$N(E) \propto E^2$
1	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{3}{4}$
2	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{3}{5}$
3	$\frac{1}{4}$	$\frac{2}{5}$	$\frac{1}{2}$

Table 2.5: The exponents  $\lambda$  from (2.170).

Variable range hopping appears to be applicable for systems with randomly distributed scattering places, covering all dimensions making the theory useful even in the nanoworld where the control over structural homogeneity is very limited. If this issue doesn't play a major role for more regular structures (such as carbon nanotubes) the wide palette of familiar structures may cause the production of very disordered compounds that are more related to non-crystalline materials than to crystalline structures in terms of long range symmetry.

# 2.6 Luttinger liquid

Strongly one-dimensional systems often exhibit different physics compared to three-dimensional, bulk material. We pointed out in the subsection 2.1.2 the spontaneous vanishing of long range order in 1D only due to space dimensionality. Similar peculiarities are observed when electronic states and excitations are explored implying very different behavior compared to the well known Fermi liquid that governs the macro world [6, 5]. Here the combination of the Pauli principle with low excitation energy (e.g.  $kT \ll E_F$ ) and the large phase space available in 3D, produces a *very dilute* gas of excitations where interactions are sufficiently harmless to preserve the 1:1 correspondence between the low-energy excitations of the free Fermi gas and those of an interacting electron liquid which are termed "quasi-particles". Roughly three basic elements can be stressed:

- 1. the elementary excitations are quasi-particles,
- 2. The transport is described by the Boltzmann equation,
- 3. The low-energy physics can be parameterized by a set of Landau parameters  $F_l^{s(a)}$ , which contain residual interaction effects in the angular momentum of charge and spin channels.

Basic properties arise from *weak correlations in the electron system even though the interactions can be very strong.* 

For 1D metal confinement this description breaks down. Due to Peierls effect some vertices, finite in Fermi liquid theory, diverge. Another argument states that when degenerate perturbation theory is applied to the coupling of the electron states at the Fermi points  $\pm k_F$ , it will split them and therefore remove the entire Fermi surface. Consequently free-electron-like metal will not be stable in 1D. We can say that the coupling of quasiparticles into collective excitations is large for 1D, no matter how small the interaction! The statement for 3D thus reads reversely for 1D: the correlations remain strong, even for weak interactions!. In other words, in 3D adding an electron or modestly exciting the liquid, doesn't affect the population and the electronic states whereas in 1D each disturbance causes the reformation of the system globally - a collective response governs basic properties.

1D metals are described as Luttinger liquids. A Luttinger liquid is a parametric onedimensional metal without quasi-particle excitations. This definition is based on the necessary condition for Luttinger liquid formation that the spin and charge excitations remain gapless, with dispersions  $\omega_{\nu} \approx v_{\nu}|q|$  ( $\nu$  denotes  $\rho$  for charge and  $\sigma$  for spin). Moreover the charge and spin modes (holons and spinons) possess different excitation energies with  $v_{\rho} \neq v_{\sigma}$  that leads to the separation of charge and spin of an electron added to the Fermi sea, in space-time, or  $q - \omega$  space, prohibiting quasi-particle excitations. Such system is now governed by power-law correlations with scaling relations between the exponents parameterized by coupling constants  $K_{\nu}$ , an equivalent to Landau parameters in Fermi liquids. Similarly as before basic elements describing the nature of Luttinger liquid can be summarized:

- 1. the excitations are not quasi-particles but collective excitations
- 2. charge and spin excitations (holons and spinons) remain gapless,
- 3. electron-electron interactions make  $v_{\rho} \neq v_{\sigma}$  leading to charge-spin separation thus prohibiting quasi-particle excitations,
- 4. two parameters  $K_{\nu}$  (the equivalent for Landau parameters in Fermi liquid theory) and  $v_{\nu}$  completely describe the physics of Luttinger liquid.

Due to bosonic nature of spinons and holons the standard approach for describing Luttinger liquid includes bosonization. The bosons are obtained as a linear combination of stable particle-hole excitations in the  $q \rightarrow 0$  regime, where the range of allowed excitations shrinks to a one-parameter spectrum  $\omega_{nu} \approx v_{\nu}|q|$  (Fig. 2.23). In addition low-energy particle-hole pairs with momenta between 0 and  $2k_F$  are not allowed. The route leads



Figure 2.23: a) Particle-hole excitations in 1D. b) The spectrum of allowed states has no low-energy states with  $0 \le |q| \le 2k_F$ .

through the Hilbert space of states and includes utilization of bilinear forms in bosons for free fermions, describing the *excitations*. We just write the general form of the Hamiltonian but we don't follow the derivations any further:

$$H = \sum_{\nu = \rho, \sigma} \sum_{q} v_{\nu} |q| \left( b_{\nu, q} b_{\nu, q}^{\dagger} + \frac{1}{2} \right), \qquad (2.171)$$

where  $v_{\nu} = v_F$ . Theoreticians were dealing also with the calculations of basic charge transport properties and via the mentioned bosonization they obtained the result [3]<sup>18</sup>:

$$I = I_0 T^{1+\alpha} \sinh\left(\frac{eV}{2kT}\right) \left|\Gamma\left(1 + \frac{\alpha}{2} + i\frac{eV}{2\pi kT}\right)\right|^2, \qquad (2.172)$$

where  $\alpha$  depended on the Luttinger parameter  $g = v_F/v_\rho$ . Since experiments inevitably included macroscopic leads, the results include also the charge transfer from Fermi liquid to Luttinger liquid (FL-LL) and also realistic cases of impurities inside of wires with adequate Luttinger liquid - Luttinger liquid connections (LL-LL). Both cases give different  $\alpha(g)$  dependence:

$$\alpha_{\text{LL-LL}} = (g^{-1} - 1)/4,$$
  

$$\alpha_{\text{FL-LL}} = (g + g^{-1} - 2)/8.$$
(2.173)

In realistic cases g proves to be small and the exponents appear to be connected via  $\alpha_{\text{LL-LL}} = 2\alpha_{\text{FL-LL}}$ . From the experimental point of view a closer inspection of the curve (2.172) is needed to successfully extract the parameters. The basic characteristics emerge:

1. all IV curves for different temperatures collapse to a single curve with typical knee when  $I/T^{\alpha+1}$  is plotted against eV/kT (Fig. 2.24),



Figure 2.24: The collapsed curve with typical knee emerges when  $I/T^{\alpha+1}$  is plotted against eV/kT.

- 2. at low temperatures the LL-LL junctions become most resistive governing the conduction power-law in the low-voltage regime as  $G \propto T^{\alpha_{\text{LL-LL}}}$ ,
- 3. at high voltages the FL-LL junctions dominate and  $I \propto V^{\alpha_{\text{FL-FL}}+1}$ .

<sup>&</sup>lt;sup>18</sup>In literature one may find different manifestations of the expression, sometimes even mistyped. The correct formulation includes in the imaginary part of the Gamma function  $\pi$  also in the fraction, otherwise the curve exhibits very different behavior.

Often [10, 11] the exponents are renamed,  $\alpha_{\text{LL-LL}}$  to simply  $\alpha$  and  $\alpha_{\text{FL-LL}}$  to  $\beta$ . Since the dominant junction prevails, the voltage V in the expression (2.172) denotes the actual voltage drop over such a junction and not the high bias pressed over a system. For this reason their ratio in form of parameter  $\gamma$  is introduced to the characteristic so that the final formula reads:

$$I = I_0 T^{1+\alpha} \sinh\left(\frac{\gamma eV}{2kT}\right) \left| \Gamma\left(1 + \frac{\beta}{2} + i\frac{\gamma eV}{2\pi kT}\right) \right|^2.$$
(2.174)

This is also the core result for Luttinger liquid applications in terms of charge transport along 1D confined systems.

With this rather exotic theory we conclude our journey through the theories that apply to confined and nonuniform systems. In the following chapters we focus on the experimental part i.e. the manufacture of the measurement chips, sample preparation, post-production treatment and the measurement itself. Finally the results are discussed in the spirit of the theories presented here, thus deducing the nature of the electron transport along our nanowires.

# Chapter 3

# Sample preparation and measurements

Before we describe the experimental work in detail let us first present the aim of our research in terms of practical realization. As mentioned in the introduction of this report our goal was to determine/measure the electrical conductivity properties of thin MoSIx nanowire bundle as schematically depicted on (Fig. 3.1a). This basically means that we have to plug ends of the device under test to an electrometer and measure the current vs. voltage (IV) characteristics of the system. In the macro word this presents a rather trivial task since the standard measurement equipment can be used along with the macroscopic connections to the measured sample in form of different pins, crocodile clamps or we can even solder the electrodes to the sample.



Figure 3.1: a) A simplified sketch of IV measurement as a function of temperature for some arbitrary sample and b) the artistic expression of electrodes introduced over a thin, single nanowire bundle and c) a bundle (dielectrophoretically) attached over a narrow prefabricated gap between two electrodes.

The situation changes severely as the sample size decreases to nanoscale especially when the objects can be observed only with modern microscopy techniques such as electron microscopy or atomic force microscopy. In the nanoworld the question of contact introduction to the measured structure becomes a technological issue accompanied with a myriad of peripheral factors that affect the whole process. We have two possibilities of wiring minute structures: the selected object is located under a microscope, followed by a targeted placement of metal contacts over it (Fig. 3.1b) or reversely, the object is guided and pinned over prefabricated electrodes with a narrow gap between them (Fig. 3.1c). Also the handling of the sample demands an epopee of efforts since such minute objects need special attention even to be observed, seen and defined as chemical compounds not to mention the manipulation and targeted pinning of structures needed in order to connect them to the macroelectrodes. In this chapter we focus on the issues of minute electrode/device manufacture, processing of the sample and the procedures for bundle attachment to the circuit electrodes that lead to a successful measurement. Let us first summarize all the steps needed to reach the goal of measuring current - voltage characteristic of a thin, single nanowire bundle:

- nanolithographic manufacture of microchip devices,
- sample preparation,
- attachment of the bundle to the electrodes,
- temperature annealing,
- measurement.

## 3.1 E-beam lithography

The manufacture of simple microchip devices that served as the contact electrodes of nanowire bundles is step one of our experimental procedure since without the skill to produce electrodes the measurements aren't possible. We addressed this problem with standard e-lithographic procedure widely used across the world in other research facilities. Depending on the budget the whole technique, along with the accompanying equipment and the know-how, can be commercially acquired. This high performance instruments are specially developed for the task of minute structure production with high accuracy, stability and quality. In many cases such systems are modified for the purpose of similar electronic measurements and even nanoparticle manipulation [32, 33]. Moreover such tasks demand special research laboratories and facilities in order to reach the highest nanoscale performance along with the quality and reproducibility. Custom built vibrationally isolated rooms and clean rooms with controlled air flow that require strict working policies for the researches are required for such quality. Due to limited funds we started with a modest 40 000 EUR second hand electronic microscope (Fig. 3.2) that operated fully analogically without the built-in lithography electronics. Moreover the whole lithographic procedure needed to be introduced and developed from scratch: the resists and accompanying chemicals, e-beam writing, chemical treatment, metal introduction and the finalization of the process. Also the laboratories weren't optimal since we had only a very

general chemical laboratory as the center for lithographic techniques. All these factors predetermined our best resolution but for structures of several hundreds of nanometers in size (length) it was sufficient and we carried on with the development. Even though our pre-graduate work [1] made first steps and roughly introduced the technique, the goal of measuring one single and thin bundle by far exceeded the performance and skills of the acquired procedures. We spent most of the research time tinkering, modifying and refining the whole lithographic procedure in order to reach the desired performance level. Let us stress that according to before-mentioned lithographic and system limitations we didn't pursue developing the approach of contacts over a bundle but we concentrated solely on the attachment of a bundle over a gap between the electrodes. We mentioned both cases since the first one is dominantly used.



Figure 3.2: The electron microscope JEOL JXA-840a modified to perform e-beam writing. We used software that guides the electron beam through an interface whereas other settings are adjusted manually over the control panel.

What lithography actually is? The word comes from German "die Lithographie" that is coined from Greek "lithos" stone + "graphein" write and can be thus translated as "to write or draw on stone". The technique was used in 19th century for fast printing and the reproduction of images and is practiced even today by many artists [34] to imprint the features into a stone using hydrophobic ink followed by a special chemical treatment. When the ink is applied afterwards with a roller it attaches only to the pre-drawn areas whereas unspoiled areas remain pure<sup>1</sup>. If a paper is pressed against the surface the ink leaves a trace of the image on the paper (the mirror image, of course). You can think of it as a very sophisticated and heavy stamp. This differentiation between written and unwritten areas is the basic concept also in electron- or photolithography.



Figure 3.3: a) A layer of an e-beam resist is spun on a substrate and a predesigned pattern is written with an e-beam over it. b) In the process of development the electron treated areas are dissolved leaving trenches of exposed substrate c) so that the sputtered metal attaches directly to it in the desired and pre-written shape d) that remains after the lift-off.

The process namely starts with the writing of desired circuit patterns over an electron or photon sensitive resist layer on top of a nonconductive substrate (Fig. 3.3a). Afterwards the chemically changed written areas are dissolved in appropriate solvents producing trenches in the shape of the desired circuit in the resist (Fig. 3.3b). In those trenches the substrate is totally exposed whereas elsewhere it remains covered with the resist. The following process of metal deposition covers the entire substrate with a thin layer of desired metal thus depositing metal inside the trenches as well as on top of the resist (Fig. 3.3c). During the lift-off the entire remaining resist is dissolved along with the metal deposited on top and washed away, leaving only the metal in the trenches which remained unaffected by the lift-off process. The end result are the metal electrodes shaped in the form of the pre-written pattern (Fig. 3.3d). The smallest feature limit using such

<sup>&</sup>lt;sup>1</sup>Children utilize similar but reverse technique for fast painting of background with water based colors on pre-painted wax crayon picture.

a procedure is determined by the resolution of the trench production, which is directly related to the method used. In the case of photolithography the lower limits are at several hundreds of nanometers (related of course to the wavelength of the light), whereas in the electron beam writer the smallest feature can reach even several decades of nanometers with the best equipment.

Let us itemize the e-lithographic steps we needed to acquire:

- 1. e-resist handling and spinning,
- 2. e-beam writing,
- 3. developing,
- 4. metal sputtering,
- 5. the lift-off.

Since we used this wide spread and standard procedure as a tool to serve the prime goal of single bundle measurement we discuss only the relevant points that affected the shape and quality of the circuits and consequently the measurements.

#### 3.1.1 Substrate and e-resist spinning

Successful circuits must be fabricated on a nonconductive substrate in order to prevent the obvious short circuit between the features via the substrate. On the other hand ebeam writing is most successful on better conducting substrates so we have to make a compromise. A good balance can be achieved by using a silicon wafer with a thicker oxide layer to make the surface non-conductive, but with the sufficiently conductive core to prevent high charging that disables accurate e-beam writing. The plates can be bought with arbitrarily thick oxide layer<sup>2</sup>. We selected 600 nm of oxide on top of 300  $\mu$ m thick wafer, extra polished to reduce the surface roughness to minimum so that small bundles would be clearly spotted on the surface.

For controllable and even reproducible production of circuits a uniform layer of well defined thickness must be deposited on the substrate. One of the best ways to achieve this is spin casting. A droplet of resist dissolved in an appropriate solvent is put on a substrate and spun for several minutes. The surplus liquid is then (centrifugally) ejected from the surface leaving a trail of thin layer over the whole substrate area. The thickness can be controlled and is proportional the spinning frequency and inversely proportional to the concentration of the e-resist.

When we mastered the basics of the lithography we preliminarily modified a general centrifuge into a spinner, which worked satisfactorily for early tests and also for bigger circuits/bundles later on. As we approached the scales relevant for our nanoscale objects it became clear that a professional spin coater was required<sup>3</sup> (Fig. 3.4). We acquired an adequate unit that not only simplified the resist deposition but also enabled full control and perfect reproducibility.

<sup>&</sup>lt;sup>2</sup>The web page of the distributor: www.universitywafer.com.

<sup>&</sup>lt;sup>3</sup>The unit was bought from Laurell Technologies corporation: www.laurell.com.



Figure 3.4: WS-400B-6 NPP/LITE spin coater was used in order to reproducibly deposit a thin and uniform layer of e-resist over the silicon wafer.

The e-beam resists were picked according to the suggestions of our e-beam lithography chemicals provider<sup>4</sup>. Commonly researchers use two different layers of e-resist on top of each other, the upper one slightly less sensitive then the lower one. For the bottom layer we used a 2% solution of poly(methyl methacrylate) (PMMA) MAA/33% in ethyl acetate spun at 4000 rpm for two minutes (the resulting thickness was ~190 nm) followed by 10 minutes of baking on a hot plate at 200°C and 1% solution of PMMA 950k in chlorobenzene spun at 6000 rpm for two minutes (the resulting thickness was ~90 nm) followed by 10 minutes of baking on a hot plate at 160°C. As we discuss in the section 3.1.3 this choice was necessary and even inevitable since the deposition of metal via sputtering isn't as successful as one might hope or expect.

## 3.1.2 E-beam writing and developing

In the e-beam illumination step the stage is set for the production of the final circuit. As described above the electrons bombard the substrate/e-resist in the predesigned pattern in the form of the desired circuit (Fig. 3.3a). We used a scanning electron microscope modified with the help of the company LPKF<sup>5</sup>, and succeeded to directly implement

<sup>&</sup>lt;sup>4</sup>The web page of the e-resist and the accompanying chemicals provider: www.allresist.de.

<sup>&</sup>lt;sup>5</sup>LPKF Laser & Elektronika d.o.o., Polica 33, SI-4202, Naklo, Slovenia

their laser guidance software (Fig. 3.5) used in laser cutters through the development of an adequate computer-microscope control panel interface that converts signals from the software output into analog signals that directly control the position of the e-beam in the microscope. We also needed to learn how to use our system and to determine basic operational parameters along with the basic procedures. Even though we spent a considerable amount of time acquiring the new technology we will not discuss the details further since they are rather technical and specific.



Figure 3.5: A CAD program (SCAPS) enables to draw arbitrary patterns and to transfer them directly to the e-beam guidance of the electron microscope. Additional features such as beam speed and hatching greatly simplified the design and the writing steps, thus lowering the production time of circuits.

In the process of writing the backscattered electrons play a decisive role in trench production since the resist gets illuminated also from beneath (Fig. 3.6a). This effect actually dominates the final width of the channel making it roughly proportional to the e-beam current; the phenomenon is known as the proximity effect[35, 36] and must be carefully taken into account when we deal with the chemical development step. The chemically altered illuminated areas are more soluble in developer (in our case a mixture of methyl isobutyl ketone and isopropanol in ratio 1 : 3) and dissolve faster leaving behind the voids that form the trenches. Since also the unspoiled areas dissolve slowly a treatment in stopper (in our case pure isopropanol) is needed. This fact along with the poorly defined limits between the illuminated and unspoiled areas due to the proximity effect makes the time of development crucial for the successful production of channels; in our case  $50 \pm 2$  s. Let us stress at this point that the step exhibits extraordinary sensibility, narrowing the parameter margins of previous processes (spinning, writing, developing, stopping).

Since our machine along with the rest of the procedures shows some intrinsic instability accompanied with a residual uncertainty, the overall yield of successful trench production gets reduced. If everything goes well the resulting channel has the edges of the form of a roof edge that sticks outwards from a supporting wall Fig. 3.6b.



Figure 3.6: a) The electrons scatter backwards illuminating the e-resist also from beneath. b) A successful development gives a channel with roof-like edges.

The proximity effect doesn't have an important role in the production of big structures, whereas for the smaller ones the relative discrepancy between designed and actual structure grows with the size reduction of the features. The effect especially starts to become a problem when we would like to create two trenches close together. In this case the proximity effect stretches also to the nearby feature illuminating the wall between them two times as much. This often results as the overexposure of the separation e-resist wall in many cases also as its collapse sometimes even fusing together both channels. This issue affects our circuit production directly since the electrode design includes a narrow channel between the metal contacts and consequently writing of two wide trenches close together. The production yield is reduced even more in this case since the optimal time of development for normal edges differs from the one for nearby trenches. Practically this means that the separation walls collapse before the other edges get adequately developed. On Fig. 3.7 the AFM amplitude images of successful trench production along with typical failed attempts are presented. In most cases the top e-resist layer of the wall structure gets dissolved partially or completely (Fig. 3.7b and 3.7c), or the sharp edges get rounded raising the probability of electrodes getting fused in the process of metal deposition (Fig. 3.7d). This combined with poor stability of the electron microscope writer makes the production of circuits extremely demanding and pain staking already at this point stretching our research time more then expected.



Figure 3.7: The AFM images of typical trenches carved in the e-resists: a) successful, b) collapsed top e-resist layer of the wall in the middle, c) e-resist collapse throughout the entire length leaving only a narrow stripe of bottom layer and d) rounded edges of the top layer that can result as contact fusion after metal deposition.

## 3.1.3 Sputtering and lift-off

In previous steps we were able to optimize the procedures in order to manufacture adequate trenches in the layers of e-resist. Since we didn't possess our own metal deposition unit we were forced to seek collaborations in the group for thin metal coatings at our institute<sup>6</sup>. The group has an accurate, reliable and diverse metal sputtering system that enabled us to perform uniform and reproducible metal deposition over our carved e-resist layers. Unfortunately their procedure is optimized so that the metal gets deposited at every possible angle so that even holes, indentations or complex shaped objects get uniform coating without any shades or missed spots. This however was a serious obstacle for our

<sup>&</sup>lt;sup>6</sup>Department for thin films and surfaces. Their webpage: http://www.ijs.si/ctp/ijs-dept-f3A.html-l2.

deposition since we were hoping for a perpendicular introduction of the metal in order to create confined depositions in the middle of the trenches with metal attached to the edges. As depicted in Fig. 3.8a the metal nicely forms a narrow and well defined stripe if the metal falls perpendicular to the surface (as in the case of metal evaporation), whereas in the case of omnidirectional sputtering the metal attaches even to the edges, widening the features to larger size defined by the proximity effect (Fig. 3.8b).



Figure 3.8: a) The perpendicularly deposited metal falls in the middle of the trenches without touching the edges whereas b) for omnidirectional sputtering the metal is thrown also in the cavities beneath the wall's roof-like top reducing the gap between two electrodes from the c) nominal width of the upper e-resist wall to d) the actual width determined by the base size of the e-resist wall.

Alternatively one could propose to reduce the cavities created by this effect but this would backfire immediately since the metal deposition would create steep, almost vertical edges at the contact ends endangering the successful circuit production or in the case of narrow channel production it would result as fused contacts. In truth not even the last process of lift-off, when the rest of the e-resist is dissolved in remover (in our case N-Methyl-2-pyrrolidone for 12 hours) and disposed together with the overlying metal,

influences much the end result so we were forced to use this inadequate but uniform and accurate sputtering technique. Fortunately we had more freedom in the choice of the sputtering metal. Due to limited lithography performance we were forced to sputter only thin, up to 50 nm thick layers of preferably softer metal to ensure successful lift-off. The metal adhesion to the surface also needed to be strong enough to withstand all the processes during the later bundle integration procedures and measurements. Titanium has good adhesion and can be sputtered in a thin layer but it is rather hard thus obstructing the lift-off. Moreover it shows high chemical reactivity especially with oxygen resulting in non-conductive oxides lowering the conductivity of contacts in the circuit itself. One alternative is gold that appears soft and inert, but unfortunately it sticks extremely poorly to the silicon oxide wafer making it necessary to use a sticky layer of nickel, titanium or chrome to act as a form of glue for better adhesion of gold. In this way the overall thickness increases and the contacts show only limited durability since the gold layer wears down when mechanically stressed. Best results were achieved by using nickel or palladium. Both exhibit high chemical inertia, high adhesion to the substrate surface and also show great resilience towards mechanical stress. The difference between them is that the palladium contacts appear to have a higher low-limit of contact thickness than nickel. We observed that palladium shows a strong tendency to wear off when sputtered in layers thinner than 50 nm whereas nickel preserves its integrity to the limits of sputtering procedures; the thinnest layers were 15-20 nm thick. For this reason we chose nickel to produce measurement circuits<sup>7</sup>.

Despite the described drawbacks we continued with the production of the circuits with relatively low yield of 10 - 20% and the production time of roughly one week. The minority of the produced contacts had a well defined gap between both electrodes and were considered successful (Fig. 3.9a) whereas the majority carried the legacy of poorly created trenches that resulted as extremely narrow gaps with possibility of connection between the electrodes (Fig. 3.9b) or even more unexpected features when metal was pushed beneath the upper layer creating a soft transition from one electrode to another with some well defined areas in between (Fig. 3.9c). Often the electrodes were surrounded by a metallic crown (Fig. 3.9d) that could be washed away with a cotton stick, making the circuit workable but only if the contacts weren't fused at any point.

# 3.2 MoSIx Nanowires

Armed with adequate circuits we focused our attention to the sample preparation. We were hoping to get a monodispersed solution of the thinnest nanowire bundles or perhaps even only single nanowires. In this section we introduce the chemical structure of our MoSIx nanowires along with a brief introduction to their synthesis and a recipe for the successful preparation of the nanowire dispersion in acetone and isopropanol.

<sup>&</sup>lt;sup>7</sup>Some aspects of metal choices are presented also in the sections of dielectrophoresis and the annealing procedure.



Figure 3.9: The AFM images of typical final circuits: a) successful, b) extremely narrow gaps with possible fused points, c) soft transitions of metal from one contact to another and d) typical metal crown surrounding the metal contacts.

# 3.2.1 The synthesis and the chemical structure of MoSIx nanowires

MoSIx is actually a trademark name for this type of nanowires produced and distributed by the company Mo6 d.o.o.<sup>8</sup>. These wires form a structural family of inorganic nanowires composed of three different elements: molybdenum, sulfur and iodine under the formula:  $Mo_6S_xI_{9-x}$ . The structure is closely related to Chevrel phases with the general formula  $M_xMo_6X_8$  where M stands for a metal and X for a chalcogen. In fact at the discovery there was a debate whether these wires weren't just simply a new species in this rich family of structures. It turned out [14, 13] that indeed there was a close resemblance between the atomic arrangement in the nanowires and in most related crystal structures

<sup>&</sup>lt;sup>8</sup>Mo6 d.o.o., Tehnološki park Ljubljana, Teslova 30, SI-1000 Ljubljana, Email: info@mo6.com

such as  $Mo_6S_6I_8$ ,  $Mo_6S_2I_8$  and  $Mo_6S_8$ . The basic structural cells are closely related but with a major difference that in the case of MoSIx nanowires the lateral cross link bonds between the molybdenum octahedra via sulfur or iodine are missing (Fig. 3.11). Thus an interesting compound of many chemically separated wires is formed, held together only by weak van der Waals forces making them easily dispersable in various solvents. The individual wires on the other hand have a stable but soft structure since the molybdenum octahedra get longitudinally connected via sulfur planes surrounded by iodine ions. With other words: the MoSIx nanowires have the molybdenum backbone, that consists of molybdenum octahedra clusters connected via 3 sulfurs in the linkage plane altogether surrounded by iodine or sulfur ions (Fig. 3.10). Their close resemblance to Chevrel phases makes them come in greater packs of nanowires, in thicker bundles of various sizes.



Figure 3.10: The MoSIx nanowire structure consists of molybdenum backbone formed by the octahedra clusters with 3 sulfurs in linkage plane, surrounded by iodine. a) The side view reveals the linkage planes and b) the cross section depicts the iodine arrangement around the molybdenum octahedra.



Figure 3.11: a) The basic structural cell of separated MoSIx nanowires in a bundle and b), c), d) of most similar Chevrel phases with pointed cross links.

Basic properties have also been studied using density function theory [37]. The calculations reveal finite density os states at  $E_F$  for longitudinal direction (3.12a) thus predicting the material to be conductive. For the Drude peak damping of  $\Gamma = 0.1eV$  the conductivity at room temperature is estimated to be around  $5 \times 1000$  S/cm, which is two orders of magnitude lower than for carbon nanotubes. Soft bonds between the Molybdenum atoms
and the linkage planes suggest possible distance modulation that can be denoted as *the accordion effect*. The calculations confirmed that assumption and determined two stable minima even in a flawless nanowire (3.12b).



Figure 3.12: a) The density of states calculated using density function theory. b) The free energy calculation predicts two stable positions for the linkage sulfur towards the molybdenum octahedron.

The described resemblance between various structures induced considerable uncertainty and sensitivity to the synthesis and dispersion preparation. Even though the synthesis follows a rather simple procedure, defining, controlling or even pinning the relevant parameters appear to be rather slippery tasks. Basically all the elementary ingredients in targeted stoichiometry mass ratio<sup>9</sup> are put in a quartz ampoule, vacuumized (pressure  $2 \cdot 10^{-5}$  mbar), sealed and put in an oven with homogeneous temperature<sup>10</sup> of 720°C for 3 days. The resulting material has a puffy, wool-like appearance that contains residual iodine that evaporates spontaneously in 24 hours after the extraction from the ampoule. As pointed out the similarities of different stoichiometries and even to Chevrel phases make it rather hard to determine the proper structure of the resulting material. We can speculate that the thermodynamic growth conditions allow multiple structures ( $Mo_6S_6I_8$ ),  $Mo_6S_2I_8$  and  $Mo_6S_8$ ) to be formed making the end material a multi-phase mixture. Unfortunately also the X-ray analysis cannot distinguish sharply between them so the material type is never completely certain. Also the growth mechanism and the environmental conditions aren't well understood, thus reducing the reproducibility of synthesis. We were not directly part of material production research and had very little influence on the synthesis outcome so we focused intensely on sample dispersion in different solvents. Other groups dealt also with material post processing trying to determine the basic solubility properties of our material [24, 23]. Despite their elaborate work we couldn't reproduce

<sup>&</sup>lt;sup>9</sup>This sets the x in the  $Mo_{9-x}S_xI_{9-x}$  formula.

<sup>&</sup>lt;sup>10</sup>An oven without temperature gradients.

the dispersions according to their recipes at least not in the desired terms of small mean bundle diameter and of proper concentration. In addition to that the dispersions showed vivid agglomeration dynamics that expelled the wires from the solution to the bottom of the reservoir.

After many failed attempts and the synthesis crisis we came up with a procedure that appears to have overcome all indicated problems. We have to keep in mind that our final goal of single bundle/nanowire integration demanded high quality dispersion, much higher than needed for average solutions suitable for population studies (UV-vis spectra, Röntgen analysis, sedimentation studies). Let us itemize the basic dispersion properties we needed to achieve in order to use it for single bundle integration:

- a monodisperse solution,
- low mean diameter of bundles,
- few impurities,
- high concentration,
- low agglomeration and high stability of solution,
- a dispersion in a solvent suitable for single bundle trapping over prefabricated circuits<sup>11</sup>.

The final recipe, that overcomes the itemized terms may sound rather simple, but it is based on many dead-end procedures. We discovered that we have to use the whole amount of material from the ampoule without any washing, dispersing, homogenizing or any kind of pre- preparation. Our initial attempts namely included all facts about the poor reproducibility of syntheses so we tried to use small amounts of given sample generation, learn the material handling for some specific synthesis and then to use it to prepare final solution for the experiment. As we discovered later using small amounts (< 5 mg) inhibited our sample preparation from the start since the population of targeted small bundles appears in the solution in rather small quantities. Using larger amounts (or as stated above, all of it) pays off since the results truly fulfill the demands by a large margin.

The best solvent for initial dispersion of the bundles turned out to be acetone with a special emphasis on its purity. We believe that commonly used chemical reservoirs contain many impurities that influence the agglomeration and stability of the solution so we suggest to use fresh, perhaps even filtered or distilled chemicals if possible. For the dispersion we used an ultrasonic tip (small tip at a maximum allowed power for 10 minutes) to thoroughly disintegrate the initial material in a plastic reservoir with 50 ml of acetone to smaller meshes and single bundles (Fig. 3.13a). Afterwards the dispersion almost immediately separated into two phases: soluble and stable dispersion and the completely non soluble sediment that formed again a puffy phase on the bottom of the

 $<sup>^{11}\</sup>mathrm{We}$  discuss this later in the section of dielectrophores is.

reservoir (Fig. 3.13b). The upper dispersion had a yellow-orange appearance and was left for several days (7 days) to separate from the remaining non soluble phase. Afterwards the upper dispersion was carefully poured (10 ml) into a fresh glass reservoir and tightly sealed. We used glass beaker because we observe that the material tends not to stick heavily to the glass walls as in the case of the plastic (polypropylene) ones.



Figure 3.13: a) The ultrasonic tip (Cole Parmer CP750 750W) was used to disperse assynthesized material in acetone. b) The resulting solution clearly shows the soluble and non-soluble phases sharply separated.

As we explain in 3.3 the proper solvent for the bundle incorporation into the circuit wasn't acetone but isopropanol. To change the solvent we dried the nicely sedimented dispersion on a hot plate and immediately poured the isopropanol (10 ml) into the cooled reservoir. To redissolve the dried material stuck on the walls we used an ultrasonic bath at 100 % power for 2 minutes (Fig. 3.14a). The result was again a yellow-orange solution without sediments that appeared stable for months. We emphasize the color of the solution since we believe that it's a strong indicator of dispersed bundles in the solution. The resulting yellowish tan (Fig. 3.14b) indicates thin and long bundles whereas more greyish, dark blue color (Fig. 3.14c) marks solutions with small amounts of single bundles, filled with crystalline objects that sediment extremely fast leaving the solution almost empty in terms of desired single bundles. Naturally we allow the possibility that the thinnest bundles exist even in this solutions but unfortunately they are useless for our circuit integration due to extremely small bundle concentrations.

Along with the sample preparation we derived a more accurate test to determine the consistence of the dispersions. We simply measured the UV-vis spectrum of a solution and analyzed the peaks. We observed that at least one of the peaks appears to be connected to the small bundle population. As presented on the graph from (Fig. 3.15) the position



Figure 3.14: a) The ultrasonic bath (Transsonic digitalS ELMA T490HD, 2x40W, 40 kHz) was used to redisperse dried material in isopropanol. b) The successful final solution has yellow-orange color whereas c) dispersion with lower concentration of single thin bundles appears grey or dark blue.

of the peak around 700 nm gives the information about the sample consistence. If the peak appears at lower wavelengths (between 690 nm and 700 nm) then thin bundles are present in strong concentration in the solution. The alternative cases of the peak appearing at higher wavelengths (greater then 700 nm) give smaller concentrations of the thinnest bundles. We have to admit that we constructed this test on the experience basis of also other researchers and we didn't look more into it since we still had a long way to go till the successful measurement.



Figure 3.15: Successfully prepared samples (black curve) appear to have the most left peak of UV-vis spectrum pushed above 1.77 eV (700 nm) and don't shift in time, whereas the failed ones (red curve) show the peak at 1.69 eV (732 nm) or lower. Also the upper peak follows same shift - 2.73 eV vs. 2.56 eV.

Let us summarize the whole recipe once more:

- 1. the whole content of the synthesis ampoule is sonicated in 50 ml of acetone in an elongated plastic reservoir with a thin ultrasonic tip for 10 minutes (Fig. 3.13),
- 2. the dispersion is let to sediment for seven days,
- 3. the upper stable dispersion is carefully poured into a glass reservoir (10 ml),
- 4. to replace the acetone with target solvent the dispersion is dried on a hot plate  $(60^{\circ}C)$  immediately followed by the introduction of the final solvent,
- 5. the material stuck to the glass walls of the reservoir is redissolved in an ultrasonic bath at 100% power for 2 minutes (Fig. 3.14).

## 3.3 Dielectrophoretical attachment of single bundles over a narrow gap

The integration of a single, thin bundle into a circuit became the core of our research since the final measurements could have been performed by using standard measurement techniques. We were interested in electronic properties, particularly in the direct transport measurements that are perhaps the most demanding to perform since individual bundles have to be connected to the macro-electrodes. With this approach the preparation of the measurement chip is the hardest part since the technological skills to manufacture such circuit hybrids are pushed to a new level. The interpretation of the measurements on the other hand is quite straight forward and requires very little data post-processing in order to get the raw results for further analysis. In contrast to this individual approach there are population, statistical techniques that count on homogeneity of a sample since a collective response is measured. In the past we tried to determine the conductivity properties of a bulk pellet [22, 21], other researches tried to measure the transport through a thin foil of compressed sample [20]. Bulk sample approach is widely used also in other basic property measurements such as SQUID magnetic susceptibility scans of a sample capsule, laser absorption of a sample foil for the determination of electronic states [15, 16, 18, 19, 17]. The sample preparation for these experiments is rather simple but the measurement results demand careful analysis since the properties are tested on a group, burying the individual response. This problem widens even more if the sample contains a palette of different phases as in our case, since the overall response becomes a sum of all different structures making it impossible to distinguish directly between them. This was actually the main reason for our ambitious goal to manufacture a single, thin bundle connected to macroelectrodes so that the conductivity measurements bring us as close as possible to the true transport properties of our material.

As discussed at the beginning of this chapter the two basic strategies involve the introduction of the contacts a over prelocated bundle (Fig. 3.1b) on a substrate or the attachment of a bundle from a dispersion over a prefabricated electrodes with appropriately narrow gap (Fig. 3.1c). Our lithographic techniques together with poor repositioning capabilities enabled us to use the underlying-bundle technique only for the thickest bundles [1] whereas for the thinnest ones the most promising alternative was the overlying-bundle approach. In this section we discuss the technique of dielectrophoretical attachment of an individual bundle from a dispersion over two electrodes.

#### 3.3.1 Theoretical considerations

Perhaps more natural approach of particle attraction in a solution would be the electrophoresis where constant potential is pressed over the contacts gathering the charged particles form the solution (Fig. 3.17a)[38]. Our initial attempts showed that the resulting depositions resulted as huge amounts of non-bundle material that totally covered both electrodes without a trace of separated single bundles. This together with the underlying work of our colleges [26] pushed us to utilize the alternating potential or the *dielectrophoresis* (Fig. 3.17b) as the source of the attraction force. In contrast to the electrophoresis the force is governed by the electric field gradient rather than by the field itself and for that it naturally requires a non-uniform electric field, generated around the contacts as simulated on the Fig. 3.16.



Figure 3.16: a) The 3D simulation of the non-homogenous electric field around two oppositely charged stripes b) the top view of and c) the cross section in the middle of the stripes, perpendicular to the gap.

A dipolar moment  $\vec{p}(\omega)$  is induced in neutral objects when inserted in an alternating electric field  $\vec{E}(\omega)$  resulting as a dipolar force  $\vec{F}(\omega)$  in the present field gradient (Fig. 3.17b). We can write the force as:

$$\vec{F}(\omega) = (\vec{p}(\omega) \cdot \nabla) \vec{E}(\omega). \tag{3.1}$$

The dipolar moment depends on the material polarizability per unit of volume  $\alpha(\omega)$ :

$$\vec{p}(\omega) = V \,\alpha(\omega) \cdot \vec{E}(\omega), \tag{3.2}$$



Figure 3.17: a) In electrophoresis the charged particles are strongly pulled in constant electric field towards the opposite charged electrodes whereas neutral particles remain ignored. b) In an alternating, non-homogeneous field of dielectrophoresis the charged particles oscillate around a fixed point, hardly moving in the solution, allowing only neutral particles to feel the dielectrophoretical force.

that further depends on the complex permittivities  $(\varepsilon^* = \varepsilon + i\frac{\sigma}{\omega})$  of media  $\varepsilon^*_m$ , on the particle  $\varepsilon^*_p$  and on the shape of the particle manifested in the factor  $f(\varepsilon^*_m, \varepsilon^*_p)$ :

$$\alpha(\omega) = \varepsilon_m f(\varepsilon_m^*, \varepsilon_p^*). \tag{3.3}$$

Now we modify the expression (3.1) to:

$$\vec{F}(\omega) = V \,\varepsilon_m \operatorname{Re}\{f(\varepsilon_m^*, \varepsilon_p^*)(\vec{E}(\omega) \cdot \nabla)\vec{E}(\omega)\},\tag{3.4}$$

which can be rewritten to the final expression:

$$\vec{F}(\omega) = \frac{1}{2} V \,\varepsilon_m \,\operatorname{Re}\{f(\varepsilon_m^*, \varepsilon_p^*) \nabla \vec{E}(\omega)^2\}.$$
(3.5)

Theoreticians calculated the factor  $f(\varepsilon_m^*, \varepsilon_p^*)$  for some general shapes including rods and elongated, cylindrical objects that adequately describe our bundles with lengths l, radii r and the volume  $V = \pi r^2 l$ :

$$f(\varepsilon_m^*, \varepsilon_p^*) = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_m^*}.$$
(3.6)

This gives the result for our bundles in form:

$$\vec{F}(\omega) = \frac{\pi}{2} r^3 l \,\varepsilon_m \operatorname{Re}\left\{\frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_m^*} \nabla \vec{E}(\omega)^2\right\}.$$
(3.7)

The described phenomenon conveniently annuls the dominant electric force by utilizing an alternating signal instead of a constant potential leaving the smaller charged particles to oscillate around a fixed position, hardly traveling in the solution (Fig. 3.17b). The bigger and elongated objects carrying small charge such as our nanowires are being pulled by the field gradient toward the electrodes eventually ending up bridging them. This scenario was the core of our dielectrophoretical attachment approach.

#### 80 3.3 Dielectrophoretical attachment of single bundles over a narrow gap

#### 3.3.2 The attachment procedure

Gathering all the ingredients and setting the strategy we reached the point of actual bundle attachment to the circuit - bridging a pre-manufactured gap between two electrodes (Fig. 3.1c). Let us stress that dielectrophoretical attachment was optimistically attempted at every intermediate research results (different circuits, different syntheses and dispersion strategies) but with only limited success. We concluded that well defined and narrow gaps ( $200\sim300$  nm in width) along with stable dispersion containing sufficient amount of thin single bundles accompanied by few impurities are the imperative before realistically expecting successful single bundle attachment. As introduced in the brief theoretical consideration all we had to do was to press an external alternating electric field to the gap electrodes, pour a droplet of solution for couple of seconds over it, blow dry the surplus solvent and check the circuit under the AFM (Fig. 3.18).



Figure 3.18: An artistic rendering of a dispersion droplet over the two electrodes with signal pins pressed onto the circuit pads.

Other researches have been studying this phenomenon more thoroughly from the theoretical point of view, revealing the complex nature of such attachment attempts [39]. Many effects are present that we will not discuss here since we used the technique as a tool to produce the circuit, not studying the process itself. The core dielectrophoresis is accompanied by the mechanisms such as gravity, electrothermal and light-electrothermal heating, buoyancy effects, Brownian displacement, electrolysis and AC-osmosis.

Even though this rather simple technique hides a variety of processes we boldly proceeded with bundle attachments, having in mind only successful single bundle attachment. As depicted on Fig. 3.19 we constructed a simple mechanical press contacts that were controlled with micro-manipulator (Fig. 3.20b). The contact pins were made out of a 100  $\mu$ m thin wire that can be found in some fine electronic cables. Thicker or more robust contact pins turned out to scratch the circuit, destroying it during the attachment process. The whole assembly from Fig. 3.20b) was placed under the magnifying glass mount (Fig. 3.20a) so that the circuit pads and the contact pins could be precisely aligned and the approaching monitored until the contact was established. Due to the statistical nature of the procedure we were expecting numerous attachment attempts before succeeding and



Figure 3.19: The pins are pressed on the circuit pads manufactured on a silicon wafer.

due to the shortage of circuits we were forced to repeatedly use the same ones. That is why we needed to design a fast, accurate and simple method to perform many depositions and to check them under the AFM. Such press contacts from Fig. 3.20b) proved to be the right way. The alternative of permanently attaching contacts onto the circuit pads wasn't practical since the silver paste, that was used to stick the wire to the circuit, turned out to slowly dissolve in the nanowire solvent leaving a messy trail over the circuit making it useless. Moreover the minute objects that we were targeting could have been observed only under the AFM and a macro-circuit with attached macro-wires became very difficult to be mounted into the microscope.

The first attempts quickly showed that even though all the necessary ingredients were present, along with a promising single bundle strategy, the integration was still far from reaching the goal and actually producing a working circuit. First we encountered the issue of selecting a suitable solvent for dielectrophoresis. Being totally dependent on of statistics and laws of probability for a successful utilization of dielectrophoresis the dispersions had to contain a sufficient amount of target material (the thinnest bundles), low amount of impurities that would be naturally deposited as well and low agglomeration tendencies that would result as big deposition clumps and would destabilize the solution over longer periods of time. Moreover it turned out that a quickly drying droplet disables any kind of deposition control since the material becomes denser as the liquid volume decreases with evaporation enabling only extremely dense depositions. From this point of view the acetone even though being most suitable solvent for sample dispersions as mentioned in section 3.2 isn't the right way to go. Since we were familiar with the work of other researches [24, 23, 26] we tried to dissolve the material in water as an opposite to the acetone regarding droplet formation on the wafer and regarding the evaporation rate. Unfortunately the necessary high density, low impurity content and stability were not achieved, thus failing all dielectrophoretical attempts. The most suitable candidate turned out to be isopropanol that appeared to possess both qualities of acetone and water:



Figure 3.20: a) The dielectrophoretic setup consisted of a magnifying glass mount with an in-built illumination and b) the press-electrodes controlled by a vertical micro-manipulator.

the dispersion could be produced with same quality as for acetone but with slower evaporation rate. Thus with proper procedures the adequate dispersion could be prepared (see section 3.2) and the favorable physical properties enabled dielectrophoresis in a relatively controllable way.

The next step was to determine the proper frequencies and amplitudes of the AC signal along with the appropriate timing. At the beginning we plugged in a sinus signal generator with the aim to control the depositions. Unfortunately it turned out that regardless of the signal settings the depositions appeared to be very dense. Remarkably the density didn't decrease even when the generator was totally unplugged. After closer look we noticed that all our setup appeared to have been catching the background electro-magnetic (EM) signals from different electric instruments and even the electric wiring. By a simple process of elimination we succeeded to isolate the magnifying lamp illumination, or better, its power supply transformer as the major cause for the EM-signals. Amazingly even after total disconnection of all possible EM-sources the signal on the contact pins of the press contact still had enough power to attract single bundles form the dispersion at the most optimal rate. The final step was of course to ground the mount and the manipulator which killed the EM signals and no attachments were observed. In the process we tried also the chance deposition meaning that a droplet was poured over the circuit without the press contact in floating  $mode^{12}$  and no depositions were observed. Intrigued by the situation we tested the background EM-signals and determined the expected quasisinus signal of 50 Hz and the amplitude of 100 mV for the plugged and 10 mV for the unplugged illumination to be present; the signal vanished after the grounding. We also tried to simulate this favorable signal via signal generator with grounded mount but with no success. We concluded that the grounding of the whole mount influences the signal

<sup>&</sup>lt;sup>12</sup>The mount was not grounded.

from the signal generator and no depositions are observed. Since we had been under huge time pressure with the core of our research still ahead of us and since the successful attachment conditions were achieved we consciously abandoned further modifications of the dielectrophoresis setup.

Let us stress that the seemingly trivial grounding actually becomes a nightmare especially when the background influences the experiments in such a profound matter. We believe that special measures would be required in order to fully separate the background EM radiation and the external signals from the signal generator and since we found the proper parameters we devoted our research to the production of the circuits for the final measurement.

As mentioned, many attempts were needed to obtain one successful single bundle attachment. In order to use the same circuit several times we cleaned it carefully after each attempt with cotton, dipped in isopropanol followed by flash drying with compressed nitrogen gas. Such a circuit was then placed under the magnifying glass, aligned with the contact pins followed by careful descent of the pins via a micro-manipulator until the contact was confirmed. As described, the illumination was turned off afterwards and a 5  $\mu$ l droplet was poured with a micro-pipette extremely cautiously over the circuit avoiding the delicate wire pins. After 10 seconds the liquid was flash dried with compressed nitrogen gas and the circuit was ready for the AFM examination. To summarize once more the procedure in the compact form:

- 1. a circuit is gently cleaned with isopropanol dipped cotton and flash dried using compressed nitrogen gas; this step is repeated after each failed deposition,
- 2. the circuit is aligned under the magnifying glass, followed by monitored pins' descent until the contact with the circuit is confirmed,
- 3. the illumination is disconnected from the power socket,
- 4. a 5  $\mu$ l droplet of a dispersion is carefully poured over the circuit,
- 5. a 50 Hz signal of 10 mV amplitude is generated in the circuit,
- 6. after 10 seconds the solution is flash dried with compressed nitrogen gas,
- 7. after raising the contact pins the circuit is ready for AFM examination.

Before we discuss the outcome of the procedure let us briefly comment on the metal used to manufacture the circuits. As described in the section 3.1.3 the choice of metal facilitated successful circuit production along with reliable measurements. It is clear that the mechanical stress resilience turns out to be more of a necessity than a virtue. Having in mind the several nanometer thick bundles also the upper thickness limit of the metal becomes an issue. Thinner layers are preferable on one hand due to the AFM imaging since the minute nanowire strands get lost quickly in the high and vivid topography of the circuit gorge and on the other hand due to the tendency to keep the bundle as straight as possible. Naturally, soft bundles tend to accurately follow the underlying surface topography thus not literally bridging the gap between the metals but bending

#### 84 3.3 Dielectrophoretical attachment of single bundles over a narrow gap

over both edges, touching the bottom of the gorge. These bends, also known as kinks, are believed to affect the electron transport through similar systems [40] so we wanted to keep these bends as flat as possible by keeping the metal thickness to a minimum. We came to the conclusion that that 20-25 nm thick nickel contacts would optimally satisfy all the mechanical stress resilience here and in the lithography section.

Regarding the performance of our single bundle attachment procedure we realized that even under the best possible conditions the attachments still resulted in a wide palette of possible outcomes. Most often (~50 %) we observed multiple bundle depositions (Fig. 3.21a) that varied in density, mean diameter and the position of the bundles; sometimes not even a single one bridged the gap (Fig. 3.21b). Also agglomerates (Fig. 3.21c) and extremely thick bundles (Fig. 3.21d) found the way to our electrodes (~25 %) only proving that probability and statistics dominate the process. Luckily for us in quite some cases (~20 %) only several bundles bridged the gap (Fig. 3.21e) enabling tedious postprocessing using the AFM to cut specific wires leaving only one wire intact as described below. Our preferred outcome was present only in the minority of cases (up to 5 %) (Fig. 3.21f) and the rest were cases of impurities bridging the gaps (Fig. 3.21g and 3.21h or random junk attachment (Fig.3.21 i). The impurity bridges often lead to the destructions of the circuits since they couldn't be cleaned and recycled again; this was also the end of many circuits. As pointed out before, images like Fig. 3.21e caused a great deal of





Figure 3.21: The AFM images of typical depositions: a) most common dense deposition of many wires b) sometimes without bridging. c) Also frequently present deposition of agglomerates and d) extremely thick bundles, e) only few thin single bundles bridging the gap, f) the desired single bundle attachment, g) and h) the intriguing impurity bridges, i) the mixed deposition of all possible junk.

frustration, since by finding a way to cut the surplus wires we would considerably widen the amount of favorable outcomes. The opportunity lies of course in the utilization of the AFM tip as the precise cutting tool. From the experiences with scanning the surfaces with the AFM tip we knew that our wires showed high adhesion to the surface and appeared to be rather soft, so we needed to scan the samples in tapping mode. In contact mode we were namely cutting or destroying the integrity of the bundles. Even the attempts of other colleagues to manipulate them on the surface ended the same way. So it was only natural to use the contact mode as the possible bundle cutting procedure or a route to destroy the particle bridges such as on the Fig. 3.21g, 3.21h and especially 3.21e where on the upper left corner a bridge distorts otherwise perfect deposition. More different outcomes were present here as well.



86 3.3 Dielectrophoretical attachment of single bundles over a narrow gap

Figure 3.22: The AFM images of typical AFM tip cleaning:  $a1) \rightarrow a2$ ) a successful disconnection of three features,  $b1) \rightarrow b2$ ) a frequently observed gathered material after cleaning and  $c1) \rightarrow c2$ ) a undesired deformation of the selected bundle along with the slight material gathering.

The most valuable and desired scenario contained a clean and precise cut of a bundle/feature in a specific location without interfering with other entities. A successful cut is presented on the Fig. 3.22a1 and 3.22a2, before and after the operation. The bundle on the right of the images was picked and the features marked with black arrows on Fig. 3.22a1 were recognized to have possible unwanted bridging between the contacts and were disconnected as presented on Fig. 3.22a2. In many cases the material after cleaning appeared to have gathered at the end of scanning lines making the situation even worse, especially when the features formed close to the picked bundle as on Fig. 3.22b1 and 3.22b2 or 3.22c1 and 3.22c2. Interestingly the amount of material appeared to have surpassed the material quantity in the features suggesting that some parts could have come from the AFM tip while roughly scratching the area. As also noticed in the macroscopical cotton cleaning of the circuit some bridges exhibited extraordinary resilience towards mechanical scratching and AFM cleaning procedure only confirmed that, as depicted on the image sequence of Fig. 3.23 where the nasty bridge from Fig. 3.21e was attempted to be cleaned.

We can conclude that even though the AFM cleaning process was shown to be a



Figure 3.23: The AFM images sequence of unsuccessful bridge cleaning: a1) the initial situation with the target bridge on the left side of the gap, a2) the first attempt and a3) the widened cleaning area with bridge still intact.

promising way to improve the single bundle attachment yield, the overall success turns out to be rather modest. Upon reflecting the outcomes we could establish a correlation between the AFM tips used but systematic study on this subject hasn't been done. We noticed that the common silicon nitride (the product name OTESPA<sup>13</sup>) tips tend to get worn out easier producing additional deposits on the surface whereas platinum/iridium (the product name OSCM-PIT) covered tips not only didn't leave any traces, the residual material of the cleaned features disappeared. We believe that an intrinsic potential is applied on the tip through the AFM apparatus attracting and cleaning particles from the surface. Such a case is depicted on Fig.3.21 a) where after cleaning the material simply vanishes. Perhaps the best demonstration of the procedure is presented on Fig. 3.24 where we succeeded to cut two out of three bundles.



Figure 3.24: The sequence of AFM images of exemplary bundle cutting: a) the initial situation, b) the blowup from the previous image clearly showing the initial three bundles and c) the selected bundle on the right after cleaning is completely intact whereas the other two are disconnected.

<sup>&</sup>lt;sup>13</sup>http://www.veeco.com

Dielectrophoresis turned out to be the best way to attach a single bundle over a gap thus integrating it into a measurement circuit. The technique combines a number of phenomena that can be tempered in the desired manner only if all important parts exhibit adequate properties. We have to emphasize especially the dispersion's quality and the choice of the solvent. To fully understand and utilize the technique, also the pin design, signal introduction and especially grounding must be taken into account. We saw the dielectrophoretical attachment only as a route to achieve our goal of measuring electronic properties a single bundle and we were not going into a deeper investigation of the concept itself.

### **3.4** Measurements

After laying a pathway for manufacturing single bundle circuits we were ready to perform conductivity measurements. As announced in the beginning of this chapter our interest lies in the current vs. voltage characteristics as a function of temperature. In this section we describe the measurement setup followed by the unforseen temperature pre-treatment of the circuits, which was not planned initially.

#### 3.4.1 Measurement setup

Current vs. voltage is perhaps the most basic measurement in the determination of electronic properties and gives a profound view into the mechanisms that govern the transport of electrons. As widely debated in the theoretical sections many effects might affect the electrons traveling along the wire and our goal was to experimentally measure our system and compare the results to the theoretical possibilities.

All we needed in order to perform such a measurement was a voltage source and a current measurement unit. Since the temperature plays an important role in the electron dynamics a thermostat was included; a schematics of the setup is depicted on Fig. 3.25.

We also needed to construct a custom measurement setup, but this time we had a very good standard measurement equipment at our hands. The core conductivity measurement was performed by Keithey 238 electrometer, a source-measure unit. For temperature setting and control we used a cryostat (Oxford Instruments) connected to a cryodrive (Edwards cryodrive 1.5) and driven by ITC 503 temperature controller. All components were controlled by the computer program that was specifically designed for the task of temperature controlled current vs. voltage characteristic measurements. The setup is presented on the photograph Fig. 3.26.

The program had full control of the measurement scan and at the same time enabled custom data patterns designed for a specific system measurement (Fig. 3.27).

Let us add a full description of the measurement procedure along with measurement conditions even though the whole technique hardly needs a deeper description. The silicon plate carrying the sample circuit was glued onto a copper cryostat holder to ensure high temperature conductance and proper control of the temperature in the sample. The circuit pads and the external socket pins were connected with a 25  $\mu$ m thick gold wire that was



Figure 3.25: A voltage is pressed over the sample circuit and the resulting current is measured. The sample is closed in a cryostat under high vacuum with controllable temperature.

glued onto the pads using silver paste and carefully soldered to the connector plug (Fig. 3.28a).

Before mounting it in the cryostat (Fig. 3.28b) the holder was left for at least 12 hours to dry otherwise the glue gets swollen resulting in an unreliable temperature control. After plugging the external wires to the holder plug the cryostat was covered with a radiation shield and finally sealed with the external cover. A two stage vacuum system composed of rotational and turbo-molecular pump was engaged to depressurize the cryostat chamber below  $10^{-3}$  mbar. Finally the program had been set and the measurement could begin. The temperature range was swept step-by-step while stabilizing below the tolerance of 0.1 K at each temperature point before measuring the current vs. voltage curve. During the conductance scan the prescribed source voltage was pressed over the sample for 5 seconds before reading a sequence of the current values with 20 ms integration time and exporting the average value along with standard deviation error into a digital data file. The temperature scan interval stretched form the room temperature of 295 K till 18 K and backwards to get a comparison between cooling and heating data<sup>14</sup>.

Surprisingly the setup was able to measure with the accuracy down to several pA, reliably measuring resistances up to 50 G $\Omega$  with the leakage resistance of about 100 G $\Omega$ . As presented in the results in the following subsections the stability and accuracy of the measurement also surpassed our expectations thus making the data gathered with the system credible and accurate.

#### 3.4.2 The process of temperature annealing

The story so far was presented as a sequence of research stages that were encountered before finally reaching the point of the measurement. That is entirely true for the desired thinnest samples but for the thicker ones several studies have been made revealing

<sup>&</sup>lt;sup>14</sup>The duration of a cycle was roughly 14 hours.



Figure 3.26: The measurement setup, controlled by the custom made computer program, consisted of Keithley 238 measurement unit, Oxford Instruments cryostat, driven by the Edwards cryodrive 1.5 and two step vacuum system (rotational and turbo-molecular pump).

the full perspective of the goal assignment. As mentioned earlier the measurements were performed at some intermediate level mainly with the purpose to test the manufacture techniques (circuits, contact metals) and to become acquainted with the measured material. Let us stress that we could abandon the idea of a thin bundle measurement and obtain some results using the thicker bundles of several 100 nm, but we continued in the direction of thinnest ones since we believe that the basic nanowire nature could be revealed much better with only a few nanowires in a bundle. Nevertheless the experiences gathered by dealing with bigger, even macroscopical bundles were priceless since many aspects of the final measurement procedure have been revealed, while unfortunately opening yet another research battlefield.

Looking at similar systems like carbon nanotubes and molybdenum selenide nanowires [10, 11, 2, 4] we were expecting relatively low resistances in the range of resistance quantum for some arbitrary bundle, even more so since many nanowires in the bundle would conduct in parallel reducing the common conductance roughly by a factor of nanowire number in the bundle compared to a single nanowire conductance. The first results were



Figure 3.27: The program sets the measuring sequence on the individual level for the voltage as well as for the temperature.



Figure 3.28: a) The silicon plate carrying the circuit was glued onto the copper cryostat holder and connected to the in-built connector socket via gold wires. b) The holder was screwed onto the cryomount and plugged to the measurement wires.

shocking since the values of resistance proved to be in the order of several  $G\Omega$ , far from

the most optimistically expected fraction of 1.3 k $\Omega$  in ballistic transport through one nanowire. Repeated experiments only confirmed this behavior even more dramatically for the thinnest bundles. Comparing the measurement procedures we discovered that the post-productional treatment is needed in order to evoke current through the sample. The process is called *annealing* and is usually performed simply by baking the circuit in the oven. We wanted to go a step further since the process is not well understood and we can only speculate about what is happening. One can look at the phenomenon from two different points of view: the contact between the bundle and the metal from the circuit guides changes (improves) or the bundle itself undergoes a structural change. From the basic chemical properties we knew that the material appears stable in the atmospheric conditions up to 300°C (the material tends to get disintegrated due to oxygen) and in vacuum up to  $900^{\circ}C$  [13, 21]. Relying on that, we performed an annealing effect survey on the circuit resistance for different circuit production techniques, different contact metals and for different MoSIx stoichiometries [25]. The circuits were produced and measured accordingly in several different ways: a macro bundle suspended on a glass plate (1  $\mu$ m diameter and 2 mm in length) directly connected with silver paste (Fig. 3.29a), four probe measurement for the contacts over a 220 nm thick, 2  $\mu$ m long bundle and two probe measurement of dielectrophoretically attached bundles (DEP) of different stoichiometries. Desperately trying to reach thinnest bundles we even designed a measurement using special conductive atomic force microscopy (CAFM) techniques provided by our AFM microscope. As depicted on the artistic expression on Fig. 3.29b a deposition of bundles over a silicon oxide wafer was lithographically covered with a stripe contact hoping to partially imbed single bundles beneath. The metal contact acted as one measurement pole and the conductive (platinum/iriduim covered) AFM tip as the other. This experiment turned out to be quite demanding and in the end destructive. The most challenging was as expected the positioning of the tip over the bundle, obstructed by the intrinsic tip drift, and the contact formation. Initial mechanical and voltage treatment was necessary in order to evoke current through the bundle, often resulting in a total destruction of the bundle. This was the main reason why we couldn't compare the effect of annealing on the same circuit and used two for each condition. Since the structural integrity needed to be preserved the annealing temperature was set to 700°C for an hour in vacuum. The circuits got annealed after the raw material was integrated into a circuit except for the macro-bundle where the raw material got thermally treated and afterwards connected directly with silver paste to the measurement contacts (Fig. 3.29b).

The results gathered in the table 3.1 clearly show that for the dielectrophoretically deposited bundles the annealing improved the conductance by roughly three orders of magnitude for three different stoichiometries; the comparison of data before and after annealing is presented on Fig. 3.30b. This huge conductance improvement implies that indeed the connection between the bundle and the metal plays an important role in the electron transport. Also the four probe measurement supports this assumption since the measurement by design pushes out the contact resistances revealing the bare conductivity of the sample; the comparison of data before and after annealing is presented on Fig. 3.30a, where only modest modification of the conductance improvement was noticed. We can draw the same conclusion from the CAFM measurements since the conductivity for



Figure 3.29: a) A suspended macro-bundle is glued directly to the measurement wires with silver paste. b) Partially covered thin bundle is tested for conductance at several points using a conductive AFM tip as one pole and the metal stripe contact as the other.

both cases ranged in the same magnitude even though the conductivity on the titanium changed dramatically (point B on Fig. 3.31b and point 4 on Fig. 3.31c).

	Before annealing $[\mathrm{Sm}^{-1}]$	After annealing $[\mathrm{Sm}^{-1}]$
Material (measurement method)	(contact metal)	(contact metal)
$Mo_6S_3I_6$ (2-probe freestanding)	/	9.5 (Ag)
$Mo_6S_3I_6$ (4-probe lithography)	0.07 (Ti) - 0.3 (Pd)	2.5 (Pd)
$Mo_6S_3I_6$ (CAFM)	0.37 (Ti) - sample 1	0.52 (Ti) - sample 2
$Mo_6S_3I_6$ (DEP)	$1.3 \ge 10^{-4}$ (Ti)	0.135 (Ti)
$Mo_6S_{4.5}I_{4.5}(DEP)$	$3.7 \ge 10^{-5}$ (Ti)	0.057 (Ti)
$Mo_6S_2I_8$ (DEP)	$2.3 \ge 10^{-5}$ (Ti)	0.048 (Ti)

Table 3.1: Single bundle conductance at 295 K.

As briefly pointed out earlier this survey addressed also the issue of metal choice for the production of circuits. A thin metal layer can exhibit special and unforeseen properties when introduced to high temperatures. Under such conditions material migration can be expected especially for softer metals or metals with poor adhesion. Also chemical properties can play an important role since many substances otherwise inert at room temperatures become vividly reactive when heated. We totally abandoned the idea of using gold in combination with some adhesive layer (nickel, chromium, titanium) mainly due to poor lithographic properties (see section 3.1.3). The alternative was pure titanium or more inert palladium. We knew that titanium oxidizes fast at high temperatures but we were hoping that our vacuum (low amount of oxygen) was good enough to reduce this effect so that the measurements wouldn't be affected. If titanium worked after annealing for the



Figure 3.30: a) A current vs. voltage characteristics for the four probe measurement of a bundle before and after annealing; the conductivity raises by roughly one order of magnitude b) whereas for the DEP circuits three orders of magnitude improvement was observed. The insets are the AFM images of the circuits with the scale bar of 2  $\mu$ m length for the left and of 250 nm for the right image.

DEP circuits it proved to be totally inadequate for the sensitive CAFM measurements. As depicted on the resistance vs. length (the distance between the contact point between the AFM tip and the bundle) diagram in Fig. 3.32b the linear curve includes contribution from the bundle and from the metal. The extreme value of  $R_0 = 4.2T\Omega$  gives the raw contribution of the titanium contact the alarming range of T $\Omega$ . Even direct measurement on the titanium (point 4 in Fig. 3.31c) confirmed that value. We believe, that the metal oxidized at high annealing temperatures covering otherwise good conducting electrode with a non-conductive oxide film.

One might argue that to the total resistance also the narrow AFM tip contributes along with its touching point but as seen from the conductance curve of pure titanium before annealing (point B on Fig. 3.31b) the resistance is estimated at around 20M $\Omega$  thus negligible compared to overall resistance of the whole circuit (G $\Omega$  for the point A on Fig. 3.31b or T $\Omega$  for annealed sample from Fig. 3.31c).



Figure 3.31: a) The conductance AFM cross section scheme of the experiment. b) The measurement of the non-annealed (70 nm diameter) and c) of the annealed circuit (6.5 nm diameter).



Figure 3.32: a) Resistance as a function of distance form the titanium contact for the annealed circuit from Fig. 3.31b). b) Current vs. voltage characteristic of the titanium contact and the bundle for the non-annealed sample from Fig. 3.31c.

We concluded that the titanium contacts oxidize severely transforming otherwise metallic and conductive material into poor conductor even into an insulator; the oxide can even be identified with the ball-shaped structures on the surface of the metal see on the AFM images from Fig. 3.31c. Let us add that for thin bundles the CAFM technique proved not to be an adequate method for conductance measurements partially due to hard positioning and mechanical destruction hazard but mainly due to extremely difficult current awakening in the bundle with or without annealing. In fact the activation stress turned out to be too violent and the bundles got often destroyed even before performing any measurements. These results convinced us to return to the path of dielectrophoretical attachment as the only strategy with good prospects for the measurement of the thin bundles. Once more we changed the metal for the production of the contacts from titanium to nickel since thin contacts required for thin bundles cannot be produced with favorable palladium (see section 3.1.3).

While performing first measurements on thin bundles we were confronted with similar problems as for the CAFM since the current through the circuits wasn't detectable with our setup (upper resistance limit was several hundreds of  $G\Omega$ ) and the process of annealing became a necessity. As presented in Fig. 3.33 ideally after the treatment the bundle survives and the metal contact doesn't show severe feature formation. Moreover we can even observe bundles submerging into the metal (Fig. 3.33c) establishing a better electric connection. This unique and exciting effect is present only on nanoscales since thin metal films possess new and unfamiliar properties compared to the bulk material. Most relevant in our case is of course the lowering of the melting point of thin films [41], that most probably in combination with surface tension and atmospheric conditions mediates the reformation of topographic structure of the layer.



Figure 3.33: The sequence of AFM images of ideal annealing outcome: a) the initial situation, b) the blowup from the previous image and c) the circuit after temperature treatment shows slight buckling of the metal surface with the unspoiled bundle submerging under the metal.

Unfortunately this favorable annealing property had also the downside since the perilous nature of high temperature treatment caused the destruction of many circuits and even bundles (Fig.  $3.34a1 \rightarrow 3.34a2$ ). Mostly we observed vivid buckling of the metallic surface manifested extremely high topographic features sometimes causing even the contacts to fuse and create short connections (Fig.  $3.34b1 \rightarrow 3.34b2$ ). Even strange crystalline formations (Fig.  $3.34c1 \rightarrow 3.34c2$ ) were observed only proving yet again another poorly controllable and understood circuit preparation. This final bottleneck pushed the whole experiment to a new level. Many times we got excited over finally being able to produce a bundle integrated into a circuit but faced a cold shower such as in the case of bundle exemplary cutting, where perfect circuit had been produced but got completely destroyed; the sad ending of that circuit is depicted on Fig. 3.35.



Figure 3.34: The AFM images of typical annealing downsides:  $a1) \rightarrow a2$ ) the bundle disintegrated,  $b1) \rightarrow b2$ ) contacts were fused together creating short connection and (c1)  $\rightarrow$  (c2) crystalline formations on top of metal layer.



Figure 3.35: The sequence of AFM images of a circuit destruction: a) the initial situation, b) the destruction of the bundle and c) a view of the whole buckled contacts with extreme topography.

#### 3.4.3 Measured samples

The necessary annealing process comes in package with great circuit losses but we were still pushing towards a successful measurement knowing that we couldn't expect many repetitions. Let us itemize the finale recipe of required steps to produce and post-treat the circuits in order to make successful measurements:

- 1. the whole amount of sample from the synthesis ampoule is sonicated for 5 minutes in acetone using an ultrasonic tip, left to sediment for seven days, dried and redispersed in isopropanol in glass reservoir using ultrasonic bath,
- 2. with e-beam lithography 25 nm thick nickel electrodes with 200 500 nm wide gaps are produced on a silicon wafer with 600 nm of silicon oxide on top,
- 3. a thin bundle is deposited from a droplet over the gap using 50 Hz signal with the amplitude 10 mV for 10 seconds before flash drying it with nitrogen gas,
- 4. the circuit is annealed in vacuum (in a sealed ampoule vacuumized till  $2 \cdot 10^{-5}$ ) mbar at 700°C for an hour,
- 5. finally the circuit is glued with heat conductive resin to a cryostat and the pads are connected using silver paste to 25  $\mu$ m thick gold wires that are soldered to the electronic socket.

Countless attempts finally paid off and we produced and successfully measured four samples. On the Fig. 3.36 are presented the AFM images of the samples with their diameter and length gathered in table 3.2. The nomenclature was left original and is composed of the prefix "na" that denotes the abbreviation for "nanos" (in English "deposition"), and the identification number.

sample signature	diameter[nm]	length[nm]
na12	5	530
na23	4.2	265
na27	4	200
na28	12.5	190

Table 3.2: The diameter and the length of the measured samples.



Figure 3.36: The gallery of all successfully measured samples: a) na12, b) na23, c) na27 and d) na28.

These four samples represent the core of our work and the results of their currentvoltage measurement are presented and discussed in the next chapter. All other measurements on thicker bundle chips were manufactured and prepared by the procedures described in this chapter.

# Chapter 4

# **Results and discussion**

In the previous section we described in detail the experimental background that lead to the successful current vs. voltage measurements of four nanobundle integrated chips at various temperatures. Despite reaching our predetermined goal of testing the thinnest wires, the obtained results don't promise reliable statistics. On the other hand in the case of homogeneous sample with stable and uniform structures of single nanowires one can expect reproducible results with slight discrepancies among them, making only few measurements sufficient to explore the properties of target structures. Unfortunately when dealing with real systems this is hardly the case. As already debated in the chemical structure section 3.2 our material shows multi-phase stabilities in terms of stoichiometries, allowing also a great number of structural defects in an individual wire. Each nanowire is thus a unique system with unique transport properties that can vary widely as debated in theoretical section 2. This awareness was our main motivation to continue with painstaking sample production in order to get as many repetitions as possible, since in the worse case scenario the measured chips would exhibit unrelated characteristics, which would be exciting from a theoretical point of view.

As presented further in this section our palette of the thinnest four samples makes a statistical compromise by separating them roughly into two groups according to the basic shape of the IV curves at low voltages also exhibiting different underlying transport laws. Later on we add results of thick bundle measurements that again appear to form a separate group. We conclude the chapter with the discussion of the annealing effect and the overall comparison of measurements, justifying the term "integrated chip" over simply a "nanowire circuit".

## 4.1 The thin bundles

We consider nanowires thin if their diameter falls below 15 nm. Since these minute objects cannot be directly examined in terms of their composition and fine chemical structure, the data about their shape comes only from their AFM images. Our nanobundles were individually introduced in Fig. 3.36 of the previous section, with their sizes gathered in table 3.2. The raw IV characteristics for each sample are presented in Fig.4.1. The close-to-linear curves at higher temperatures tend to bend as the temperature drops. Plotting

the normalized curves (Fig. 4.2), we observe two distinct shapes:

- 1. the "S" shape the VI curves remind of the letter "S" the samples na12 and na27,
- 2. the "J" shape the high voltage regime appears linear with smooth step leading towards zero voltage slope the samples na23 and na28.



Figure 4.1: The current vs. voltage characteristics from the room temperature till 18 K (from top till bottom): a) na12; the error bars depict high accuracy (0.5 % - 1 %) of the measurements and are omitted in all other graphs, b) na23, c) na27 and d) na28.

We introduced many transport mechanisms in the theoretical section but here we confine ourselves to the most likely ones also suggested and discussed in literature [10, 11, 4]: variable range hopping (section 2.5), environmental Coulomb blockade (sections 2.4 and 2.4.2) and the Luttinger liquid behavior (section 2.6). Mathematical expressions for each law can be tested on measurement data: the Luttinger liquid behavior law (2.174) allows all curves over all voltage ranges to collapse onto a single curve. Unfortunately the equivalently general result for the variable range hopping 2.159 has to be tested in low voltage limit that gives the known hopping behavior 2.170. The most tedious is the environmental Coulomb blockade theory that cannot be solved analytically for the general case, but demands temperature and voltage limitations in order to utilize quantitative analysis 2.144. Qualitatively the properties emerge only through numerical treatment,



Figure 4.2: The normalized current vs. voltage characteristics from the room temperature till 18 K (from top till bottom). The curves' development with dropping temperature are clearly seen. a) na12, b) na23, c) na27 and d) na28.

revealing linear dependencies for high voltages and smooth transition of the slope from zero voltage to high voltage regime (numerical depiction on Fig. 2.18). Let us describe the numerical treatment we follow in the analysis:

- Luttinger liquid The collapsing diagram of underlying law 2.174 is obtained by plotting  $I/T^{\alpha+1}$  against eV/kT (2.24). The  $\alpha$  is the slope of zero voltage conductivity against temperature in the loglog plot. The  $\beta$  is the exponent for the high voltage ( $eV \gg kT$ ) limit since the general law exhibits power law behavior  $I \propto V^{\beta+1}$ . The  $\gamma$  stands for the fitting parameter and adjusts the voltage drop over the circuit.
- Variable range hopping The plot  $\ln(G)$  (for low voltage) against  $T^{-\lambda}$  yields curves that become linear for the correct hopping exponent (table 2.5). To extract the most adequate mechanism the fits are tested for Pearson's correlation (values close to unity prove the best fits).
- **Environmental Coulomb blockade** Qualitatively the IV curves should exhibit linear dependence for high voltages with a smooth transition to zero voltage slope and the

derivative dI/dV approaches an asymptotic value. For low voltages and temperatures the dependance follows a power law behavior  $I \propto V^{2/g}$  (2.144).

#### 4.1.1 The "S" curves

The curves remind strongly of the Luttinger liquid sinh dependency. The loglog plot G vs. T for the **na12** reveals only remote resemblance to a straight line. We still fit a linear curve extracting the  $\alpha$  for three instances: low temperatures, high temperatures and over all points (Fig. 4.3a). The curves for the overall slope with  $\alpha = 2$  collapse relatively well, especially since we plot throughout the entire temperature range (Fig. 4.3b). We tested the collapse resilience of the other values of parameter  $\alpha$  for low and high temperatures (1.3 and 2.7), but the curves diverge severely for both cases (Fig. 4.3c and d). To obtain the Luttinger law fit the parameter  $\beta$  was extracted from the curve



Figure 4.3: a) The zero voltage conductance G vs. T gives three values of  $\alpha$ : 1.3 for the low temperatures, 2.7 for the high temperatures and 2 for the overall fit. b) The collapse diagram of all IV characteristics shows relatively good overlapping of the curves for  $\alpha = 2$ , especially if compared to very diverged plots of c) and d) for  $\alpha = 1.3$  and 2.7 respectively. The fit in the diagram b) was obtained using:  $I_0 = 1.1 \cdot 10^{-14}$ ,  $\alpha = 2$ ,  $\beta = 1$  and  $\gamma = 23^{-1}$ .

steepness of the IV curves, plotted in loglog scale (Fig. 4.4a). As mentioned, the power law should prevail at high voltage limit  $(eV \gg kT)$  that can be reached much easier at

lower temperatures. From the diagram  $\beta + 1$  (Fig. 4.4b) as a function of temperature we select the highest value at the lowest temperature ( $\beta + 1 = 2 \rightarrow \beta = 1$ ), since it should be the closest approximation to the correct value. It can also be seen that the zero voltage slopes remain constant and close to 1, thus in agreement with Ohm's law. The plot Fig.



Figure 4.4: a) The current vs. voltage characteristics are gathered on a LogLog plot, suggesting values for  $\beta + 1$  in the form of slopes at high voltages. b) The slopes  $\beta + 1$  are increasing with decreasing temperature as a result of departing from high voltage limit  $(eV \gg kT)$ , where the power law  $I \propto V^{\beta+1}$  holds. The arrow points the value of  $\beta + 1 = 2$  that was selected for further analysis.

4.3b with relatively good fit suggests that Luttinger liquid behavior probably contributes to the electron transport. Remarkably even the  $\alpha = 2\beta$  (Eq. (2.173)) prediction holds, reinforcing the suspicion that Luttinger liquid could be the most likely candidate for the electron transport through the system. Of the remaining possibilities only variable range hopping stands out, since the linear behavior for high voltages in the IV curves isn't observed, dismissing the environmental Coulomb blockade as the governing transport phenomena.

In Fig. 4.5a the conductance G is plotted against  $T^{-\lambda}$  for various exponents (from the table 2.5), together with the linear function fits in order to test the behavior. The values at low temperatures were not taken into account since noise-to-signal ratio increases for the lowest voltages and lowest temperatures yielding uncertain conductance values. Since different  $\lambda$  lie close together, a correlation<sup>1</sup> value between the fits and the data is compared in the histogram Fig.4.5b for each exponent, suggesting onedimensional hopping with the exponent 1/2, if the density of states is taken to be constant. Since this mechanism is also in a reliable agreement with the theoretical prediction, a definite answer cannot emerge.

Following the described analysis also the **na27** can be tested in a similar way. In this case the graph in Fig. 4.6a, yielding the Luttinger liquid parameter  $\alpha = 2.3$ , follows a straight line much closer to that in the previous na12. Moreover, the IV curves overlap even closer (Fig. 4.6b) suggesting that the Luttinger liquid could be the dominant transport mechanism. More disperse plots for other testing values of  $\alpha = 1.8$  and  $\alpha = 2.8$  (Fig.

<sup>&</sup>lt;sup>1</sup>High correlation yields the value closer to 1.



Figure 4.5: a) The G against  $T^{-\lambda}$  plots in a logarithmic scales shows tests of is different  $\lambda$  by comparing the linear fits for each curve. b) For quantitative comparison the Pearson's correlation between the fits and the data is compared. The values closest to 1 reveal the closest fits, in this case 1/2, suggesting 1D transport.

4.6c and d respectively) similarly prove the sensibility of curve collapsing, supporting the theory since the fitted  $\alpha = 2.3$  gives the best results. The loglog plots of the IV curves also show the Ohmic behavior at zero voltage and the increase of slopes for high voltages. In this case the value  $\beta + 1$  is taken to be 2.6 and thus  $\beta = 1.6$ . Here the equality  $\alpha = 2\beta$  isn't followed any more. When comparing the data to the variable range hopping the characteristic plots in Fig. 4.8a exhibit different behavior, since in this case the closest fit exponent is 1/4 according to Fig. 4.8b, suggesting 3D hopping as in opposite to 1D hopping found in the case of the na12.

Similar results were reported also by other researchers when measuring the transport properties of the molybdenum selenide nanowire bundles [10]. Their analysis of several samples comparable in size and structure<sup>2</sup> to ours shows two types of transport when compared to Luttinger liquid:  $\alpha \approx 2\beta$  and  $\alpha \approx \beta$ . The cases are related to the presence of the defects in the bundle; for a uniform structure the second equality holds, whereas breaking of the conducting channels may result closer to the first case. Our na12 appears to be closer to the disrupted channel structures, whereas the na27 contains fewer irregularities.

Also variable range hopping could be a part of transport mechanism since the characteristic plots follow theory's predictions. The dimensionality that is the main issue here appears to be different for both samples: na12 follows 1D and na27 3D hopping. This coexistence of both theories doesn't appear to be intrinsic for other nanowire samples. A report [11] on transport measurements of NbSe<sub>3</sub> nanowires dismisses the variable range hopping as a satisfactory possibility and focuses on the Luttinger liquid approach. Their samples on the other hand exhibit also the Peierls transitions with charge density wave properties, that yield falling conductance as a function of temperature; this was also the main reason for omitting the Wigner crystal theories in this report. We can speculate that in the mesoscopic systems the transport is governed by many effects resulting as a mixture of different mechanisms. Moreover the underlying phenomena exhibit qualitatively very

<sup>&</sup>lt;sup>2</sup>Both have molybdenum octahedra forming the backbone.



Figure 4.6: a) The zero voltage conductance G vs. T approximately follows a straight line with the slope  $\alpha = 2.3$ . b) The collapse diagram of all IV characteristics shows better overlap of the curves than for the sample na12. The diverging plots of c) and d) for the testing  $\alpha = 1.3$  and 2.7 make the results even more consistent since the ideal value turns out to come from the slope on the graph a). The fit in the diagram b) was plotted using:  $I_0 = 7.7 \cdot 10^{-16}$ ,  $\alpha = 2.3$ ,  $\beta = 1.6$  and  $\gamma = 18^{-1}$ .

similar behavior and follow strongly the level of impurities and disorder. These assumptions are supported by the data gathered for the na23 and na28, that show environmental Coulomb blockade behavior together with variable range hopping mechanism.



Figure 4.7: a) The IV curves in loglog plot suggest Ohmic law for zero voltage regime and power law for the high voltage regime. b) Also here the arrow points to the highest value of  $\beta + 1 = 2.6$  that is the closest to the real value.



Figure 4.8: a) The G against  $T^{-\lambda}$  plot in logarithmic scale shows a test of different  $\lambda$  by comparing the linear fits for each curve. b)  $\lambda = 1/4$  produces the closest fit, suggesting 3D hopping.

### 4.1.2 The "J" curves

In this group the IV curves from Fig. 4.1b and 4.1d and even especially the scaled data from Fig. 4.2b and 4.2d strongly resemble the numerical solutions of environmental Coulomb blockade (Fig. 2.18a). The diagram shows curves for different parameters g that are inversely proportional to the environmental resistance (Eq. (2.137)). For low resistances (or general impedances) the curves come close to straight lines or Ohmic behavior, whereas for the highest impedances a smooth transition between zero voltage slope and high voltage linear law is predicted<sup>3</sup>. Even though the theoretical results demand low temperatures, we can assume that the temperature dependence is hidden in the parameter g, consequently bending the curves with changing temperature. With this we actually allow the environmental resistance to change with temperature, which is quite plausible if not

<sup>&</sup>lt;sup>3</sup>With a bit of imagination the curves form the letter "J".

even predictable since our system resembles only remotely the quantum dot coupled to a Fermi reservoir as debated in the Coulomb blockade theory. The quantum dot (perhaps even more of them) would be in our case embedded within the nanobundle (Fig. 2.9b), thus profoundly changing the nature of the electron reservoirs. From the S-shape curves we learned that even Luttinger liquid and variable range hopping govern the resistance in the nanobundle leads, thus modifying the g and the shape of the curves. To test the theory the curves are normalized with the conductance prefactor that scales the curves according to the governing transport phenomena and thus the temperature.

Since the introduction plots from Fig. 4.2b and 4.2d are hard to read, we plot once more the curves (Fig. 4.9a and 4.9b for the samples na23 and na28), only that this time we pick fewer representative curves at proper temperatures and, following the numeric result, confine the data to the first quadrant with positive voltage and current. Despite



Figure 4.9: Normalized representative IV curves for the samples a) na23 and b) na28. Both diagram closely resemble the numerical predictions for the environmental Coulomb blockade theory shown on Fig. 2.18a.

the resemblance we are aware that the temperature drop wasn't severe enough and that the charging effect would be observed even more profoundly at lower temperatures. Nevertheless the shapes are reasonably convincing to confirm the environmental Coulomb blockade as an important transport mechanism. Even more convincing are the derivative plots from Fig. 4.10 since the transition from low to high voltage becomes more visible. From these graphs also the charging energy  $E_C = e/2C$  could be estimated, because at that voltage the transition of the slopes stands roughly in the middle between the low and high voltage value. Since the derivative graphs come with high errors, a completely numerical fit is used to extract the trends of the curves. We took the sum of the exponential approaching and the linear function:  $a + bx + c \exp[-x]$ . The plots are shown in Fig. 4.11 with the charging voltages 0.15 V and 0.13 V for na23 and na28 respectively that set the capacitance to  $\sim 5 \cdot 10^{-19}$  F. Just for the taste we plot also all curves' fits in the Fig. 4.12. If we take a step forward and totally omit the charging energy, the energy needed to enable transport equals only to the gap of the energy states on the dot (see section 2.4) instead of their sum. Now we can calculate the lowest limit of the dot size, since the omitted charging increases the size of the dot due to smaller quantum state


Figure 4.10: The derivatives of normalized curves from Fig. 4.9 for a) na23 and b) na28 show resemblance with the trends from numerical prediction of 2.18b.



Figure 4.11: Numerical fits of Fig. 4.10 reveal the core curve trends for a) na23 and b) na28.

gap. Assuming the dot is a potential well cube with edge length  $x_0$  and by taking the lowest occupied quantum number energy gap from Eq. (2.8), we get roughly  $x_0 \approx 1.7$  nm. The value is consistent with the diameters of both bundles (4.2 nm and 12.5 nm) since it physically allows a dot of that size to get formed inside of the nanobundle.

To test the power law of IV curves  $(I \propto V^{2/g})$  for low voltages we plot, same as in the case of the "S" curves, loglog plot of the characteristics (Fig. 4.13a for na23 and Fig. 4.14a for na28), only that this time we focus on the slopes around zero. The inner and outer slopes plotted on Fig. 4.13b for na23 and Fig. 4.14b for na28 expectedly gather around unity for high temperatures, since the curves become almost linear. The highest exponents are thus for the lowest temperatures with  $2/g \approx 2.1$  for na23 and 1.1 for na28. The discrepancy of the outer slopes towards linear unity, even exceeding the inner slopes, may again indicate other transport mechanism to be present.

Next we test the Luttinger liquid law. The central slope plots from Fig. 4.15a and Fig. 4.16a give hope due to linearity, but the actual collapse plots on Fig. 4.15b and Fig. 4.16b aren't as convincing. At least for the na23 the Luttinger liquid can be dismissed,



Figure 4.12: To complete the picture we plot the derivative fits for all measured curves of a) na23 and b) na28. Interestingly the asymptotic curves are not constant values, as expected form the core of the theory, but linear curves that imply other transport mechanism to be present.



Figure 4.13: Predicted power law for na23 at low voltages has the exponent around 2 and falls close to unity for the temperatures, when the curves become close-to-linear. The power law growth for higher voltages again suggest other transport mechanisms.

whereas the curves for the na28 do overlap reasonably with a successful fit using  $\beta \approx 0.27$ , which is close to values from Fig. 4.14b (the maximum value is 0.22). Compared to the general Luttinger liquid law, the typical knee in the collapse plot is smeared out, mainly as a consequence of low  $\beta$ . The variable range hopping testing plots for na28 from Fig. 4.18a reveal good agreements with the theoretical predictions, with the 3D hopping for constant density of states sticking out (Fig. 4.18b). The treatment for the na23 on the other hand isn't as convincing, since the data gets more scattered around the linear fit (Fig. 4.17a). The correlations from Fig. 4.17b promotes 1/3 or even 2/5 to be the correct exponent  $\lambda$ , implying 2D hopping with a constant density of states or 3D hopping with linear density of states to be present.

By observing all measured samples we can conclude that in nanobundle integrated



Figure 4.14: The predicted power law for the na28 at low voltages has the exponent around 1.1 for the lowest temperature that we have reached. The high voltage slopes, similarly than for the na23, imply another transport mechanism but less vivid, since the slopes never exceed the value of 1.2.



Figure 4.15: a) The zero voltage conductance G vs. T approximately follows a straight line with the slope  $\alpha = 3.5$ , but b) the collapse diagram of all IV characteristics shows no overlap of the curves.

chips a variety of physical phenomena govern the electron transport through the system. Impurities, stoichiometric disorder, growth and structural defects are the main factors that set the transport properties of the material not only globally but also locally since each individual object exhibits unique behavior. Very surprising is the observation of multiple mechanisms acting in the system simultaneously, almost never individually. Most commonly observed is the physics of the Luttinger liquid, since fundamentally the system is strongly onedimensional or composed of strongly onedimensional objects. This comes as a surprise, since the theory we used to test this behavior uses a different model as a basis for the calculation. There a onedimensional strand, with few or none broken spots, is connected to Fermi liquid reservoirs, whereas in our cases, the strands are gathered in a thick and disordered bundle. The equally powerful mechanisms evoke through the size and density of disorder, usually in the form of variable range hopping and environmental



Figure 4.16: a) The zero voltage conductance G vs. T again follows a straight line with the slope  $\alpha = 2.3$  and b) The collapse diagram of all IV characteristics shows better overlap of the curves than for the sample na23. The typical knee in the fit is smeared out compared to na12 and na27. The fitting parameter are:  $I_0 = 1.9 \cdot 10^{-15}$ ,  $\alpha = 2.3$ ,  $\beta = 0.27$ and  $\gamma = 17^{-1}$ .



Figure 4.17: a) The tested variable range hopping plot suggests this mechanism to present even though the relatively scattered points make the b) correlation histogram less reliable. The best fit appears to be 1/3 or perhaps even 2/5.

Coulomb blockade. The first one could be the consequence of random onedimensional channel discontinuities forcing the electrons to hop according to the disorder topography (thus setting the hopping exponent and the dimensionality) between the strands, whereas bigger and bulkier islands or topological kinks could split the bundle entirely, thus forming a quantum dot that allows the electrons to pass only by paying the charging energy which results as the environmental Coulomb blockade. The environment plays an important role, since in the raw theory the dot gets connected to rigid Fermi reservoirs as opposed to our case, where the island separates two Luttinger liquid (also disordered) leads. In the end we could say that the systems behave as disrupted Luttinger liquid coupled to Fermi liquid and sometimes to a quantum dot. As mentioned, theoretically only the coupling Fermi liquid - Luttinger liquid has been studied and was also used for our analysis. Based



Figure 4.18: a) Once more the variable range hopping appears to be present with more reliable b) correlation histogram, that predicts the exponent to be 1/4.

on the described models, the nanobundles from samples na12 and na27 are composed of disordered Luttinger liquid Fig. 4.19a, whereas the second set of na23 and na28 includes a huge isolated island with disordered Luttinger liquid reservoirs Fig. 4.19b. Now it is not hard to accept the observed result that variable range hopping and Luttinger liquid behavior govern the "S" group and the "J" group includes environmental Coulomb blockade and variable range hopping. The vanishing or at least diminishing of Luttinger liquid transport mechanism in the "J" group could be a consequence of the high disorder that might chop the onedimensional nanowires to short strands, obstructing Luttinger liquid formation. Similarly we can say that for the na12 the disorder already severely disrupts the nanowires in the bundle, whereas in the case of na27 the strands remain mostly intact, facilitating better agreement with the Luttinger liquid law.



Figure 4.19: a) The proposed model predicts disrupted onedimensional strands connected to Fermi liquid reservoirs for the "S" curve group and for the group "J" a radical disorder (on the scheme an isolated island forms a quantum dot) splits the entire bundle causing charging effects for the electron transport.

In general the conductance properties are presented by the conductivity  $\sigma$  at room temperature and by the maximum current density value. The table 4.1 contains the data and calculated values.

sample	D[nm]	l[nm]	I[nA] (295 K,1 V)	$\sigma = \frac{I}{V} \frac{l}{S} [\text{S/m}]$	$j_{\rm max} = \frac{I}{S} [{\rm GA}/{\rm m}^2]$
na12	5	530	300	8100	1.5
na23	4.2	265	622	11900	4.5
na27	4	200	233	3710	1.6
na28	12.5	190	469	730	0.4

Table 4.1: The basic conductive properties of measured samples.

#### 4.2 The thick bundles

The preliminary measurements were performed on thick bundles above 500 nm in diameter [25]. In contrast to the thin bundles they show totally straight IV characteristic, thus following Ohm's law. This was one of the reasons why obtaining thin bundle data became our primary goal since we expected that if one dimensional properties are to be observed, thin bundles would reveal them. The temperature dependence on the other hand still shows variable range hopping behavior which again supports the thesis of disorder in the bundles affecting if not dominating the transport. Also the issue of low conductivities before annealing was addressed. The temperature treatment at 700°C for an hour improved the conductivity by three orders of magnitude, from 0.1 nS (10 G $\Omega$ ) to  $\sim 100 \text{ nS}$  (10 M $\Omega$ ). We also compared the measurements of samples before and after annealing to get the insight into transport mechanisms. Two different samples were tested on variable range hopping in the same way as for the thin bundles. Fig. 4.20a and Fig. 4.21a before and after annealing prove the hopping to be present in both cases, but with different dimensionality. Correlation histograms from Fig. 4.20b and Fig. 4.21b suggest 3D hopping before ( $\lambda = 1/4$ ) and 1D ( $\lambda = 2/3$ ) after annealing, with different density of states dependence (constant before and linear after annealing, according to the table 2.5) If change in conductivity is indisputability observed, the variable range hopping



Figure 4.20: a) Before annealing the variable range hopping plots are in relatively good agreement with the theory. b) The correlation histogram predicts the exponent to be 1/4 thus 3D hopping with a constant density of states.



Figure 4.21: a) Also after annealing variable range hopping is present, but the hopping dimension changes according to b) correlation histogram to 1D with the exponent 2/3 and linear density of states.

dimensionality transition isn't definite. We have to keep in mind that these were two different samples (650 nm and 500 nm in diameter) and based on the individual properties of different bundles observed in thin samples, this transition could be simply an intrinsic property of each bundle, not being induced by annealing. To get better insight into this effect same circuit was measured before and after annealing. In order to do that the technological issues, that arose from relatively high annealing temperature, needed to be solved. Namely the silver paste and the thermally conductive varnish used to attach and glue the chip onto the cryoholder and to connect the chip pads to gold wires (see section 3.4) were unstable at high temperature and would evaporate during the annealing, thus destroying the chip. We were forced to compromise and to totally omit the use of any heat conductive media and to connect the chip pads through press contacts similar to the ones used in dielectrophoresis from Fig. 3.19. Of course the whole mechanical connector assembly needed to fit into the cryomount from Fig. 3.28b so we constructed it in the form of round plastic disc with contact pins<sup>4</sup> placed on three springs that enabled the positioning of the pins' height through three screw bolts; the photograph of the connector is shown in Fig. 4.22a and 4.22b. We are aware that omitting the heat conductive varnish would result as progressive temperature discrepancy from the nominal value set by the measurement temperature controller and the actual value, thus obstructing full quantitative analysis used in other measurements. On the other hand due to the same experimental conditions the data could be compared for qualitative change. In Fig. 4.23 an improvement in conductivity by a factor of 300 is observed which is consistent with other measurements. When compared to variable range hopping laws, the curves depart from a straight line for low temperatures as expected, especially true for the curves after annealing (Fig. 4.24a before and Fig. 4.25a after annealing). The correlation histograms from Fig. 4.24b and Fig. 4.25b show in both cases convincingly 1D hopping law with the exponent 1/4. The graphs after annealing were fitted until 110 K, to get complete comparability with the data before annealing, and also throughout all points, to check for

<sup>&</sup>lt;sup>4</sup>The pins were taken from a mobile phone.



Figure 4.22: a) The press pin connector assembly enabled the measurements without the use of varnish or the silver paste and b) most importantly, it fits in the cryostat making the temperature scans possible.



Figure 4.23: The IV curve slopes before and after annealing show an improvement in conductivity by almost three orders of magnitude. The scan before annealing ends at 110 K since we didn't want to risk any damages to the chip.

possible change in the exponent also when the data is treated as a unity. No discrepancy was found.

We even went a step further and tried to determine the influence of the thermoconductive paste that we omitted. For that we measured the same chip twice, first "non-glued" and "glued". As presented in Fig. 4.26 the measured conductances at the same nominal temperatures differ severely, indicating that the real temperature of the sample is much higher than the measured one and therefore we cannot reliably extract the main transport mechanism from the data. We can conclude that also thick bundles are submitted to variable range hopping, but neither Luttinger liquid behavior nor Coulomb blockade phenomena were observed. We believe that due to high dimensionality, perhaps even different internal structure, the onedimensional strands, if present, do not contribute to the



Figure 4.24: a) The variable range hopping plots could be present with 3D hopping according to b) the correlation histogram.



Figure 4.25: a) Also after annealing variable range hopping could be present at least until 110 K. For lower temperatures the data points naturally depart from a straight line due to discrepancy of real temperature over the set temperature. b) Correlation histograms for fits over all data and until 110 K suggest 3D hopping with the exponent 1/4 to govern the hopping.

overall transport or the contributions aren't sufficiently strong. Possible isolated islands could separate the bundle only at bigger sizes (approximately the bundle diameter) but in that case the charging, while passing through it, wouldn't play any decisive role thus dismissing any form of Coulomb blockade. Importantly the annealing experiments indisputably confirmed substantial conductance improvement and even suggest that the transport mechanism through the bundle doesn't change upon annealing and consequentially that the structure remains unaltered. The change in conductance could be a consequence of the connection improvement between the bundle and the metal contact. We believe that since the material gets in contacts with many chemical compounds during sample preparation, the bundle surface might react, forming a thin layer of isolative molecules that prevent injection of electrons in the bundle. High temperatures could disintegrate such molecules thus facilitating better electronic contacts.



Figure 4.26: The data depart severely implying temperature discrepancy form the nominal towards the actual value. Since the lowest conductance for the non-glued sample aligns with the value at  $\sim$ 130 K for the glued one, the temperature never dropped below this temperature in the non-glued case.

Unfortunately the story doesn't end here. For some bundles we observed what we call "the cycling" effect, where the conductance vs. temperature curves change several times after each temperature scan before settling. This observation is discussed in the following subsection.

#### 4.2.1 The cycling effect

This phenomenon was observed two times, based on pure chance since all circuits' manufacture procedures were identical. In Fig. 4.27a and 4.27b the observed cycling curves of the conductance G vs. T are presented for the samples na\_double (two bundles of 40 nm and 50 nm both bridging the gap) and na13 (a single bundle with 60 nm in diameter). In the first case the transition appears to occur at room temperature, just before starting a new cycle, whereas in the case of the na13 the first transition happened at 110 K and the others again after starting new scan. By looking at the IV curves we noticed in the first case (Fig. 4.28a) that the characteristics were completely linear for each measured temperature, whereas for the na13 the curves show familiar bending for the first cycle until the transition at 110 K where they straighten up and remain linear for all other points. On the Fig. 4.28b the bending trend<sup>5</sup> for the last point before transition (point A for the Fig. 4.27b) is shown along with the straight curve at the lowest point (point B for the Fig. 4.27b) in the last cycle at 15 K, where the curvature, if present, should have been the most expressed. We can even notice that during the IV scan at point A, for the positive voltages, the current values start to scatter, implying that some change is occurring in the bundle/chip. This suggests that the transition at 110 K is different, perhaps more profound compared to all other ones. Our suspicion is confirmed when the data get tested on variable range hopping behavior. From the Fig. 4.29a we notice that the data before transition appears to be in agreement with the 1D variable range

<sup>&</sup>lt;sup>5</sup>Not surprisingly, since the bundle isn't very thick.



Figure 4.27: The conductance curves tend to change upon each temperature scan before settling: a) for the sample na\_double and b) for the na13. Also the shape of the curves is different compared to what we observed for other chips, since the conductance appears to reach some minimum value at each cycle.



Figure 4.28: a) The IV characteristics for the na\_double are completely linear as for the most measured points of na13 except for the beginning of the first cycle, where the curves exhibit familiar bending. b) On diagram are presented the curved characteristic for point A and the linear dependance for point B from Fig. 4.27b.

hopping (the exponent  $\lambda = 1/2$  from histogram Fig. 4.29b), whereas all other curves tend to depart for a straight line, following some other transport law. The sample na\_double, on the other hand, doesn't show this profound transition (Fig. 4.30a), but appears to have two regimes: the variable range hopping at high temperatures with the exponent 1/4, thus 3D hopping (from the histogram Fig. 4.30b) and the constant conductance at low temperatures.



Figure 4.29: a) For the na13 the variable range hopping appears to be present only in first part of cycle 1, whereas all others depart severely form straight lines. For clearer depiction the variable range hopping plot is shown only for the optimum exponent  $\lambda = 1/2$ , read from b) the correlation histogram of cycle 1 form room temperature until 110 K.



Figure 4.30: a) For the na\_double the variable range hopping is present only for higher temperatures. We present only the plot for the settled last cycle 5 since all other resemble closely. b) the correlation histogram implies the 3D hopping with the exponent 1/4 to be present for all cycles.

These observations can be explained qualitatively if we take a look at the fundamentals of the variable range hopping theory (section 2.5). We learned that in general the disordered systems form a band with the localized states in the extremities and the nonlocalized ones in the middle, forming a continuum of states (Fig. 4.31). The conductive properties are related to the position of the Fermi energy inside of the band. If it lies deep in the non-localized region the conductance should have metallic properties with constant conductance<sup>6</sup> with respect to temperature, but if it is surrounded by many localized states, the variable range hopping governs the transport. Since our nanowires/nanobundles structurally differ form each other, also band structure and consequently the position of the

<sup>&</sup>lt;sup>6</sup>We overlook the phonons.

Fermi energy alters for individual samples. To explain the cycling effect we have to go one step further by assuming that the bundle structure changes during temperature scans, resulting as the formation/vanishing of localized and non-localized states. To observe such transitions the Fermi energy must lie close to the mobility edge<sup>7</sup>  $E_C$  so that the conversion of states would change the Fermi level neighborhood, thus altering the conductance properties. In general, there are three possibilities of the Fermi level position (Fig. 4.31): I.  $E_F^{\rm I}$ is in the lower localized state extremity, II.  $E_F^{\rm II}$  is in the middle of the continuum band and III.  $E_F^{\rm III}$  is in the upper localized extremity. In the first case, a semiconductor behavior at high temperatures could be observed, since the electrons can get excited into the continuum band, passing the gap  $E_C - E_F^{\rm I}$  (2.157), and the variable range hopping for lower temperatures, where the electrons remain confined in the localized states. The second



Figure 4.31: For a general Fermi glass band structure, we have three possibilities for the Fermi level position: I.  $E_F^{\rm I}$  is in the lower localized state extremity, II.  $E_F^{\rm II}$  is in the middle of the continuum band and III.  $E_F^{\rm III}$  is in the upper localized extremity. If for the I. and II. the Fermi level lies close to the mobility edge, the Fermi function could excite the electrons above the gap  $E_C - E_F^{\rm I,II}$  to the neighboring region.

case should result as metallic behavior, due to the continuum nature of the surrounding states, with the conductance proportional to the number of states of at the Fermi level. If the level is placed close to the upper mobility edge, also the upper localized states would be initialized at higher temperatures, adding variable range hopping to the transport. In the last case the variable range hopping should be present exclusively, since the electrons remain confined to the localized states for the entire temperature range. This is also the most observed behavior, suggesting high disorder, with many localized states and with Fermi level in the upper localized extremity. If we now apply the transitions of localized to non-localized states and place the Fermi energy closer to the mobility edge (Fig. 4.32a), then indeed the broadening on the continuum states could overpass the Fermi level, thus changing its surrounding states from localized to non-localized (Fig. 4.32b).

<sup>&</sup>lt;sup>7</sup>The energy that separates the localized and non-localized states.

Consecutively also the initial variable range hopping is replaced by metallic behavior, expressed as constant conductance at low temperatures. Realistically, only limited amount of states becomes non-localized, thus placing the Fermi level still close to the mobility edge. At high temperatures in such a situation the electrons would, according to the Fermi function, get excited also to the upper localized states (Fig. 4.32b), adding also the variable range hopping to the overall transport, but not in the strict form, since also the temperature dependance of the Fermi function adds to the behavior. By looking at the cycling data, this scenario could be recognized: at the beginning in the sample na13 the Fermi energy is lying in the upper localized states extremity, close to the mobility edge (the scheme in Fig. 4.32a). During the first cycle it follows variable range hopping until 110 K (Fig. 4.29), where some of the localized states become non-localized, with the mobility edge passing the Fermi energy, but with the Fermi function still reaching into the localized states region, thus contributing to the conductance, but only at higher temperatures, where the overlapping of the Fermi function and the localized extremity is substantial (the scheme in Fig. 4.32b).



Figure 4.32: a) In special cases the Fermi energy lies in the upper extremity of the localized states, just after the continuum of the non-localized states. b) Upon structural change in the bundle some of the localized states become non-localized, effectively causing the mobility edge to travel outwards, passing the Fermi level.

The subsequent cycles don't exhibit such profound changes, since new non-localized states only push the mobility edge away from the Fermi level, thus only changing the limiting conductance at low temperatures due to the reformation of the band states, that influences also the density of states at the Fermi energy and thus the conductance. The sample na\_double could be explained in similar way, only that here the Fermi energy lies from the beginning in the non-localized part of the band (as on scheme in Fig. 4.32b), with cycling influencing only the low temperature conductance limit. In contrast to the na13, here the variable range hopping is confirmed for high temperatures with the exponent  $\lambda = 1/4$  remaining constant for all cycles, thus placing the mobility edge close to the Fermi level.

The assumption of localized to non-localized transitions is based on high structural disorder that may facilitate soft localized states, which can become non-localized even for slight modification in structure<sup>8</sup>. The driving force, that induces such changes, could be the dissipative electric energy in form of heat that could rearrange the structure. We believe that it is more likely for a localized state to become non-localized, since changes always tend to improve structural order by minimizing the free energy, thus sometimes passing the Anderson localization criterion from localized to non-localized state. This suggests the transitions to be irreversible, which was supported also by the measurement data.

Just to show that these structural changes can produce a variety of cases we report on the most intriguing measurement we came across (Fig. 4.33). The data exhibits in one scan from the lowest till room temperature three transitions, the second one even to lower conductances which is in contrast to our observations in the cycling data. At the end the system didn't settle down and the conductance continued to wobble. Each section has its



Figure 4.33: The most intriguing measurement shows three jumps (at 123 K, 140 K and 170 K) in the same temperature scan, each time changing the slope and the hopping exponent (Fig. 4.34)

own slope, implying that the conductance regions differ quite severely when we tested the data on variable range hopping<sup>9</sup>, even the exponents changed profoundly, since  $\lambda$  started with 3/5 or 1/2, jumped to 1/4, raised to 1 and finally returned to 1/4, as in contrast to e.g. na\_double where the hopping dimensionality remained constant.

We can only speculate about the scenario that could explain such a sequence, we can only say that the structural changes appear to be rather radical, vividly changing the neighboring states of Fermi levels, perhaps even producing disorder and new electron traps.

Considering all presented results, a general picture emerges regarding the MoSIx nanowires from the perspective of the electron transport measurements. The highly dis-

 $<sup>^{8}\</sup>mathrm{This}$  could happen if such states include weak electron traps, that could vanish upon structural change.

<sup>&</sup>lt;sup>9</sup>Lets keep in mind that the regions are quite short thus following closely a straight line.



Figure 4.34: a) The regions appear to be governed by variable range hopping, but b) with different exponents: I - 2/5 or 1/2, II - 1/4, III - 1 and IV - 1/4.

ordered tendency, predicted by general chemical properties and the synthesis procedure, was confirmed, since no transport mechanism was found to exclusively govern the system. For the thin ones, this is particularly true and the combinations of variable range hopping and Luttinger liquid properties or environmental Coulomb blockade phenomenon were observed. For the thicker bundles mostly the variable range hopping is observed, with no convincing indications that other mechanisms are involved. From the cycling effect we can deduce that thicker bundles can have more ordered structure, enabling the formation of continuum states inside the bands, thus expressing yet another type of transport that involves simple metallic behavior and variable range hopping mechanism. We can get this impression also by looking at the AFM images where thin wires and a majority of the thicker ones appear to be soft and bendy. We believe that these are the ones with higher disorder and are also mostly observed in the experiments. But there are also some rigid bundles among the thick ones above  $\sim 50$  nm, which we believe could be some other stable phases, perhaps even elongated crystalline structures with crosslinks between the bundles. The necessary annealing process used in the chip production also confirms the reports of stability of the material in vacuum at least up to 700°C and suggests an intrinsic wrapping of bundles with an isolative layer. Its chemical nature is still a matter of debate, all we can say is that from our perspective this contamination can be a good explanation for poor electric connection to the contact metal and its dramatic improvement as the film disintegrates at high temperature during the annealing process.

# Chapter 5 Conclusion

The presented work on electronic transport properties included steps form the sample preparation, the circuit manufacture using electron beam lithography, single bundle integration into the measurement chips with annealing procedure, the actual measurements and finally the result analysis according to relevant transport mechanisms. Unfortunately searching for successful sample preparation took most of our research time, since the material composition wasn't clear, nor were the basic chemical properties that would help us prepare single bundle dispersions. The task proved to be even more demanding because our main goal was to test the thinnest bundles which were especially hard to find. Nevertheless we found a recipe to prepare an extraction of single bundle by using big amounts of initial material and by dispersing it in acctone, that turned out to be the best solvent for our material. Modifying the electron beam lithography technique we manufactured measurement electrodes on the oxidized silicon wafer. We determined the optimal distance of the gap between the channels to be several hundreds of nanometers, based on the observation that smaller distances would facilitate multiple objects to bridge the gap, whereas in the opposite case the thinnest bundles prove to be to short to reach both electrodes. When dealing with bundle attachment over prefabricated electrodes, gentler dielectrophoresis turned out to be the best way to extract single and thin bundles from a dispersion as in opposite to the aggressive electrophoresis that attracts charged particles, resulting as extremely dense depositions even using low voltages. In fact, both methods turned to be much more effective than we needed and even 10 mV, 50 Hz AC background signal was sufficient to isolate only few bundles from a dispersion. Not only the AFM was an irreplaceable way to monitor sample preparation and dielectrophoretical attachment, it proved to be a powerful tool to clean the circuits, cut selected bundles and even to perform conductance measurements. If for primer imaging a general silicon nitride tips in tapping mode provided sharp and noninvasive images, for cleaning and measuring platinum/iridium covered tips were the most suitable for the job. The second one for the obvious reason of establishing an electric contact, whereas for cleaning the slight potential on the conductive tip turned out to pick up the unwanted debris altogether, not only pushing them aside. To finalize the bundle integration into a chip, an unexpected annealing procedure was necessary in order to improve conductance (or conductivity) into the accessible measurement ranges. The high temperature during annealing turned out to be

quite destructive, since in many cases the bundles got disintegrated or the contacts fused together, creating short circuits. In successful treatments, on the other hand, the bundles remained intact that implies unaltered structure after annealing. Closer examination for all bundle thicknesses revealed up to three orders of magnitude improvement, but with different values. The thicker ones showed conductivity between 0.05 and  $10 \text{ Sm}^{-1}$ , whereas for the thinnest the value increased up to  $11900 \text{ Sm}^{-1}$  for the absolute champion. From the relative improvement we could conclude that the connection between the metal and the bundles gets altered, most probably on the account of impurity wrapping, that could cover the bundles due to relatively high reactivity and substantial use of different solvents in the process of sample preparation. The enormous discrepancy in absolute value between thick and thin bundles could be explained, if only nanowires in direct contact to the electrodes or in their vicinity actually carry the current; the fraction is estimated below 1 % for the thick bundles. This relatively low conductivity for the preliminarily measured thick samples was also one of the main reasons to push our research towards measuring the properties of the objects with the lowest diameters. When we finally succeeded to measure several thin samples we found, along with higher conductivities, also different transport properties. If the thick ones showed linear IV characteristics, the curves got severely bent for the thin bundles. Studying the work of other researches we tested our data on three main theories: the variable range hopping, the environmental Coulomb blockade and the Luttinger liquid. Since we were expecting for our material to include disorder, the variable range hopping was on the top of the list. Indeed we confirmed its presence in thick and also in thin bundles, but with different hopping dimensionalities/exponents. Mostly for the thick ones the variable range exponents 1/4 and 1/2 or 3D and 1D hopping were observed, thus with constant density of state. Annealing also appeared to have no effect on the dimensionality, confirming the assumption that the bundles preserve their structure during temperature treatment. When we turned our attention to the thin samples we observed two groups according to the IV curves. For the "S" group we got convincing confirmation that the Luttinger liquid applies as well, whereas in the "J" group there was strong evidence of charging effect implying that also the environmental Coulomb blockade also governs the transport. This combination of transport mechanisms could be perhaps explained by assuming that a bundle is composed of onedimensional nanowires, broken randomly in many places, sometimes even with an isolated island separating bundle in half. The first case could hold for the "S" curves and the charging from the "J" group could come from the separation island that acts as a quantum dot. These possibilities have never been theoretically explored, most probably due to tedious treatments involved. The cycling effect found for some thick bundles made the measured results even more exciting, since the conductance changed for each temperature scan and even during scans. By looking at the fundamentals of the variable range hopping theory we propose a transition of some localized states to non-localized states to explain the behavior. We believe that if in such a case the Fermi energy would be close to the mobility edge and the effect of several localized states turning to non-localized states would be observable. For the drastic transition during scans we believe that the mobility edge passes the Fermi level, placing it into the continuum part of the band, resulting as profound temperature dependance change. In other cases the level is falling deeper into the continuum, only changing the

conductivity limit at low temperature as the theory predicts. This explanation qualitatively fits the results perfectly, but for quantitative analysis we believe that a theoretical treatment would be needed.

We can conclude by saying that we succeeded to develop all necessary steps from the raw sample in form of black wooly dust till the final measurement of integrated chips. The obtained results were reliable and showed a combination of transport mechanisms. For the future work we propose additional measurements, since perhaps also other phenomena could be revealed, and also additional theoretical exploration of the transport mechanisms combinations for disordered onedimensional wires.

### Razširjeni povzetek v slovenščini

## Poglavje 6

### Uvod

Nanotehnologija vedno bolj prodira med klasične in moderne znanstvene discipline. Posebej se uveljavlja v temeljnih raziskavah v medicini, elektroniki, fiziki, biokemiji, kemiji,...; kjer odpira nove možnosti na področjih diagnostike, informacijske tehnologije, zdravljenja raka, pri sintezi novih kompozitov. Tej novi tehnologiji daje posebno moč in potencial velikostna skala delcev. Ce obvladujemo in razumemo svet atomov preko kemije in njej sorodnih disciplin ter makro svet od astronomskih razsežnosti do mikrosveta skozi veje fizike in inženirskih znanosti, potem nanotehnologija zapolnjuje vrzel med molekulami in mikronskimi razsežnostmi, zato pravimo, da se ukvarja z mezoskopskimi sistemi. Kar ji daje poseben potencial, je ravno združitev zahtev mejnih svetov: visok fizični nadzor nad delci velikosti nekaj nanometrov z natančno predpisano sestavo na atomskem nivoju. Približevanje temu idealu bi omogočilo oblikovanje novih rešitev in razširitev razumevanja ustroja sveta. Če je sinteza teh novih nanomaterialov že močno razvita (nanoprahovi, nanocevke, nanožice, fine membrane), je področje vodenja in nadzorovanega vgrajevanja nanogradnikov v večje sestave še vedno v primežu laboratorijskih raziskav in je zaenkrat še na nivoju eksperimentalnega dela. V prvi vrsti izziv zahteva zanesljivo opazovanje nanoelementov, ki ga omogočajo šele modernejše tehnike mikroskopiranja (elektronski mikroskop, mikroskop na atomsko silo, tunelski mikroskop), primarna manipulacija posameznih objektov pa v večini primerov sloni na modificiranih napravah z vgrajenimi mikromanipulatorji. Takšen pristop se največkrat uporablja pri temeljnih raziskavah merjenja osnovnih fizikalnih lastnosti snovi, medtem ko se spontano samourejanje kljub omejenemu nadzoru kaže kot možna pot k splošnejši uporabi in nenazadnje k novim aplikacijam tako v znanosti kot v industriji. K zaokrožitvi področja spada gotovo še razvoj ustreznih perifernih tehnik izdelave mikrovezij, instrumentalnih naprav in novih tehnik merjenja, ki jih v makrosvetu sicer ne poznamo. Predvsem gre tukaj za pomemben vpliv okoljskih motenj in približevanja svetu kvantne mehanike, ki mnogokrat vpliva na meritve in izvedbe eksperimentov. Prav posebej pa je treba poudariti razvoj rokovanja z materialom, ki ga največkrat zaradi praškastih oblik priročno razpršujemo v izbranih topilih. Takšen pristop povleče za sabo kopico novih možnosti in obenem pasti, saj ne smemo pozabiti da gre za drobne delce z drugačnimi kemijskimi in fizikalnimi lastnostmi. Tako se velikokrat večino raziskav usmerja v iskanje ustreznega postopka (pred)priprave vzorcev materialov, ki omogočijo uspešno sestavo in izvedbo eksperimentov z zanesljivimi in natančnimi rezultati. V svetu je močno razvito področje raziskav ogljikovih nanocevk

in sorodnih kompozitov, kar je potisnilo razvoj miniaturnih vezij na osnovi elektronske [1] in fotolitografije na višji nivo ter s tem omogočilo izdelavo vezij z integriranimi nanoobjekti. Meritve elektronskih lastnosti ogljikovih nanocevk so pokazale enodimenzionalno obnašanje Luttingerjeve tekočine [2, 3, 4, 5, 6] in efekte impedančne Coulombove blokade, ki jih napovedujejo teoretične obravnave [7, 8, 9]. Tudi študije elektronskih lastnosti anorganskih nanožic (niobijev in molibdenov selenid) so potrdile prisotnost Luttingerjeve tekočine, v nekaterih primerih pa poročajo tudi o mehanizmu spremenljivega preskakovanja [10, 11], ki ga obravnava teorija Fermijevega stekla in opisuje vpliv nehomogenosti v strukturi na lastnosti snovi [12]. V tem doktorskem delu smo se posvetili obravnavi temeljnih transportnih lastnosti anorganskih nanožic na osnovi molibdena, žvepla in joda s splošno oznako  $Mo_6S_xI_{9-x}$ , ki jih poznamo tudi pod signaturo MoSIx [13, 14]. Študije na makroskopskih tabletkah so obravnavale propagacijo zvoka [19] in optične lastnosti [15, 16, 17, 18] moritvo električnega transporta na mrožah panosvečniov [21, 22] in

Studije na makroskopskih tabletkah so obravnavale propagacijo zvoka [19] in opticne lastnosti [15, 16, 17, 18], meritve električnega transporta na mrežah nanosvežnjev [21, 22] in tankih filmih [20] pa so podobno kot pri drugih anorganskih nanožicah pokazale prisotnost preskakovalnega mehanizma pri prevajanju elektronov. Kar daje prednost anorganskim kompozitom pred organskimi je boljša kompatibilnost z osnovnimi kemijskimi topili in predvsem z vodo, kot so pokazale raziskave topnosti svežnjev MoSIx [23, 24], to pa je odločilnega pomena za vstop nanomaterialov na biokemijsko področje. Tudi njihova lastnost samourejanja in enostavne funkcionalizacije z različnimi (bio)materiali [26] jim daje poseben potencial in prednost pred drugimi spojinami in to je bil eden temeljnih razlogov za usmeritev raziskav v to družino nanožic. Meritve prevodnosti na posameznih debelejših svežnjih (s premerom nad 50 nm) so prav tako pokazale prisotnost preskakovalnega mehanizma [1, 25], nas pa so zanimale električne transportne lastnosti najtanjših svežnjev. S fizikalnega vidika so zanimive zaradi svoje strogo nizkodimenzionalne zgradbe, ki predvideva obstoj faze Luttingerjeve tekočine, pričakovane nehomogenosti pa bi še dodatno vplivale na transport elektronov.

Pričujoče doktorsko delo vsebuje dopolnitev in nadgradnjo izdelave vezij z elektronsko nanolitografijo, iskanje postopkov za pripravo razpršin nanožic oz. nanosvežnjev v katere se povezujejo, njihovo integracijo v miniaturna vezja, izvedbo meritev in analizo rezultatov skozi napovedi nekaterih temeljnih teoretičnih obravnav električnih lastnosti enodimenzionalnih sistemov.

## Poglavje 7

### Teoretične napovedi

Efekti kvantne mehanike postajajo izrazitejši šele na nizkih, (sub)nanometrskih skalah, zato so nanožice, nanocevke, tanki filmi, nanodelci zanimivi tudi iz teoretičnega vidika. Ker je naše delo vključevalo tudi meritve električne prevodnosti na realnih objektih, v tem razdelku predstavljamo nekatere možnosti elektronskega transporta, predvsem skozi nizkodimenzionalne, prostorsko omejene sisteme, obenem pa se posvetimo še obravnavi vpliva naključnih sipalnih mest na transportne lastnosti skozi sistem.

### 7.1 Kvantne pike in (impedančna) Coulombova blokada

Pod tem izrazom mislimo na izoliran, z nekim potencialom omejen prostor v katerem se prosto gibljejo elektroni. Obravnava takšnega sistema [27] [28] v osnovi zahteva izračun energijskih stanj in pripadajočih valovnih funkcij preko Schrödingerjeve enačbe:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi = E\,\psi,$$
(7.1)

kar da za primer enodimenzionalnega harmonskega potenciala

$$V = \frac{1}{2}m\omega^2 x^2 \tag{7.2}$$

ekvidistančno lestvico energijskih stanj s kvantnim številom n:

$$E_n = \hbar\omega(n + \frac{1}{2}). \tag{7.3}$$

Lastne funkcije  $\psi_n$  so Hermitovi polinomi oblike:

$$\psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} (2^n n!)^{-\frac{1}{2}} H_n\left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}x\right].$$
(7.4)

Grafično so stanja in verjetnostna porazdelitev za prvih nekaj lastnih funkcij prikazane na sliki 7.1.



Slika 7.1: Energijska stanja za enodimenzionalni harmonski oscilator (levo) in verjetnostna porazdelitev prvih nekaj lastnih stanj (desno); barve črt na obeh diagramih pripadajo istemu kvantnemu številu n.

Ker so realni otočki tridimenzionalni zapišimo še rešitve, ki jih za nesklopljene dimenzije dobimo kar iz enodimenzionalnih rešitev z dodajanjem novih kvantnih števil. Tako dobimo tri kvantna števila  $n_x$ ,  $n_y$  in  $n_z$  ter s tem dopolnitev lastnih stanj z dodatnimi členi v (7.5) in valovnih funkcij s faktorji v obliki Hermitovih polinomov v (7.6):

$$E_{n_x, n_y, n_z} = \hbar \omega (n_x + n_y + n_z + \frac{3}{2}), \qquad (7.5)$$

$$\psi_{n_x,n_y,n_z} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} e^{-\frac{m\omega}{2\hbar}(x^2+y^2+z^2)} \left(2^{n_x+n_y+n_z}n_x!n_y!n_z!\right)^{-\frac{1}{2}} \cdot H_{n_x} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}x\right] H_{n_y} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}y\right] H_{n_z} \left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}z\right].$$
(7.6)

Soroden je tudi rezultat za stopničast potencial, oz. za potencialno jamo širine  $x_0$ ,  $y_0$  in  $z_0$  le da stanja niso več ekvidistančna, funkcije pa so sinusi (v resnici linearna kombinacija sinusov in kosinusov glede na robne pogoje):

$$\psi_{n_x,n_y,n_z} = \left(\frac{2}{x_0}\right)^{\frac{1}{2}} \left(\frac{2}{y_0}\right)^{\frac{1}{2}} \left(\frac{2}{z_0}\right)^{\frac{1}{2}} \sin\left(\frac{n_x\pi x}{x_0}\right) \sin\left(\frac{n_y\pi y}{y_0}\right) \sin\left(\frac{n_z\pi z}{z_0}\right),$$

$$E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{x_0^2} + \frac{n_y^2}{y_0^2} + \frac{n_z^2}{z_0^2}\right).$$
(7.7)

Ko se velikost pike zmanjšuje, se energijska razlika med stanji povečuje dokler ne preseže tipične energije termičnih fluktuacij kT. Nad tem pragom meja med zasedenimi in prostimi stanji postane zelo ostra, kar posledično vodi pri transportnih meritvah elektronov do zanimivega pojava izmenjavanja prostega in zaprtega prevajanja glede na meritvene parametre. Pojav prepovedanega transporta imenujemo  $Coulombova \ blokada([8] 5. poglavje).$ 

Kot pri večini neposrednih meritev električne prevodnosti tudi v tem primeru na merjenec, torej kvantno piko, priključimo dva Fermijeva rezervoarja oz. dve elektrodi (izvor ter ponor), v bližino pa postavimo še elektrodo, preko katere lahko induciramo polje v merjencu in jo imenujemo vrata. Shema postavitve je prikazana na sliki 7.2. Pika je z



Slika 7.2: Kvantna pika je priključena na izvorno in ponorno elektrodo, v bližini pa so postavljena še vrata, ki s svojim potencialom vplivajo na polje merjenca.

rezervoarji sklopljena le kapacitivno, kar pomeni, da energijska stanja ostanejo nespremenjena, vendar pa obenem dovoljujemo preskakovanje elektronov iz rezervoarjev na piko in obratno. To je mogoče le (v limiti  $T \rightarrow 0$ ), kadar sta Fermijevi energiji  $E_F$  poravnani z najnižjim stanjem upoštevaje dodatne energije zaradi kapacitivne sklopitve  $e^2/C$ ter zunanjega polja vrat  $\phi_{\text{ext}}$ . Račun preko velike kanonične porazdelitve daje pogoj za prevajanje v obliki:

$$E_N + \left(N - \frac{1}{2}\right)\frac{e^2}{C} = E_F + e\phi_{\text{ext}}.$$
(7.8)

Ta pogoj razdelimo na preskok na piko (7.9) in z nje (7.10); obakrat je na piki N elektronov:

$$E_N + \frac{e^2}{2C} = E_F + e\phi_{\text{ext}}(N-1),$$
 (7.9)

$$E_N - \frac{e^2}{2C} = E_F + e\phi_{\text{ext}}(N).$$
 (7.10)

Obe situaciji sta tudi grafično prikazani na sliki 7.3.



Slika 7.3: a) Pogoj za tuneliranje elektrona na piko zahteva, da je najvišje nezasedeno stanje pike  $e^2/2C$  pod  $E_F$ . b) Zaradi kapacitivne sklopitve pike z elektrodami, elektron doda energijo  $e^2/C$ , zato se novo stanje dvigne za  $e^2/2C$  nad  $E_F$ . c) Ko elektron na koncu tunelira v ponorno elektrodo, se energijska stanja vrnejo v prvotno konfiguracijo.

Pogoji prevajanja se še obogatijo, ko dodamo vpliv vrat in natančno ločimo med posameznimi kapacitivnostmi  $C_1$ ,  $C_2$ ,  $C_g$  ter obravnavamo naboj  $q_1$ ,  $q_2$ ,  $q_0$  na stikih med piko in elektrodami, kakor je prikazano na sliki 7.4.



Slika 7.4: Kvantna pika s tunelskima stikoma med izvorom na potencialu  $V_S$  in ozemljenim ponorom. Tuneliranja skozi vrata ne dovolimo, pač pa na piki preko kapacitivne sklopitve inducirajo dodaten zvezni naboj.

Da bo transport omogočen, mora biti razlika proste energije pri tuneliranju dodatnega elektrona  $n_1 + 1$  na piko ter enega s pike  $n_2 - 1$  negativna. Rezultat računa so premice, ki omejujejo območja blokade za parametra  $V_S$  in  $V_g$ , obenem pa ločijo med sabo še število elektronov na piki med posameznimi odprtimi režimi prevajanja. V diagramu 7.5  $V_S$  proti  $V_q$  pogoje za prevajanje zapišemo v obliki:

$$V_S > \frac{C_g}{C_2 + C_g} V_g + \frac{e}{2(C_2 + C_g)} - \frac{ne}{C_2 + C_g},$$
(7.11)

$$V_S < -\frac{C_g}{C_1} V_g - \frac{e}{2(C_1)} + \frac{ne}{C_1}.$$
(7.12)



Slika 7.5: V diagramu družine pogojev (7.11) in (7.12) svetlejši paralelogrami označujejo območje blokade. Strmini  $k_1$  in  $k_2$  pripadata posameznemu številu elektronov na piki n z ničlami  $-e/2C_g + ne/C_g$ .

Vendar pa tudi ta opis sistema za realne meritve toka v odvisnosti od napetosti še ni zadosten, saj moramo v splošnem upoštevati še končno impedanco merilnega sistema([8] 2. poglavje). Jedro teorije, ki jo imenujemo *Impedančna Coulombova blokada*, se ukvarja z vplivom poljubne impedance  $Z(\omega)$  na prehajanje elektronov skozi tunelski stik, kakršni se tvorijo med kvantno piko in izvorno oz. ponorno elektrodo. Simbolna shema na sliki 7.6b ponazarja takšno dopolnjeno obravnavo priključitve napetosti V na tunelski stik z neko splošno končno impedanco  $Z(\omega)$ . Problem se rešuje preko hamiltoniana, sestavljenega iz kvazidelcev v elektrodah, zunanje impedance ter tuneliranja:

$$H = H_{\rm qd} + H_{\rm imp} + H_T.$$
 (7.13)

Tok skozi stik je sorazmeren z razliko stopenj tuneliranja v eno in drugo smer:

$$I(V) = e(\overrightarrow{\Gamma}(V) - \overleftarrow{\Gamma}(V)), \qquad (7.14)$$



Slika 7.6: a) Shema tunelskega stika s stopnjo prehajanja elektronov  $\Gamma$  v smereh, kot jih nakazujejo puščice. b) Tunelski stik s kapaciteto C in upornostjo  $R_T$  je sklopljena z zunanjo napetostjo V preko splošne zunanje impedance  $Z_{\omega}$ .

ki ju dobimo iz Fermijevega zlatega pravila upoštevajoč prehod iz začetnega stanja  $|i\rangle$  v končno stanje  $|f\rangle$ :

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | \widetilde{H}_T | i \rangle \right|^2 \delta(E_i - E_f).$$
(7.15)

Problem je analitično rešljiv le v limitah nizke temperature in nizke oz. visoke napetosti:

$$I(V) = \frac{e^{-2\gamma/g}}{\Gamma(2+2/g)} \frac{V}{R_T} \left[ \frac{\pi}{g} \frac{e|V|}{E_C} \right]^{\frac{2}{g}} \text{ pri } T = 0 \quad \text{K} \quad \text{in } V \to 0, \qquad (7.16)$$

$$I(V) = \frac{1}{R_T} \left[ V - \frac{e}{2C} + \frac{g}{\pi^2} \frac{e^2}{4C^2} \frac{1}{V} \right] \qquad \text{za} \qquad V \to \infty,$$
 (7.17)

kjer je  $g = R_Q/Z(0)$  ter  $R_Q = h/e^2$ . Zaradi teh omejitev pri analiziranju meritev globalnih prilagoditvenih krivulj nimamo, tako da se moramo zadovoljiti le z ocenami ter kvalitativno primerjavo z rezultati numerične analize, prikazane na sliki 7.7. Ta teoretična napoved torej predvideva za nizke temperature in napetosti potenčno odvisnost toka od napetosti (7.16) z eksponentom  $2/g = 2Z(0)/R_Q$ , nato pa prehajanje preko kolena v linearno funkcijo s strmino  $1/R_T$  (7.17).



Slika 7.7: Numerične krivulje pri T = 0 za  $g = \infty, 20, 2, 0.2$  in 0 od zgoraj navzdol. a) IV karakteristike s b) pripadajočimi odvodi dI/dV, ki se za visoke napetosti približujejo konstantni vrednosti  $1/R_T$ .

#### 7.2 Preskakovanje spremenljivega dosega

V realnih sistemih so nehomogenosti, nečistoče in ostali strukturni defekti neizogibni. V predhodnjem razdelku smo obravnavali primer izoliranega otočka, tudi segmentiranega sistema, ki združuje še vedno veliko število gradnikov nanostruktur. Bolj subtilni defekti na nivoju atomov imajo drugačen vpliv na transportne lastnosti, ki jih obravnava teorija Fermijevega stekla[12]. V osnovi dodajanje nereda vpliva na periodičnost in homogenost potenciala, ki vodi iz začetnih nelokaliziranih do lokaliziranih stanj preko Andersonove lokalizacije. Konkretno lahko rečemo, da se idealni kristalni potenciali, s popolnoma določeno periodo in konstantno globino z nehomogenostmi preoblikujejo v neperiodične oz. nekristalne potenciale. Ena izmed možnosti obravnave predvideva modifikacijo globin posameznih potencialnih jam, kar močno vpliva na strukturo energijskega pasu, kot je prikazano na slikah 7.8a in 7.8b.

Razmerje  $V_0/B$  opisuje odmik od popolne kristalne strukture in je temeljni parameter te teorije. Izkaže se namreč, da z njegovim povečevanjem valovne funkcije, ki popisujejo takšen nekristalen potencial, potanejo lokalizirane. Za takšne funcije tudi rečemo, da izpolnjujejo Andersonov kriterij, pojav pa imenujemo Andersonova lokalizacija. Še več, ne glede na vrsto ali množino nehomogenosti se lokalizirana in nelokalizirana v energijskem pasu ne mešajo, pač pa se slednja koncentrirajo v centralnem delu, medtem ko prva tvorijo razširivene repe, obe območji pa sta ločeni z ostro mejo  $E_C$  oz.  $E'_C$ , imanovano tudi rob mobilnosti. Opisana zvonasta oblika gostote stanj je prikazana na sliki 7.8c.

Lastnosti sistema so seveda odvisne od položaja Fermijeve energije. Ce leži znotraj nelokaliziranih stanj, je prevodnost kovinska, če pa leži na koncéh oz. med lokaliziranimi stanji, lahko dobimo polprevodniško obnašanje ali pa transport teče v celoti preko prostih lokaliziranih stanj in sledi zakonu *preskakovanja spremenljivega dosega*. V prvem primeru se elektroni zaradi termične energije vzbujajo v nelokaliziran del pasu, kar opišemo s



Slika 7.8: a) Potencialne jame popolne kristalne strukture s pripadajočim energijskim pasom širine B. b) Vnos nehomomgenosti naključno spreminja globine potencialnih znotraj maksimalne magnitude  $V_0$ . Rečemo, da se kristalna mreža transformira v Andersonovo mrežo. c) Nelokalizirana stanja v Andersonovem modelu so centrirana v središču pasu, medtem ko lokalizirana stanja zapolnjujejo repa pasu in so ostro ločeni z robom mobilnosti  $E_C$  oz.  $E'_C$  on nelokaliziranih stanj.

poznanim izrazom za prevodnost polprevodnikov, le da širino reže $E_g$ nadomestimo z $E_C-E_F$ :

$$\sigma(0) = \sigma_{\min} e^{\frac{E_C - E_F}{kT}},\tag{7.18}$$

kjer  $\sigma_{\min}$  označuje prevodnost kontinuuma. Tudi v drugem primeru je dinamika preskakovanja odvisna od temperature, vendar je močno povezana z dimenzijami sistema d in disperzijo gostote stanj  $N(E) \propto E^{\mu}$ . V približku nizkega polja prevodnost popiše izraz:

$$\sigma = \sigma_0 e^{-\left(\frac{T_{\text{VRH}}}{T}\right)^{\lambda}} \quad \text{in} \quad \lambda = \frac{\mu + 1}{\mu + d + 1}.$$
(7.19)

Eksponenti  $\lambda$  za nekatere osnovne primere sistemov so zbrani v tabeli 7.1.

dimenzija	N(E)=konstanta	$N(E) \propto  E $	$N(E) \propto E^2$
1	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{3}{4}$
2	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{3}{5}$
3	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$

Tabela 7.1: Eksponenti  $\lambda$  iz izraza (7.19).

Ta teorija je nepogrešljiva pri obravnavi realnih sistemov, saj je strukturni nered vsaj na nivoju posameznih atomov prisoten že pri sintezi kompozitov in ga moramo upoštevati kot del temeljnega ustroja strukture.

#### 7.3 Teorija Luttingerjeve tekočine

Ce v makrosvetu teorija Fermijeve tekočine zadovoljivo opiše lastnosti elektronskega plina, v enodimenzionalnih sistemih temu ni več tako. Ne moremo namreč več govoriti o elementarnih vzbujenih stanjih kot o kvazidelcih, ampak le o kolektivnih vzbujenih stanjih. Rečemo lahko tudi, da v eni dimenziji korelacije med delci ostajajo močne, kjub šibkim interakcijam, torej ravno naprotno od tridimenzionalne obravnave, kjer korelacije ostajajo šibke, kjub močni interakciji. Nov opis sistema tako zajema teorija Luttingerjeve tekočine [6, 5]. Naštejmo nekaj njenih temeljnih lastnosti:

- 1. vzbujena stanja niso več elementarna, pač pa kolektivna,
- 2. vzbuditve naboja in spinske vzbuditve (holoni in spinoni) nimajo energijskih rež,
- 3. zaradi elektronskih interakcij se vzbuditvi (tudi hitrosti) za naboj in spin ločita, kar onemogoči kvazidelčni opis,
- 4. parametra  $K_{\nu}$  (ekvivalent Landauovim parametrom v teoriji Fermijeve tekočine),  $v_{\nu}$  popolnoma popišeta fizikalne lastnosti Luttingerjeve tekočine.

Preko obravnave na osnovi bozonizacije je moč izpeljati izraz za prevodnost v obliki toka v odvisnosti od napetosti:

$$I = I_0 T^{1+\alpha} \sinh\left(\frac{\gamma eV}{2kT}\right) \left| \Gamma\left(1 + \frac{\beta}{2} + i\frac{\gamma eV}{2\pi kT}\right) \right|^2.$$
(7.20)

V izrazu nastopata parametra  $\alpha$  in  $\beta$ , ki se nanašata na stik med dvema Luttingerjevima tekočinama ( $\alpha$ ), če je sistem iz kakršnihkoli razlogov prekinjen in pa na stik med Fermijevo in Luttingerjevo tekočino ( $\beta$ ) na mestih, kjer je sistem povezan z zunanjimi elektrodami. Parametra sta povezana še z razmerjem Fermijeve ter holonske hitrosti  $g = v_F/v_{\rho}$ :

$$\begin{aligned} \alpha &= (g^{-1} - 1)/4, \\ \beta &= (g + g^{-1} - 2)/8, \end{aligned}$$
(7.21)

kar da v realnih sistemih z majhnim g zvezo  $\alpha = 2\beta$ . Parameter  $\gamma$  v izrazu (7.20) reskalira padec napetosti na dejansko vrednost, ki se v realnih meritvah razlikuje od nominalne vrednosti na instrumentu med meritvijo. Zberimo še temeljne lastnosti krivulj, ki so nam v vodilo pri obdelavi rezultatov meritev:

- 1. vse karakteristike pri različnih IV temperaturah se združijo v eno krivuljo, kadar jih predstavimo na diagramu  $I/T^{\alpha+1}$  v odvisnosti od eV/kT (slika 7.9),
- 2. pri nizkih temperaturah stik med Luttingerjevima tekočinama prevlada, zato pri nizkih napetostih prevodnost sledi potenčni odvisnosti  $G \propto T^{\alpha_{\text{LL-LL}}}$ ,
- 3. pri visokih napetostih prvlada stik med Fermijevo in Luttingerjevo tekočino, kar se izrazi v potenčni odvisnosti toka od napetosti  $I \propto V^{\alpha_{\rm FL-FL}+1}$ .



Slika 7.9: Združitvena krivulja za vse IV odvisnosti na diagramu  $I/T^{\alpha+1}$  v odvisnosti od eV/kT vsebuje tudi tipično koleno.

S to precej eksotično teorijo sklenjamo krog teoretičnih napovedi. V grobem smo tako spoznali možnosti transporta skozi idealne oz. popolnoma homogene sisteme ter skozi realne strukture, ki lahko vsebujejo tako defekte na nivoju posameznih atomov, kakor tudi v obliki izrazitih nehomogenosti, ki vodijo do izoliranih segmentov znotraj kompozita.

### Poglavje 8

# Nanožice MoSIx in izvedba eksperimenta

Glavni cilj doktorskega dela je bila meritev prevodnosti nanožic oz. svežnjev z distribucijskim imenom MoSIx. Sinteza materiala ni bila del raziskav, saj smo ga dobili od podjetja Mo6 d.o.o.<sup>1</sup>, vse druge korake priprave vzorca, izdelovanja vezij, intergracije svežnjev v merilna vezja in končne meritve pa smo izvedli sami. V tem razdelku predstavljamo kemijsko stukturo nanožic ter pripravo in izvedbo eksperimenta.

### 8.1 Nanožice MoSIx

Kemijsko gre za širšo skupino anorganskih nanožic molibdena, žvepla in joda s sorodno stihiometrijo pod skupno formulo  $Mo_6S_xI_{9-x}$  [14, 13]. Posamezne nanožice so kompoziti molibdenovih oktaedrov, zaporedno povezanih preko treh žveplov v vezni ravnini z atomi joda, ki obdajajo osnovni skelet (slika 8.1). Struktura je podobna veliki skupini



Slika 8.1: Zice MoSIx sestavljajo molibdenovi oktaedri, povezani z vezno ravnino treh žveplov in obdani z atomi joda. a) S strani je povezava med oktaedri preko vezne ravnine lepo vidna. b) Prerez preko oktaedra prikazuje možno konfiguracija joda okoli molibdena.

Chevrelovih faz s splošno formulo  $M_xMo_6X_8$ , kjer M označuje kovino, X pa enega izmed halkogenidov. Poleg tega se posamezne nanožičke zdužujejo v svežnje, vendar med seboj niso povezane preko kemijskih vezi, kakor je to običajno pri Chevrelovih fazah. Na sliki 8.2 so prikazane celice nekaterih sorodnih struktur s poudarkom na mrežnih vezeh. Zaradi

<sup>&</sup>lt;sup>1</sup>Mo6 d.o.o., Tehnološki park Ljubljana, Teslova 30, SI-1000 Ljubljana, Email: info@mo6.com

te množice podobnih struktur je bila sinteza naših žičk zelo delikatna, kakor tudi kasnejša priprava razpršin za integracijo žičk v merilna vezja.



Slika 8.2: a) Osnovna celica svežnja nanožic MoSIx in b), c), č) nekaterih podobnih Chevrelovih faz z označenimi mrežnimi vezmi.

Nekatere osnovne lastnosti teh žičk so napovedale tudi teoretične študije [37]. Po teoriji gostotnih funkcionalov ima gostota elektronskih stanj na Fermijevi gladini vzdolž žice končno vrednost (slika 8.3a), kar uvršča snov med prevodnike s prevodnostjo okoli  $5 \cdot 1000$  S/cm v vzdolžni smeri. Analiza mehkih vezi med molibdenovimi okatedri preko veznih ravnin žvepla je pokazala dve stabilni konfiguraciji na različnih razdaljah (slika 8.3b), kar vnaša intrinzičen in naključen nered v osnovo naše strukture.



Slika 8.3: a) Teorija gostotnih funkcionalov napoveduje končno gostoto elektronskih stanj na Fermijevi gladini. b) Analiza proste energije položajev veznih atomov žvepla med molibdenovimi oktaedri razkriva dve različni stabilni razdalji med njimi. Temu rečemo tudi *efekt harmonike*.

#### 8.2 Priprava razpršin in izdelava merilnih čipov

Za rokovanje z nanodelci je morda najprimernejša priprava njihove razpršine, saj jih je na ta način moč nanašati, ločevati na frakcije, redčiti in nenazadnje kemijsko modificirati. Naš cilj je bila meritev prevodnih lastnosti najtanjših svežnjev, morda tudi posameznih nanožičk. Kot osnovno strategijo za izdelavo merilnega čipa smo izbrali dielektroforetično integracijo oziroma nanašanje individualnih svežnjev iz razpršine preko reže med dvema tankima elektrodama (8.4a). Vezje z režo smo izdelali z elektronsko nanolitografijo [1], kjer z elektronskim curkom narišemo izbrani vzorec preko tanke plasti elektronsko občutljivega polimera (8.4b) (v našem primeru dve plasti: 190 nm PMMA/MAA/33% in 90 nm PMMA 950k) na silicijevi rezini s 600 nm debelo plastjo oksida, kamor po razvijanju (8.4c) napršimo 20 - 25 nm niklja (8.4č), ki ostane na substratu po končni odtopitvi odvečnega polimera v obliki narisanega vzorca (8.4d).



Slika 8.4: a) Shema nanosvežnja preko ozke reže med kovinskima elektrodama na neprevodnem substratu. Nanolitografski postopek sestavljajo: b) pisanje z elektronskim curkom preko elektronsko občutljivega polimera, c) razvijanje oz. odtopitev porisanih območij, č) nanašanje kovine, d) po odstranitvi preostalega polimera ostane na površini kovina v obliki risanega vzorca.

Da bi se želenemu cilju približali, je morala razpršina zadoščati nekaterim zahtevam:

- monodisperzija,
- zadostna populacija najtanjših svežnjev,
- malo nečistoč,
- nizka stopnja aglomeracije in stabilnost razpršine,
- izbira ustreznega topila glede na dielektroforezo.

Preizkusili smo različne vrste topil, koncentracij materiala, strategij razprševanja in priprave frakcij. S spektroskopijo v ultravijoličnem in vidnem območju smo izkustveno oblikovali testiranje vsebnosti nanosvežnjev v razpršinah. Kot je prikazano na spektrih na sliki 8.5a smo povezali položaje vrhov proti višjim energijam z vsebnostjo tanjših svežnjev. Tudi rumenkasti odtenki (slika 8.5b) razpršin so bili korelirani z višjimi koncentracijami drobnih svežnjev, medtem ko so modrikaste razpršine vsebovale debelejše strukture z močno aglomeracijo, nestabilnostjo razpršin in močno sedimentacijo (slika 8.5c).



Slika 8.5: a) Razpršine tankih svežnjev imajo najnižji vrh nad 1,78 eV oz. pod 700 nm, medtem ko je pri debelejših svežnjih vrh pomaknjen k nižjim energijam oz. k višjim valovnim dolžinam. Fotografiji razpršin b) tankih svežnjev s tipičnim rumenkastim odtenkom in c) debelih svežnjev z modrikasto barvo in močnejšo sedimentacijo.

Kot uspešen recept za pripravo razpšin se je izkazal sledeči postopek:

- 1. celotno količino materiala iz sintezne ampule razpršujemo 10 minut z ultrazvočno konico v 50 ml acetona,
- 2. razpršino pustimo sedem dni, da se največji delci posedejo na dno,
- 3. 10 ml stabilne razpršine dekantiramo v steklen rezervoar,
- aceton lahko zamenjamo s ciljim topilom tako, da razpršino posušimo na vroči plošči (60°C) in nato dodamo želeno topilo
- 5. posušen material razpršujemo 2 minuti v ultrazvočni kopeli.

V postopku pripenjanja posameznih svežnjev preko reže med kovinskima kontaktoma izkoriščamo privlačno silo izmeničnega električnega polja na nevtralne ali nizko nabite delce, medtem ko nabiti delci nihajo okoli praktično stacionarne točke. Izkaže se namreč, da morda naravnejša izbira elektroforeze oz. konstantnega potenciala preveč agresivno privlači neželene nabite delce, v večini nečistoče, ki popolnoma prekrijejo vezje [26, 39, 38]. Tudi izbira topila vpliva na uspešnost pripenjanja posameznih svežnjev. Če je aceton najprimernejši za pripravo razpršin, njegova visoka hlapljivost onemogoča zadosten nadzor nad pripenjem in največkrat opazimo debele nanose svežnjev. Boljša alternativa je voda,

vendar nam ni uspelo pripraviti ustrezne razpršine, zato smo na koncu izbrali izopropanol, ki kompromisno združuje topne lastnosti acetona in nižjo hlapljivost. Kot je prikazano na sliki 8.6a, smo uporabili 100  $\mu$ m kovinske žičke kot mehanske kontakte, ki smo jih upravljali preko navpičnega mikromanipulatorja slika 8.6b.



Slika 8.6: a) Tanke žičke smo uporabili kot mehanski kontakt med napetostnim generatorjem in vezjem. b) Navpični mikromanipulator pritisne kontakte na vezje.

Nanašanje svežnjev smo morali ponoviti velikokrat, zato smo isto vezje med vsakim poskusom očistili in uporabili večkrat. Od tod tudi izbira niklja za izdelavo vezij, saj je mehansko odporen in hkrati primeren za elektronsko litografijo. Koraki oz. parametri pripenjanja so:

- 1. vezje z občutkom očistimo z vatirano palčko, namočeno v izopropanol in ga posušimo s stisnjenim dušikom; vezje očistimo pred vsakim poskusom nanosa,
- 2. mehanske kontakte z mikromanipulatorjem pod lupo spustimo na vezje do prepričljivega stika žic z vezjem,
- 3. 5 µl razpršine s pipeto previdno kapnemo na vezje,
- 4. vključimo generator izmenične napetosti s frekvenco 50 Hz in amplitudo 10 mV,
- 5. po desetih sekundah kapljico posušimo s stisnjenim dušikom,
- 6. po dvigu mehanskih kontaktov lahko vezje vstavimo v mikroskop na atomsko silo.

Izkaže se, da je za uspešno integracijo potrebno še temperaturno popuščanje, da se vzpostavi dober električni stik med vezjem in svežnjem. Pri tem postopku zapremo vezje v ampulo, izčrpamo zrak do tlaka  $2 \cdot 10^{-5}$ ) mbar ter vstavimo v peč na 700°C za eno uro. Tudi v tem primeru je nikelj najboljša izbira kovine za izdelavo vezja, saj ostane kljub visoki temperaturi razmeroma inerten, kontakti pa ohranijo svojo obliko. Primer uspešne izdelave in integracije je prikazan na sliki 8.7.


Slika 8.7: Idealen nanos a) enega samega svežnja s b) prepričljivim prekrivanjem elektrod. c) Po temperaturnem popuščanju kovina zalije strukturno ohranjen sveženj in tako izboljša stik med njima.

Žal je bilo veliko vezij po popuščanju uničenih, tako da smo meritve uspeli izvesti na štirih tankih svežnjih (tabela 8.1). Vzrok za visok izmet je bila v večini oksidacija cevk ali kovine ob slabšem vakuumu v ampuli in pa nabrekanje kontaktov vezja zaradi površinskih napetosti tankih plasti ob visokih temperaturah; zmerno gubanje opazimo tudi pri uspešnih integracijah (slika 8.7c).

oznaka svežnia	premer[nm]	dolžina[nm]
no19	5	530
11a12	10	000 005
na23	$^{4,2}$	265
na27	4	200
na28	12,5	190

Tabela 8.1: Premer in dolžina uspešno pomerjenih svežnjev.

#### 8.3 Meritev

Ceprav nam prevodne lastnosti povedo mnogo o sistemu, kakor smo spoznali v teoretičnem razdelku, gre v osnovi za eno najosnovnejših meritev v fiziki: na merjenec pritisnemo napetost in odčitamo tok skozi sistem. Ker nas je zanimala tudi temperaturna odvisnost prevodnosti, smo merilne čipe vstavili v kriostat. Opazljivke so bile torej krivulje toka v odvisnosti od napetosti (IV krivulje), merjene pri različnih temperaturah. Shema merilne postavitve je prikazana na sliki 8.8a, fotografija kriostata z bakrenim nosilcem, na katerem je s prevodno smolo prilepljen merilni čip, pa na sliki 8.8b.



Slika 8.8: a) Na merilni čip v kriostatu smo pritisnili napetost in merili tok skozenj. b) Silicijev substrat z vezjem smo s temperaturno prevodno pasto prilepili na bakren nosilec kriostata, vezje in merilni konektor pa smo povezali s 25  $\mu$ m zlato žico in srebno pasto.

Da bi dobili zanesljive vrednoisti, smo pred meritvijo vsakič posebej stabilizirali temperaturo, nato pa pomerili zadostno število točk (zajemali smo povprečne vrednosti 10 zaporednih odčitavanj), ki so omogočile dober izračun strmin krivulj, ki nastopajo pri analizi. Ker smo opazili spreminjanje lastnosti merjenca med meritvami, smo temperaturne cikle ponovili večkrat in s tem termalizirali merjence. Kriostat nam je omogočal ohladitve do 18 K, vsaka ponovitev meritve na celotnem temperaturnem območju s koraki po 10 K ali 5 K pa je trajala 14 ur.

# Poglavje 9

## Rezultati

Kljub temu, da smo dosegli cilj in izmerili prevodne lastnosti najtanjših svežnjev (pod 10 nm premera), bi za zanesljivejšo analizo potrebovali še več meritev različnih svežnjev, tudi z različnimi dolžinami in premeri. Ker je bil material sorođen mnogim strukturam, smo pričakovali različne lastnosti sicer podobnih nanosvežnjev, ki bi jih opazili le pri bogatejši statistiki meritev. To je bila tudi naša glavna motivacija pri zahtevnem izdelovanju merilnih čipov, saj smo upali na bogate rezultate tudi s teoretičnega vidika.

### 9.1 Tanki svežnji

Jedro našega dela so bile meritve štirih različnih svežnjev s premeri pod 15 nm in dolžinami med 190 nm in 530 nm. Pri vseh v grobem opazimo padanje prevodnosti s padajočo temperaturo (9.1) in zvezno prehajanje skoraj linearnih karakteristik IV pri sobni temperaturi v izrazito nelinearne lihe krivulje pri nižjih temperaturah (9.2). Po obliki jih razdelimo v dve skupini:

- 1. krivulje tipa "S" karakteristike IV spominjajo na črko S; mednje uvrščamo svežnja na12 in na27,
- 2. krivulje tipa "J"- pri visokih napetostih so krivulje precej linearne, z gladkim nižanjem strmine proti nižjim napetostim; mednje uvrščamo svežnja na23 and na28.

Analiza meritev sloni na treh glavnih teoretičnih napovedih: Luttingerjeva tekočina, preskakovanje spremenjivega dosega in impedančna Coulombova blokada. Pri njihovem testiranju smo sledili strategijam:

Luttingerjeva tekočina Testiranje združevanja krivulj vseh karakteristik na diagramu  $I/T^{\alpha+1}$  v odvisnosti od eV/kT glede na izraz 7.20 (7.9). Parameter  $\alpha$  je strmina premice na loglog grafu prevodnosti G za majhne napetosti v odvisnosti od temperature T,  $\beta$  pa je eksponent v predvideni potenčni zvezi  $I \propto V^{\beta+1}$  za visoke napetosti  $(eV \gg kT)$ . Parameter  $\gamma$  uravnava dejanski padec napetosti na merjencu v primerjavi z njeno nominalno vrednostjo.



Slika 9.1: Karakteristike IV od sobne temperature do 18 K kažejo zmanjševanje prevodnosti s padajočo temperaturo (od zgoraj navzdol) a) na12; označene so tudi napake meritve (0,5 % - 1 %), b) na23, c) na27 and č) na28.

- **Preskakovanje spremenljivega dosega** Krivulje  $\ln(G)$  (za nizke napetosti) v odvisnoti od  $T^{-\lambda}$  se približajo premicam za prave eksponente preskakovanja (tabela 7.1). Linearnost krivulj za različne  $\lambda$  testiramo s Pearsonovo korelacijo med točkami in prilagoditveno premico (dobro ujemanje daje korelacijo blizu 1).
- Impedančna Coulombova blokada Karakteristike IV so linearne za visoke napetosti in gladko prehajajo k nižjim strminam za nižje napetosti. Posledično tudi odvod dI/dV narašča zvezno od začetne vrednosti do konstantne asimptote. V obeh primerih opisano obnašanje testitamo le kvalitativno oz. jih primerjamo z numerično teoretično napovedjo diagramov s slike 7.7. Za nizke temperature in napetosti krivulje IV sledijo potenčnemu zakonu  $I \propto V^{2/g}$  (7.16).



Slika 9.2: Normalizirane krivulje od sobne temperature do 18 K (od zgoraj navzdol) jasneje kažejo zvezen trend nelinearnega ukrivljanja s padajočo temperaturo: a) na12, b) na23, c) na27 and č) na28.

#### 9.1.1 Krivulje tipa "S"

Krivulje močno spominjanjo na sinh odvisnost Luttingerjeve tekočine iz izraza 7.20. Testiranje združevanja krivulj na slikah 9.3b in 9.4b zadovoljivo potrdi prisotnost transportnega mehanizma, kot ga napoveduje Luttingerjeva tekočina. Ta sklep podkrepijo še prilagoditvene vrednosti parametrov, ki se ujemajo z vrednostmi, ki jih dobimo iz teoretičnih napovedi:  $\alpha$  iz strmine v loglog grafu prevodnosti od temperature,  $\beta$  pa iz  $I \propto V^{\beta+1}$  za visoke napetosti. Prisotnost Luttingerjeve tekočine v svežnjih potrjuje notranjo zgradbo svežnjev iz posameznih nanožic, ki jih lahko tretiramo kot močno enodimenzionalne objekte. Ker se krivulje IV ne približujejo linearni odvisnosti, ne moremo govoriti o Coulombovi blokadi, zato testiramo meritve na preskakovalni mehanizem. Presenetljivo je tudi ta način transporta potrjen, kot kažeta graf in pripadajoča histograma s slik 9.5 in 9.6, čeprav je dimenzionalnost preskakovanja (parameter  $\lambda$ ) različna.



Slika 9.3: a) Strmina prilagoditvene premice  $\alpha = 2$  dobro prilagaja tudi b) združitveno krivuljo za vzorec na12.



Slika 9.4: a) Strmina prilagoditvene premice  $\alpha = 2.3$  dobro prilagaja b) združitveno krivuljo za vzorec na27.

Za sveženj na12 je preskakovanje enodimenzionalno ( $\lambda = 1/2$ ), za na27 pa tridimenzionalno ( $\lambda = 1/4$ ). Istočasna prisotnost obeh transportnih mehanizmov ni intrinzična, kot dokazuje poročilo o podobnih meritvah na nanožicah NbSe<sub>3</sub> [11], kjer preskakovalni mehanizem ovržejo in sklepajo le na transport Luttingerjeve tekočine.

#### 9.1.2 Krivulje tipa "J"

V tej skupini prisotnost Luttingerjeve tekočine ni tako prepričljiva. Testiranje združevanja krivulj za sveženj na23 kaže močno razpršitev in neujemanje karakteristik (9.7a), medtem ko sicer nekoliko boljše ujemanje pri svežnju na28 nima značilnega kolena (9.7b). Če verjamemo izsledkom skupine "S" in pričakujemo enodimenzionalno obnašanje tudi v tem primeru, potem obstaja kakšen drug, močnejši transportni mehanizem, ki preglasi efekte Luttingerjeve tekočine. Kot primeren mehanizem se kaže impedančna Coulombova blokada, saj izmerjene krivulje (9.2b in 9.2d) kvalitativno močno spominjajo na numerične napovedi te teorije (7.7a). Še prepričljivejši so odvodi krivulj, ki pa se za visoke napetosti



Slika 9.5: a) Linearne odvisnosti  $\ln(G)$  od  $T^{-\lambda}$  potrjujejo prisotnost preskakovalnega transportnega mehanizma. b) Histogram korelacij med prilagoditvenimi premicami in meritvami za posamezne eksponente izpostavlja enodimenzionalno preskakovanje z  $\lambda = 1/2$  za sveženj na12.



Slika 9.6: a) Linearne odvisnosti  $\ln(G)$  od  $T^{-\lambda}$  potrjujejo prisotnost preskakovalnega transportnega mehanizma. b) Histogram korelacij med prilagoditvenimi premicami in meritvami za posamezne eksponente izpostavlja tridimenzionalno preskakovanje z  $\lambda = 1/4$  za sveženj na27.

ne približujejo konstatni asimptoti kot pričakovano (7.7b), pač pa linearni fukciji (9.8).

Ta efekt lahko pripišemo, podobno kot v skupini "S", preskakovanju spremenljivega dosega. Tudi ta mehanizem lahko vsaj za višje temperature potrdimo, vendar z različnimi parametri  $\lambda$ . Za sveženj na23 na podlagi histograma na sliki 9.9b najboljša prilagoditev pripada  $\lambda = 1/3$  ali morda  $\lambda = 3/5$ , medtem ko je pri na28  $\lambda$  enaka 1/4, po sliki 9.10.



Slika 9.7: Testiranje združevanja krivulj Luttingerjeve tekočine za svežnja a) na23 in b) na28. V obeh primerih prisotnost Luttingerjeve tekočine ni prepričljiva.



Slika 9.8: Odvodi krivulj (9.2b in 9.2d) v prvem kvadrantu so podobni numeričnim napovedim, le da se za visoke napetosti ne približujejo konstantni asimptoti, pač pa linearni funkciji s končno strmino. Graf a) pripada svežnju na23, b) pa na28.

Na podlagi te analize lahko rečemo, da pri krivuljah tipa "S" transport elektronov teče preko mehanizmov Luttingerjeve tekočine, istočasno pa sledi tudi preskakovanju spremenljivega dosega. Kakor je prikazano na shemi 9.11a lahko tako situacijo razložimo z naključno prekinjenimi nanožicami znotraj svežnja. Transport tako teče preko enodimenzionalnega medija, vendar mora ob prekinitvah preskakovati med posameznimi nanožicami, ki pa ga popisuje preskakovalni mehanizem. Enak sklep je mogoč tudi za krivulje tipa "J", kjer znotraj svežnja vgradimo še izoliran segment, torej kvantno piko, ki poleg mehanizmov enodimenzionalnega prevajanja preko Luttingerjeve tekočine in spremenljivega preskakovanja elektrone ovira še z efekti impedančne Coulombove blokade (shema 9.11b). Tudi kemijska narava nanožic, sorodna mnogim Chevrelovim fazam, ne samo dopušča, ampak morda celo predvideva nehomogen ustroj svežnjev z mnogo napakami, defekti, celo segmentacijami.

V splošnem podajamo prevodne lastnosti snovi s specifično prevodnostjo in maksi-



Slika 9.9: a) Linearne odvisnosti  $\ln(G)$  od  $T^{-\lambda}$  tudi v tem primeru potrjujejo prisotnost preskakovalnega transportnega mehanizma. b) Histogram korelacij med prilagoditvenimi premicami in meritvami za posamezne eksponente izpostavlja preskakovanje z  $\lambda = 1/3$  za sveženj na23.



Slika 9.10: a) Linearne odvisnosti  $\ln(G)$  od  $T^{-\lambda}$  potrjujejo prisotnost preskakovalnega transportnega mehanizma. b) Histogram korelacij med prilagoditvenimi premicami in meritvami za posamezne eksponente izpostavlja preskakovanje z  $\lambda = 1/4$  za sveženj na28.

malno gostoto toka skozi merjenec. Podatke za vse štiri merjene svežnje vsebuje tabela 9.1.

sveženj	D[nm]	l[nm]	I[nA] (295 K,1 V)	$\sigma = \frac{I}{V} \frac{l}{S} [\text{S/m}]$	$j_{\text{maks}} = \frac{I}{S} [\text{GA}/\text{m}^2]$
na12	5	530	300	8100	$1,\!5$
na23	$^{4,2}$	265	622	11900	$^{4,5}$
na27	4	200	233	3710	$1,\!6$
na28	$12,\!5$	190	469	730	$0,\!4$

Tabela 9.1: Prevodne lastnosti merjenih svežnjev pri sobni temperaturi.



Slika 9.11: a) Pri krivuljah tipa "S" so svežnji pripeti na Fermijeva rezervoarja in so sestavljeni iz enodimenzionalnih vodnikov Luttingerjeve tekočine, ki so naključno prekinjeni. b) Pri krivuljah tipa "J" sveženj vsebuje večjo, izolirano nehomogenost, ki prekinja sveženj v celoti in jo obravnavamo kot kvantno piko.

#### 9.1.3 Debelejši svežnji in efekt cikliranja

Meritve debelejših svežnjev (premera nekaj sto nanometrov) niso bile tako bogate kot pri tanjših. Opažali smo preskakovalni mehanizem pri elektronskem transportu (slika 9.12) z izključno linearnimi IV karakteristikami. Zanimalo nas je predvsem izboljšanje



Slika 9.12: Preskakovalni mehanizem je zelo prepričljivo prisoten, saj so a) krivulje zelo blizu premicam. b) Po histogramu je najbližja vrednost eksponenta 2/3 ali pa 3/5.

prevodnosti po temperaturnem popuščanju, zato smo primerjali vzorce različnih kontaktov in stihiometrij: dvotočkovna (dielektroforetični nanos) meritev, štiritočkovna meritev s svežnjem pod kontakti, dvotočkovna meritev makrosvežnja, pripetega s srebrno pasto in meritev z uporabo prevodne konice mikroskopa na atomsko silo [25]; rezultati so zbrani v tabeli 9.2. Presenetljivo visoke spremembe do treh redov velikosti pri dielektroforetični izdelavi merilnih čipov so nakazovale na globljo modifikacijo povezave med svežnji in kovino. Da ni šlo za strukturne transformacije znotraj svežnja nakazuje meritev s prevodno konico, ki ni pokazala nobene spremembe. Predvidevamo, da so svežnji prevlečeni s tanko, amorfno plastjo raznih nečistoč, ki se razgradijo ob temperaturnem popuščanju in omogočijo boljši stik s kovino.

	Pred popuščanjem [S/m]	Po popuščanju [S/m]
vzorec (tip meritve)	(vrsta kovine)	(vrsta kovine)
$Mo_6S_3I_6$ (makroskopska)	/	9,5 (Ag)
$Mo_6S_3I_6$ (štiritočkovna)	0,07 (Ti) - 0,3 (Pd)	2,5 (Pd)
$Mo_6S_3I_6$ (prevodna konica)	0,37 (Ti) - vzorec 1	0,52 (Ti) - vzorec 2
$Mo_6S_3I_6$ (dielektroforeza)	$1,3 \cdot 10^{-4}$ (Ti)	0,135 (Ti)
$Mo_6S_{4.5}I_{4.5}$ (dielektroforeza)	$3.7 \cdot 10^{-5}$ (Ti)	0,057 (Ti)
$Mo_6S_2I_8$ (dielektroforeza)	$2,3 \cdot 10^{-5}$ (Ti)	0,048 (Ti)

Tabela 9.2: Vpliv temperaturnega popuščanja na specifično prevodost pri sobni temperaturi 295 K.

Najbolj zanimiv fenomen, ki smo ga opazili le dvakrat, je bil efekt cikliranja. Obakrat sta merjenca vsebovala debelejše svežnje: par s premeroma 40 nm in 50 nm s signaturo na\_double ter individualen sveženj s premerom 60 nm s signaturo na13. Kot je prikazano na sliki 9.13 se je prevodnost višala po vsakem ciklu, preden se je ustalila na končni vrednosti pri nizkih temperaturah. Karakteristike IV za vzorec na\_double so za vse mer-



Slika 9.13: Prevodnost pri istih temperaturah se spreminja za vsak merilni cikel do končne saturacije: a) na\_double in b) na13. Tudi splošna oblika krivulj je drugačna kot običajno, saj se praviloma približujejo neki limitni vrednosti za najnižje temperature.

itve linearne (slika 9.14a), medtem ko v primeru svežnja na13 v prvem delu kažejo jasno tendenco nelinearnega ukrivljanja s padajočo temperaturo, ki pa po nezveznem prehodu (točka A na sliki 9.14b) povsem zamre celo za najnižje temperature (točka B na sliki 9.14b), kjer bi morale biti nelinearnosti najbolj izrazite. Analiza meritev transportnih mehanizmov svežnja na13 kaže na oster prehod tudi v tem pogledu, saj preskakovalni mehanizem prvega dela prvega cikla kasneje (po točki A) ni več opazen (slika 9.15). Pri na\_double pa tega ostrega prehoda ni in lahko morda prepoznamo preskakovalni mehanizem le pri višjih temperaturah (slika 9.16).

Razlago za ta pojav lahko morda najdemo v teoriji Fermijevega stekla in konceptu lokaliziranih in nelokaliziranih stanj v odvisnosti od stopnje nereda v strukturi. Zamis-



Slika 9.14: a) IV karaktertistike za na\_double so linearne na celotnem merilnem območju, medtem ko za b) na13 v prvem delu prvega cikla kažejo že znane trende nelinearnega zvijanja, po ostrem prehodu v točki A s slike 9.13b pa preidejo v linearne funkcije celo pri najnižjih temperaturah (točka B s slike 9.13b).



Slika 9.15: a) Preskakovalni mehanizem je prisoten le za prvi del prvega cikla, kasneje pa zamre. b) Po histogramu je v tem delu  $\lambda = 1/2$ .

limo si lahko, da sveženj po sintezi vsebuje strukturne napetosti (kakor surovo steklo), ki se med meritvami pod vplivom električnega toka in posledičnega gretja delno anihilirajo. Na ta način struktura preide v bolj urejeno konfiguracijo oz. nekatera lokalizirna stanja postanejo nelokalizirana. Če pred strukturnim prehodom Fermijevo energijo postavimo na zgornji del pasu in med lokalizirana stanja, a v bližino nelokaliziranih stanj (slika 9.17a), lahko po prehodu rob mobilnosti prečka Fermijevo gladino (slika 9.17b). S tem se transportne lastnosti fundamentalno spremenijo, saj v prvem primeru elektroni prevajajo preko lokaliziranih stanj, torej s preskakovalnim mehanizmom, v drugem pa preko kontinuuma nelokaliziranih stanj. Tudi po prehodu lahko preskakovalni mehanizem sodeluje v prevajanju, saj se predvsem pri višjih temperaturah elektroni vzbujajo v lokaliziran del pasu. Vsak nadaljnji premik roba mobilnosti viša delež elektronov, ki prevajajo v kontinuumu, in tako višajo prevodnost sistema. Za vzorec na13 lahko torej rečemo, da je bila Fermijeva energija v prvem delu prvega cikla med lokalizanimi stanji, po prehodu pa je



Slika 9.16: a) Za na\_double opazimo preskakovanje le za višje temperature. Predstavljene so odvisnosti za cikel 5, ostali pa so mu kvalitativno podobni. b) Korelacijski histogram za vse cikle izpostavlja  $\lambda = 1/4$ .

s prehodom mobilnega roba prešla med nelokalizirana stanja. Vsak naslednji cikel je potiskal rob mobilnost še neprej stran od Fermijeve energije ter s tem povečeval prevodnost. Zadnji scenarij lahko pripišemo tudi vzorcu na\_double, kjer je Fermijeva energija ležala v kontinuumu stanj že od samega začetka.



Slika 9.17: a) V posebnih primerih leži Fermijeva energija v zgornjem repu pasu, med lokaliziranimi stanji, vendar blizu roba mobilnosti. b) Po strukturnem prehodu se rob mobilnosti pomika navzven in prečka Fermijevo gladino.

V splošnem lahko rečemo, da so nanožice oz. nanosvežnji MoSIx neurejeni sistemi, ki vsebujejo več mehanizmov transporta. Kljub temu z opažanjem Luttingerjeve tekočine potrjujemo notranjo strukturo svežnjev iz manjših nanožic, ki pa so prekinjene in tako narekujejo tudi preskakovanje elektronov. V svežnjih pa so lahko vgrajene tudi večje nepravilnosti v obliki izoliranih otokov, ki kažejo fundamentalne lastnosti kvantne pike v obliki Coulombove blokade.

### Poglavje 10

# Zaključek

Predstavljeno doktorsko delo s področja merjenja elektronskih transportnih lastnosti nanožic je vključevalo pripravo razpršin surovega materiala, izdelavo merilnih vezij z elektronsko litografijo, integracijo posameznih svežnjev v merilne čipe preko dielektroforeze in temperaturnega popuščanja, izvedbo meritve in končno analizo rezultatov na podlagi relevantnih transportnih mehanizmov. Največ raziskovalnega časa smo posvetili pripravi vzorca, saj v začetku struktura in sinteza materiala še nista bili jasno določeni, niti nismo poznali osnovnih kemijskih lastnosti, ki bi pripomogle k uspešnejši pripravi razpršin. Ker so nas zanimali najtanjši svežnji, se je iskanje primernega recepta še podaljšalo, vendar se je vložen trud poplačal. Ugotovili smo, da je razprševanje celotne količine materiala iz sintezne ampule v acetonu najprimernejši postopek za pripravo začetne razpršine, od kođer preko dekantiranja dobimo frakcijo drobnih svežnjev. Tudi končno topilo lahko zamenjamo preko sušenja in ponovne razpršitve frakcije v želeni kemikaliji; zaradi kasnejše integracije svežnja s pomočjo dielektroforeze smo izbrali manj hlapljiv izopropanol. Z razvijanjem elektronske litografije smo uspeli izdelati množico vezij na neprevodnem silicijevem oksidu, ki so služili kot temelj našim meritvam. V osnovi smo oblikovali režo širine nekaj sto nanometrov, da so jo lahko individualni svežnji premostili, obenem pa je možnost gostega nanosa ostala razmeroma nizka. Kot strategijo pripenjanja svežnjev iz razpršine smo uporabili dielektroforezo, saj se je elektroforeza izkazala za preveč agresivno, s pregostimi nanosi. Metoda se je izkazala za optimalno uspešno že pri šibkem signalu 50 Hz in amplitudi 10 mV, ki smo ga zajeli kar iz elektromegnatnega ozadja. Tudi uporabo mikroskopa na atomsko silo smo razširili, saj ga nismo uporabiljali le konvencionalno pač pa kot način finega čiščenja nanosov in odstranjevanja izbranih svežnjev v primeru večih svežnjev na vezju. Ugotovili smo, da so za zajemanje slik najbolj primerne konice silicijevega nitrida v tipalnem načinu zazanavanja topografije, medtem ko so za manipulacijo in čiščenje svežnjev primernejše prevodne konice s prevleko iz platine in iridija. Opazili smo namreč, da je intrinzičen potencial na konici že dovolj, da privlači ostanke čiščenja, tako da jih konica ne grabi le vstran, pač pa jih s površine popolnoma odstrani. Prvi poskusi merjenja pri sobni temperaturi so pokazali izredno velike, celo nemerljive upornosti surovih, torej neobdelanih čipov neposredno po dielektroforetičnem nanosu, zato smo morali vsak čip še termično popuščati v vakuumu na 700°C, da se je prevodnost povečala in omogočila merjenje. Zal sta visoka temperatura in ostanek kisika v

#### 10 Zaključek

vakuumski ampuli tega nujnega postopka dostikrat botrovali razpadu svežnjev, kovinskih kontaktov vezja ali pa sta povzročili celo zlivanje bregov reže. Pri uspešni integraciji pa se svežnji, vsaj na podlagi posnetkov mikroskopa na atomsko silo, strukturno vendarle niso spremenili. Natančnejša študija je pokazala izboljšavo prevodnosti do treh redov velikosti tako pri debelejših kot pri tanjših svežnjih. Pri prvih smo tako izmerili prevodnosti med 0.05 in 10 Sm<sup>-1</sup>, pri drugih pa celo do 11900 Sm<sup>-1</sup>. Na podlagi relativnih sprememb predvidevamo, da k višanju prevodnosti prispeva v največji meri izboljšava stika med kovino kontaktov in svežnjev, v manjši meri pa strukturne spremembe znotraj svežnja. Ta efekt pripisujemo tankim prevlekam svežnjev, ki jih morda sestavljajo nečistoče ali pa nastanejo s kemijsko reakcijo med svežnjem in topili pri rokovanju z materialom. Veliko razliko med specifičnimi prevodnostmi debelejših in tanjših svežnjev lahko razložimo, če dovolimo prevajanje le po nanožicah, ki so v neposrednem stiku s kovino. Takšen privzetek sloni na šibki vezavi med nanožicami v svežnju, tako da se elektroni med transportom zadržujejo v plašču svežnja; delež nanožic, ki prevajajo ocenimo pod 1 %. Ravno ta nizka prevodnost je bila glavni motiv naše usmeritve na tanjše svežnje, saj smo se želeli približati prevodnim lastnostim posameznih nanožic. Zares smo poleg že omenjene visoke prevodnosti opazili drugačne transportne mehanizme. Če smo pri debelejših svežnjih opažali linearne karakteristike IV, so bile pri tankih svežnjih močno zvite a še vedno lihe. Na podlagi podobnih raziskav smo rezultate meritev testirali na tri glavne teorije: preskakovanje spremenljivega dosega, impedančna Coulombova blokada in Luttingerjeva tekočina. Ker smo iz strukturnih in kemijskih lastnosti pričakovali precej neurejeno zgradbo svežnjev, se je prisotnost preskakovalnega mehanizma zdela najverjetnejša, saj smo jo opazili tudi pri debelejših svežnjih. Zares smo ta način prevajanja potrdili v vseh vzorcih, vendar z različnimi vrednostmi glavnega parametra  $\lambda$ . Pri debelejših svežnjih smo največkrat opazili vrednosti 1/2 in 1/4, kar nakazuje enodimenzionalno in tridimenzionalno preskakovanje. Sicer agresivno popuščanje ni imelo vpliva na dimenzionalnost preskakovanja, kar še podkrepi našo trditev, da struktura svežnjev ostaja nespremenjena tudi po popuščanju. Pri tanjših svežnjih smo, glede na obliko karakteristik IV, svežnje razdelili v dve skupini. Pri skupini "S" smo poleg preskakovanja pokazali še na prisotnost Luttingerjeve tekočine, medtem ko pri skupini "J" opazimo efekte impedančne Coulombove blokade. Soobstoj večih transportnih mehanizmov lahko morda razložimo, če predvidevamo, da je sveženj sestavljen in enodimnzionalnih nanožic, ki pa so naključno prekinjene, včasih celo z nehomogenim in izoliranim otokom, ki prekine sveženj v celotnem premeru. Prva predpostavka bi ustrezala svežnjema iz skupine "S", efekt Coulombovega nabijanja izoliranega otočka oz. kvantne pike pa pripišemo skupini "J". Ti kombinaciji teoretično še nista bili raziskani, morda zaradi sorazmeroma zapletene matematične obravnave. Pri vseh meritvah pa nas je najbolj preseneil efekt cikliranja pri meritvi nekaterih debelejših svežnjev, kjer se je prevodnost pri istih temperaturah za različne ponovitve temperaturnega cikla dramatično večala za vsak zaporedni cikel. Ta pojav skušamo razložiti na podlagi teorije Fermijevega stekla in koncepta lokaliziranih in nelokaliziranih stanj. Zamislimo si namreč lahko, da ob strukturnih spremembah nekatera lokalizirana stanja prehajajo v nelokalizirana. Ce pred spremembo Fermijeva energija leži v zgornjem repu lokaliziranih stanj, lahko že subtilna sprememba strukture povzroči, da rob mobilnosti ob transformaciji lokaliziranih stanj prečka Fermijevo gladino ter tako drastično spremeneni transportni mehanizem in posledično prevodnost sistema. Prevodnost se lahko spreminja tudi ob vsakem naslednjem premiku roba mobilnosti, saj Fermijeva energija počasi tone v kontinuum stanj s čimer se prevodnost veča. Ta scenarij kvalitativno razloži dobljene rezultate meritev, vendar bi za boljšo analizo potrebovali teoretično študijo predlaganega modela.

Ob koncu lahko rečemo, da nam je uspelo osvojiti in razviti vse potrebne korake od surovega materiala do končne meritve integriranih čipov. Dobljeni rezultati so zanesljivi in kažejo na kombinacijo različnih transportnih mehanizmov. Za nadaljnje delo predlagamo dodatne meritve, saj bi lahko morda opazili še kakšen nov pojav, in pa teoretične študije soobstoja različnih transportnih mehanizmov v enodimenzionalnih sistemih.

### Bibliography

- [1] M. Uplaznik. Meritev vzdolžne električne prevodnosti  $Mo_6S_4I_4$  nanožičk z uporabo elektronske nanolitografije: diplomsko delo. *In Slovene*, Sept 2003.
- [2] A. Bachtold, M. de Jonge, K. Grove-Rasmussen, P. L. McEuen, M. Buitelaar, and C. Schönenberger. Suppression of tunneling into multiwall carbon nanotubes. *Physical Review Letters*, 87(16):166801, Oct 2001.
- [3] L. Balents. Orthogonality catastrophes in carbon nanotubes. arXiv.org:condmat/9906032, Jun 1999.
- [4] M.C. Bockrath, H. David, J. Lu, A. Rinzler, R.E. Smalley, L. Balents, and P. L. McEuen. Luttinger-liquid behaviour in carbon nanotubes. *Nature*, 397:4, Feb 1999.
- [5] J. Voit. One-dimensional Fermi liquids. *Reports on Progress in Physics*, 58(8):977– 1116, Sept 1995 - revision form May 2006.
- [6] J. Voit. A brief introduction to Luttinger liquids. arXiv:cond-mat/0005114 v1, May 2000.
- [7] L. I. Glazman and Shekhter R. I. Coulomb oscillations of the conductance in a laterally confined heterostructure. *Journal of Physics: Condensed Matter*, 1:5811– 5815, Aug 1989.
- [8] H. Grabert and M. H. Devoret. Single charge tunneling. NATO ASI Series B, 294, 1992.
- [9] Coulomb blockade. http://www.dstuns.iitm.ac.in, seminar 2, 2007.
- [10] L. Venkataraman, Y.S. Hong, and P. Kim. Electron transport in a multichannel onedimensional conductor: Molybdenum selenide nanowires. *Physical Review Letters*, 96(076601), Feb 2006.
- [11] E. Slot, M. A. Holst, H. S. J. van der Zant, and S. V. Zaitsev-Zotov. Onedimensional conduction in charge-density-wave nanowires. *Physical Review Letters*, 93(17):176602, Oct 2004.
- [12] N.F. Mott and E.A. Davis. Electronic processes in non-crystalline materials. second edition, pages 7–39, 1979.

- [13] D. Vrbanić, M. Remškar, J. Jesih, A. Mrzel, P. Umek, M. Ponikvar, B. Jančar, A. Meden, B. Novosel, S. Pejovnik, P. Venturini, J.C. Coleman, and D.D. Mihailović. Air-stable monodispersed Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowires. *Nanotechnology*, 15:635–638, Nov 2004.
- [14] A. Meden, A.F. Kodre, J. Padežnik Gomiljšek, I. Arčon, I. Vilfan, D. Vrbanič, A. Mrzel, and D.D. Mihailović. Atomic and electronic structure of Mo<sub>6</sub>S<sub>9-x</sub>I<sub>x</sub> nanowires. *Nanotechnology*, 16:1578–1583, Mar 2005.
- [15] C. Gadermaier, P. Kušar, D. Vengust, I. Vilfan, and D.D. Mihailović. Equilibrium and non-equilibrium optical properties of MoSI nanowires. *Physica Status Solidi(b)*, 244(11):4152–4156, Sep 2007.
- [16] C. Gadermaier, P. Kušar, D. Vengust, and D.D. Mihailović. Femtosecond pumpprobe spectroscopy on MoSI nanowires. *To be published.*
- [17] D. Vengust, F. Pfuner, L. Degiorgi, I. Vilfan, V. Nicolosi, J.N. Coleman, and D.D. Mihailović. Optical properties of Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowires. *Physical Review. B: Condensed Matter*, 76:075106, Avg 2007.
- [18] J.J. Doyle, V. Nicolosi, S.M. O'Flaherty, D. Vengust, A. Drury, D.D. Mihailović, J.N. Coleman, and W.J. Blau. Nonlinear optical response of Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> nanowires. *Chemical Physics Letters*, 435:109–113, Dec 2007.
- [19] P. Kušar and D.D. Mihailović. Sound propagation in a highly damped Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowire network measured by femtosecond pump-probe spectroscopy. *Journal of Applied Physics*, 102(1):013510, Jul 2007.
- [20] Z. Kutnjak, D. Vrbanić, S. Pejovnik, and D.D. Mihailović. Two-channel electrical conduction in air-stable monodispersed Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowire sheets. *Journal of Applied Physics*, 99(6):064311, Mar 2006.
- [21] B. Berčič, U. Pirnat, P. Kušar, D. Dvoršek, B. Podobnik, D. Vengust, and D.D. Mihailović. Transport properties of Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowire networks. *Applied Physics Letters*, 88(17):173103, Apr 2004.
- [22] M. Uplaznik, J. Pahor, A. Mrzel, and D. Vrbanić. Conductivity of Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> bundles. conference proceeding, pages 103–106, Mar 2004.
- [23] V. Nicolosi, D. Vengust, D.D. Mihailović, W. J. Blau, and J. N. Coleman. Debundling by dilution: Observation of significant populations of individual MoSI nanowires in high concentration dispersions. *Chemical Physics Letters*, 425:89–93, Jul 2006.
- [24] V. Nicolosi, D. Vrbanić, A. Mrzel, J. McCauley, S. O'Flaherty, C. McGuinness, G. Compagnini, D. Mihailović, W. J. Blau, and J. N. Coleman. Solubility of Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> nanowires in common solvents: A sedimentation study. *The Journal* of Physical Chemistry. B: Condensed matter, Materials, Surfaces, Interfaces & Biophysical, 109(15):7124–7133, Oct 2005.

- [25] M. Uplaznik, B. Berčič, J. Strle, M.I. Ploscaru, D. Dvoršek, P. Kušar, M. Devetak, D. Vengust, B. Podobnik, and D.D. Mihailović. Conductivity of single Mo<sub>6</sub>S<sub>9-x</sub>I<sub>x</sub> molecular nanowire bundles. *Nanotechnology*, 17:5142–5146, Sept 2006.
- [26] M. Ploscaru. Self-assembly properties of  $Mo_6S_{9-x}I_x$  nanowires with different (bio)materials. *doctoral dissertation*, May 2008.
- [27] Janez Strnad. Fizika, 3.del. Državna založba Slovenije, 1988.
- [28] Albert Messiah. Quantum mechanics. 1999.
- [29] N. D. Mermin and H. Wagner. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic heisenberg models. *Physical Review Letters*, 17(22):1133–1136, Nov 1966.
- [30] F. Schreiber. Magnetism in two dimensions and mermin-wagner theorem. http://www.soft-matter.uni-tuebingen.de, Physics Lectures Course - Experimental Physics V (Solid State Physics) 2007/2008.
- [31] M.M. Fogler, S. Teber, and B.I. Shklovskii. Variable-range hopping in quasi-onedimensional electron crystals. *Physical Review. B: Condensed Matter*, 69:035413, Jul 2004.
- [32] http://lithogroup.vistec-semi.com.
- [33] http://www.nanomotor.de.
- [34] P. Croft. Stone lithography. A&C Black Publishers, London, 2001.
- [35] T.H.P. Chang. Proximity effect in electron-beam lithography. Journal of Vacuum Science Technology, 12(6):1271–1275, 1975.
- [36] A. Ouabbou, J. P. Martinez, F. Lalanne, P. Gérard, and J. L. Balladore. Proximity effects in electron beam lithography in sal 601 resists on a si-sio2-si substrate. *Microelectronic Engineering*, 20(4):255–275, 1993.
- [37] I. Vilfan and D.D. Mihailović. Nonlinear elastic and electronic properties of Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowires. *Physical Review B*, 74(235411), Dec 2006.
- [38] H.A. Pohl. Dielectrophoresis: The behavior of neutral matter in non-uniform electric fields. 1978.
- [39] A. Castellanos, A. Ramos, A. Gonzalez, N.G. Green, and H. Morgan. Electrohydrodynamics and dielectrophoresis in microsystems: scaling laws. *Journal of Physics*. D: Applied Physics, 36:2584–2597, Oct 2003.
- [40] M.J. Biercuk, N. Mason, J.M. Chow, and C.M. Marcus. Locally addressable tunnel barriers within a carbon nanotube. *Nano Letters*, 4(12):2499–2502, Oct 2004.

[41] F.O. Jones and K.O. Wood. The melting point of thin aluminium films. British Journal of Applied Physics, 15:185–188, 1964.

### IZJAVA

Spodaj podpisani Marko Uplaznik, rojen 6. 12. 1979 v Celju izjavljam, da sem avtor pričuječega doktorskega dela z naslovom "Transportne lastnosti elektronov v integriranih čipih z nanožicami  $Mo_6S_xI_{9-x}$ ".