

DNA electronics

1. Applicant

Ilias Katsouras (under the supervision of Prof. Bert de Boer)

2. Institute

Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, 9747 AG
Groningen
The Netherlands

Contact : Prof. Bert de Boer
Telephone : +31 50 363 4370
Fax : +31 50 363 8751
E-mail : B.de.Boer @ rug.nl

3. Abstract

Large area molecular junctions ^[1] have proven to be a robust and reliable system for studying electronic transport through molecules, shedding plenty of light on the parameters that affect it. We propose the use of this system for a systematic study of the charge transport properties of DNA molecules and how this depends on the molecules' structure or environment. This knowledge can not only be used to design and synthesize DNA molecules that carry desired properties, such as rectification, for use in DNA molecular electronics devices, but provide valuable information for DNA's complex role in biology as well.

4. Duration of the Project

The project will begin in September 2008 and will be concluded by September 2012, since this will be the applicant's time as a PhD student.

5. Personnel

This is multidisciplinary project combining two research groups of the Zernike Institute for Advanced Materials:

Physics of Organic Semiconductors

Polymer Chemistry – Bioengineering

The personnel working on this project are:

prof. B. de Boer (Project Leader)
I. Katsouras (Applicant / PhD Student)
A. J. Kronemeijer (PhD Student)
J. Harkema (Technician)

prof. dr. A. Herrmann
D.K.Prusty (PhD Student)

6. Cost Estimates

The funding is requested for the applicant, one PhD position. Any specifically related needs such as wafers, lithography masks and chemicals will be covered by this budget. The equipment needed for this project is already present in the laboratories of the research groups involved or within the *Zernike Institute for Advanced Materials* and no other support of this kind will be required for this project.

Budget summary of the funding requested

	2008	2009	2010	2011	2012	Total
PhD Students	1	1	1	1	1	
Postdocs	-	-	-	-	-	
Technicians	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel Costs	€ 36.000	€ 39.000	€ 43.000	€ 43.000	€ 47.000	€ 208.000
Running Budget	€ 15.000	€ 15.000	€ 15.000	€ 15.000	€ 15.000	€ 75.000
Equipment	-	-	-	-	-	-
Total	€ 51.000	€ 54.000	€ 58.000	€ 58.000	€ 62.000	€ 283.000

7. Research Programme

7.1. Introduction

7.1.1. Molecular Electronics

Moore's law, stating that the number of transistors in an integrated circuit doubles every two years^[2], requires a miniaturization of the electronic components that will soon not be attainable with current silicon-based technologies. Molecular electronics, the field that bloomed after the theoretical prediction of Aviram and Ratner in 1974 that a specially designed molecule can act as a diode^[3], presents itself as a promising successor of silicon-based technology at the end of its roadmap. Apart from the apparent advantage of being small, molecules can be synthesized and tailored so as to possess the necessary functionalities to act as electronic components.

7.1.2. DNA

Deoxyribonucleic acid (DNA) is a long polymer made from repeating units called nucleotides. The DNA chain is 22 to 26 Ångströms wide, and one nucleotide unit is 3.3 Å long. In living organisms, DNA does not usually exist as a single molecule, but as a tightly-associated pair of molecules that form a double helix (Figure 1). The helix is stabilized by hydrogen bonds between the bases attached to the two strands, made of alternating phosphate and sugar residues (Figure 2). The four bases found in DNA are adenine (abbreviated A), cytosine (C), guanine (G) and thymine (T).

Each type of base on one strand forms a bond with just one type of base on the other strand. This is called complementary base pairing. A is bonding only to T, and C bonding only to G. The double helix is also stabilized by the hydrophobic effect and pi stacking, which are not influenced by the sequence of the DNA. Pi stacking is considered important for the molecules' charge transfer characteristics^[4] (Figure 2). As hydrogen bonds are not covalent, they can be broken and rejoined relatively easily. The two strands of DNA in a double helix can therefore be pulled apart, either by a

mechanical force or high temperature. As a result of this complementarity, all the information in the double-stranded sequence of a DNA helix is duplicated on each strand, which is vital in DNA replication.

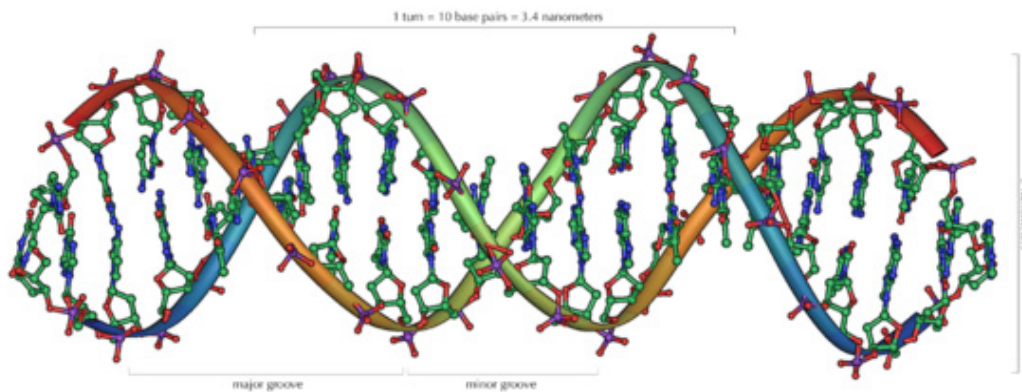


Figure 1 – The double helix structure of DNA

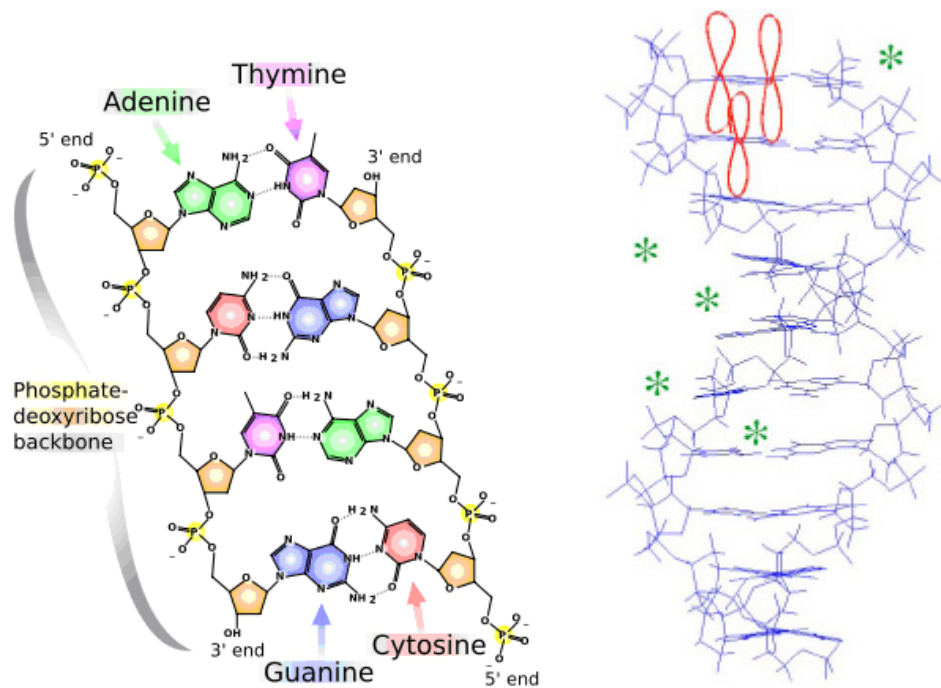


Figure 2 – Complementary base pairing in DNA, hydrogen bonds are denoted by dots (left) and a few atomic pz orbitals (vertical loops) and positive counterions (stars) in the helix (right)

DNA's electronic properties have been extensively studied and modelled [4]. Experimentally though a large spread of results have appeared on the molecule's conduction properties, presenting it as an insulator, semiconductor, conductor and even an proximity-induced superconductor [5,6,7,8]. Charge transport of a DNA molecule depends on its length, orientation, contamination, base sequence (as seen in figure 3 for example) and of course the experimental testbed used to address the charge transport properties [9].

The choice of (DNA) as a candidate for future electronics might oppose the role nature has chosen for this molecule, though the abilities to be finely engineered (in contrast to carbon nanotubes for example), to self-replicate and self-assemble can lead to nano-electronics of great precision. DNA molecules can create a self-assembled monolayer on gold substrates and double stranded DNA has a

rigid, rod-like shape with long persistence lengths [10, 11]. In addition to that, DNA molecules can be used as templates for molecular lithography [12].

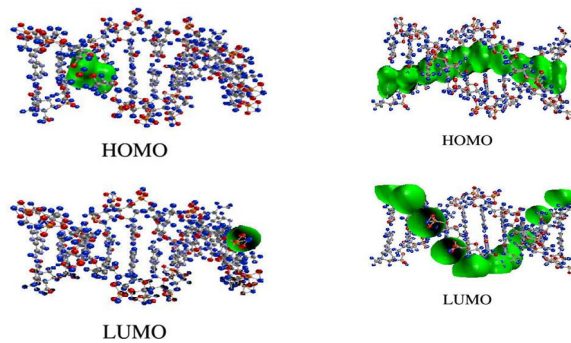


Figure 3 – Aperiodic structure of poly (A) - poly (T) DNA shows the HOMO-LUMO states demonstrate localization when compared to a periodic structure of the same molecule [13]

7.1.3. Large Area Molecular Junctions

Measuring the charge transport through molecules, even for those that have much simpler structure than DNA, has proven to be a difficult task. Different experimental testbeds have been employed, that yielded differences in the resistance value of a simple alkanedithiol of 8 orders of magnitude [14]. The basic problems of most of the methods used are reproducibility issues and the ability to be implemented in real devices.

At the Zernike Institute for Advanced Materials of the University of Groningen two-terminal devices with a self assembled monolayer (SAM) of molecules as active component have been materialized. All steps in the flow chart are conventional and industrially used processes such as spin coating and photolithography (Figure 4). The key step in this flow chart is spin coating the conducting polymer PEDOT:PSS on top of the SAM. The large, hydrophilic molecules of PEDOT:PSS (a water-based suspension) will not penetrate the hydrophobic interior of the SAM during spin coating, forming a layer on top of the SAM. This extra layer acts as a protective cushion, which prevents filamentary growth through the SAM during the evaporation of the top gold contact, that is a cause of short circuits [15].

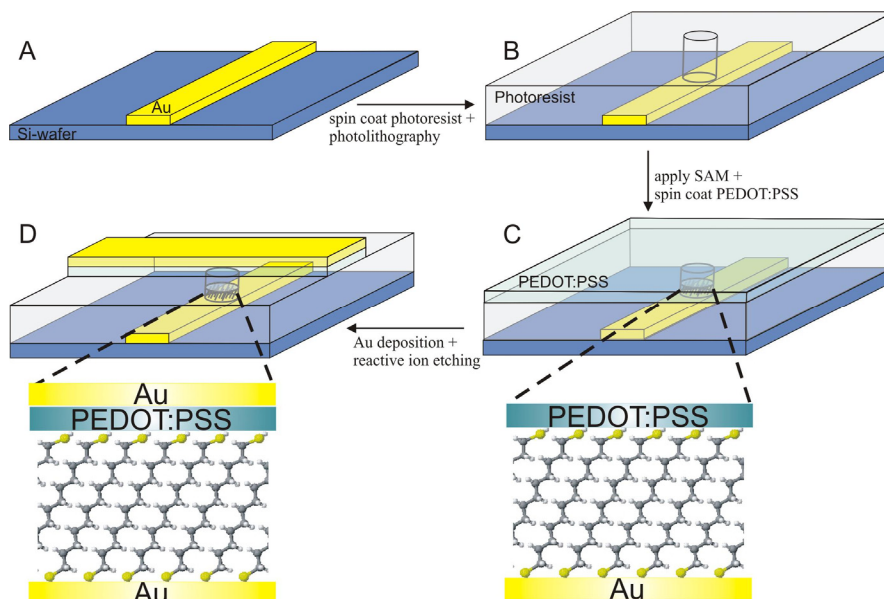


Figure 4 – Processing flow chart for the two-terminal self-assembled monolayer devices

The advantage of using the large area molecular junctions geometry for the DNA studies is that solvent-induced variations can be overcome, since the contacts are not simultaneously present while the DNA molecules self-assemble, eliminating the presence of alternative charge transport paths (i.e. salt bridges)^[16]. Moreover, the self-assembly route ensures that no external stress or conformational change is imposed on the molecules, factors that could change their electronic characteristics^[17]. Finally, this geometry allows for fast and reliable systematic studies of conductivity, owing to the high yield of working devices and the fact that it does not depend on the molecules used^[18].

7.1.4. Aim of the project

The first goal of this project is to utilize the technology of large area molecular junctions to investigate the charge transport properties of specifically engineered DNA molecules, in terms of the length/sequence or other parameters dependency of the molecule's electronic characteristics. The ultimate goal is to use this knowledge to design and manufacture functional DNA electronic components such as diodes and transistors.

7.2. DNA Molecular Rectifiers

A diode is a two-terminal device that allows an electric current to pass in one direction (called the forward biased condition) and to block it in the opposite direction (the reverse biased condition). The directionality of current flow most diodes exhibit is generically called the rectifying property. The most common type of diode in silicon technology is the p-n junction, which is formed by combining p-type and n-type semiconductors together in very close contact. Another interesting device, in which the negative differential resistance (NDR) phenomenon can also be observed, is the resonant tunneling diode. This structure is formed when a quantum well is surrounded by two thin barriers and is transparent to carriers of certain energies associated with the discrete energy levels within the well. An increase in carrier energy leads to a decrease in transmission, that is macroscopically manifested as the NDR effect.

The first molecular rectifier was conceived in 1974 by Aviram and Ratner, who proposed a model consisting of a donor π -system and an acceptor π -system, separated by a σ -bonded tunnelling bridge. This system could then, theoretically, be attached at both ends to metallic electrodes and act as a molecular rectifier, owing to its asymmetric nature (Figure 5).

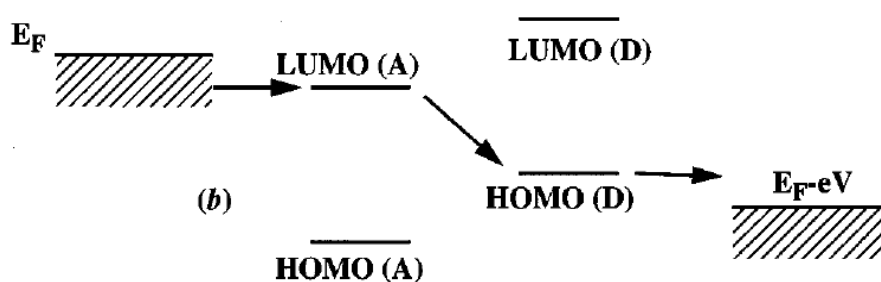


Figure 5 – Aviram and Ratner Donor-Acceptor scheme for molecular diode

A route to materialize a molecular diode using DNA is by taking advantage of the molecule's own electronic properties. It has been reported that a poly (dG)-poly (dC) DNA molecule behaves as a p-type semiconductor while a poly (dT)-poly (dA) molecule as an n-type one^[19]. This offers the possibility to manufacture a nanosized p-n junction by engineering a DNA molecule with the proper base sequence, combining a poly(dG)-poly(dC) and a poly(dA)-poly(dT) part, as shown in Figure 6. The ability to tune the molecule's electronic and thus rectifying properties by altering its overall length or creating asymmetric p and n blocks has to be investigated.

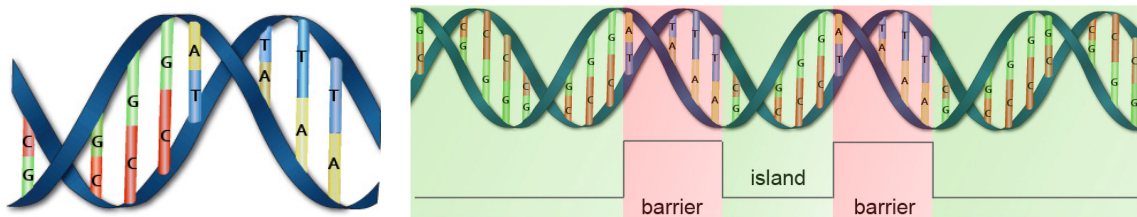


Figure 6 – A DNA molecule consisting of a poly (dG)-poly (dC) and a poly (dA)-poly (dT) part (left) and a resonant tunneling diode DNA structure (right)

The proposed structure for a DNA molecule acting as a resonant tunneling diode is also shown in Figure 6. It consists of G/C-rich donor and acceptor sequences at the ends, which are interrupted by two A/T-rich sequences and a short island of G and C. The G/C sequences can accept electrons from an electrode that could, over a certain threshold voltage, jump through the island over the A/T barriers to allow electrons flow to the other electrode. The advantage of using a DNA molecule is that the width of the barriers or the island can be precisely adjusted during synthesis.

The functional molecules described above can be easily implemented in the large area molecular diode geometry, yielding DNA-based diodes.

7.3. DNA transistor

Transistors are the fundamental building blocks of modern electronic devices. The main operating principle is that the current flowing between two contacts, the source and the drain, can be controlled by a voltage applied to a third contact, the gate. In a field effect transistor (FET) the gate controls the current flow through a semiconducting material by creating a conductive channel through the induction of charges in it.

A SAM-FET is based on the idea that a single molecular layer can play the role of the semiconducting active element. Such a monolayer can be build from DNA molecules whose electronic properties have been tuned, by sequence designing, to match those of a semiconductor. The aforementioned p-type poly (dG)-poly (dC) DNA molecule (Figure 7) is a possible candidate for field induced conductivity switching^[20].

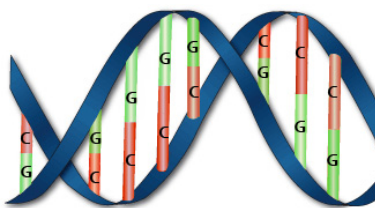


Figure 7 – A poly (dG)-poly (dC) DNA molecule

Except from the synthesis challenges, three terminal geometries in which the DNA molecules will be embedded have to be manufactured. Since there is possibly no bulk semiconducting behavior for a self-assembled monolayer of DNA molecules, the latter must be connected at their ends to the source and drain electrodes, while gated by a third electrode. Such a geometry can be achieved by using many of the technologies and processing steps developed for large area molecular junctions, a route that could yield reliable working devices in short time.

7.4. Project Outlook

Through the collaboration with the Polymer Chemistry – Bioengineering research group, the first objective of this project will be to gain a clear insight into the length and sequence dependence on the

molecules' electrical properties, and how are these manifested in the large area molecular junctions. The properties and characteristics of the DNA monolayers will be assessed using test samples and various techniques such as X-ray Photoelectron Spectroscopy (XPS), Scanning Probe Microscopy (Atomic Force or Scanning Tunneling Microscope), Ellipsometry, capacitance measurements etc. The transport characteristics (I-V measurements) will be performed in devices manufactured using the flow chart shown in Figure 4. The self assembled monolayer of DNA is formed by immobilizing thiol-terminated ssDNA (single stranded DNA) on gold, passivating the surface with a short molecule to prevent non-specific adsorption and finally hybridizing the ssDNA with the complementary strand (Figure 8).

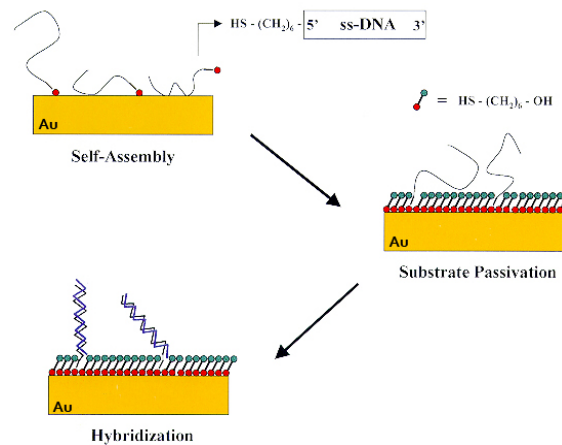


Figure 8 – DNA immobilization on gold

Once the first objective is reached, molecules with desired properties can be engineered. A DNA-based molecular diode can then be easily manufactured by assembling the DNA SAM in the two terminal molecular junction, as described previously.

The second proposed device, the DNA SAM FET can also be materialized when the appropriate functional molecules have been synthesized. These DNA transistors will provide further information into the electrical behaviour of the DNA molecules.

The first three terminal device geometry that can be used and its processing flow chart is shown in Figure 9. In this device geometry the self assembled monolayer, that acts as the active semiconducting material is formed on the vertical side of a structured Au electrode (source). The drain electrode is formed by using PEDOT:PSS to contact the other end of the molecules while the SAM is gated by applying a potential on the silicon substrate. The size of the channel can be adjusted both in length, by changing the length of the molecule, and in width, by using different masks during the lithographic process.

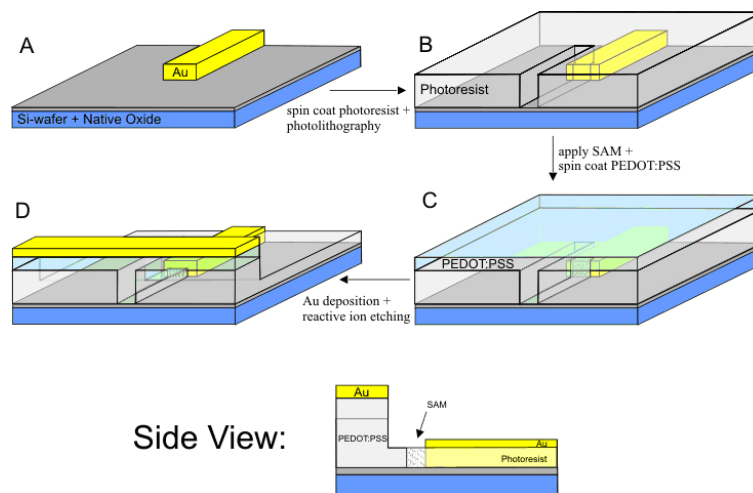


Figure 9 – Proposed flow chart for a DNA SAM FET

A second proposed geometry for a DNA SAM FET is that of the vertical transistor, where the self-assembled monolayer is formed in the holes of the large area molecular junctions and is gated by a ring electrode that is formed around the hole. The process flow of the large area molecular junctions has to be modified, as shown in Figure 10.

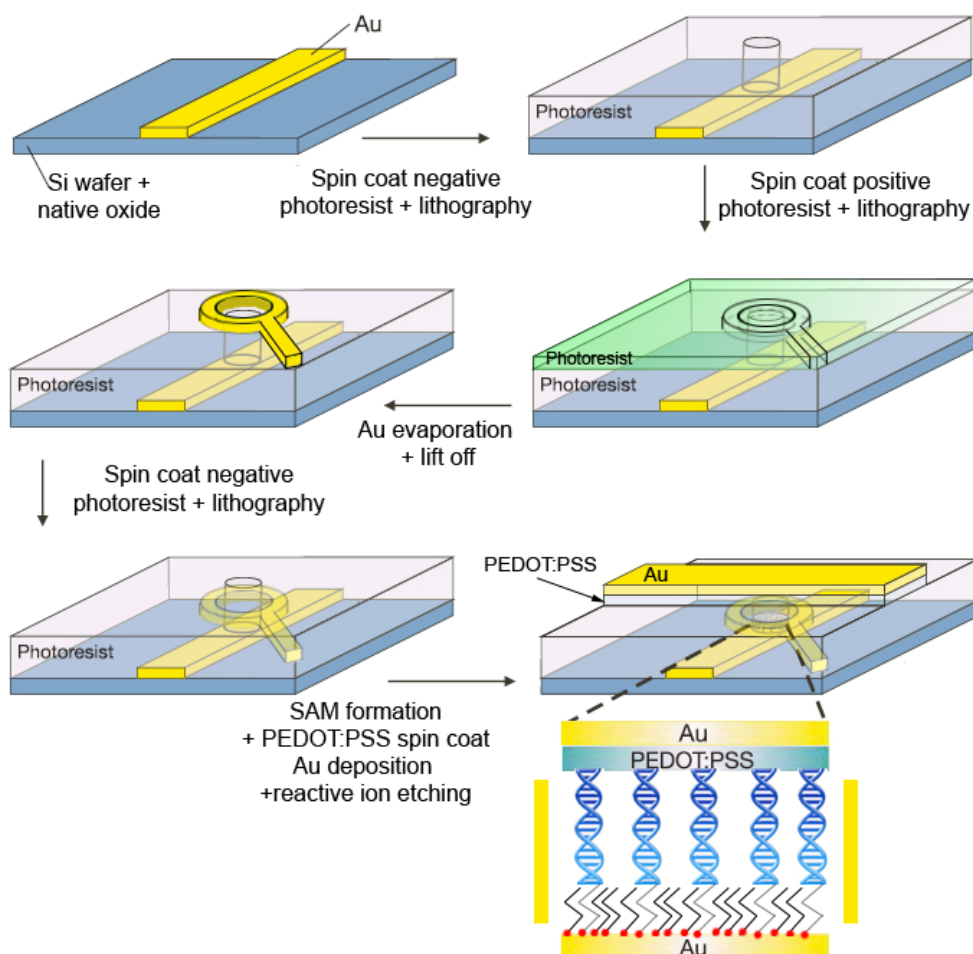


Figure 10 – Proposed flow chart for a vertical DNA SAM FET (features not shown in scale)

The operation and device characteristics of these DNA-based diodes and transistors will be inferred and also the fundamental physical processes governing their operation will be studied.

8. Infrastructure

All research equipment needed for this project is present within the research groups of *Molecular Electronics: Physics of Organic Semiconductors* and *Polymer Chemistry – Bioengineering* or the *Zernike Institute for Advanced Materials*.

9. Application Perspective

The end of the silicon roadmap seems to be approaching since the possible miniaturization, required by the need for smaller and faster electronics, faces a limit imposed by physical processes such as tunnel phenomena or ballistic transport. Molecular electronics and the idea of using tailored functional molecules can revolutionize the field, although the transition to all-molecule devices has to succeed a state of a hybrid technology.

So far, contacting and addressing the properties of molecules has proven to be anything but trivial, and many of the approaches used have yielded interesting yet contradicting results. The technology developed at the *Molecular Electronics-Physics of Organic Semiconductors* group of the University of Groningen achieved the state of reproducible and credible results, potentially allowing many open questions in the future agenda of molecular electronics to be answered.

DNA's unique properties render this molecule a promising candidate for molecular electronics. It is a molecule that can self-assemble, self-replicate and be chemically modified to carry specific properties or act as a nano-template. It is no wonder that nature has appointed DNA the task to carry the blueprint of life. A detailed study of the electronic properties of DNA will establish the end of the era when this molecule belonged entirely to the biology field and open the road towards knowledge that can eventually lead to all-molecule electronics.

10. References

- [1] H. B. Akkerman, P. W. M. Blom, D. M. de Leeuw, B. de Boer, *Nature* **441** (2006) 69
- [2] G.E. Moore, *Electronics* **38** (1965), 8
- [3] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **29** (1974) 277
- [4] R.G Endres, D.L. Cox, R.R.P Singh, *Reviews of Modern Physics* **76** (2004) 195
- [5] A. Y. Kasumov et al, *Science* **291** (2001) 280
- [6] H-W. Fink, C. Schonenberger, *Nature* **398** (1999) 407
- [7] X. Guo et al, *Nature Nanotechnology* **3** (2008) 363
- [8] D. Porath et al, *Nature* **403** (2000) 635
- [9] V. Bhalla, R.P. Bajpai L.M. Bharadwaj, *EMBO reports* **4** (2003) 442
- [10] T. M Herne, M.J. Tarlov, *J. Am. Chem. Soc* **119** (1997) 8916
- [11] H.G. Hansma et al, *Nucleic Acids Research* **24** (1996) 713
- [12] K. Keren et al, *Science* **297** (2002) 72
- [13] H. Wadati et al, *Applied Physics Letters* **86** (2005) 023901
- [14] H.B. Akkerman, B de Boer, *J. Phys.: Condens. Matter* **20** (2008) 013001
- [15] B. de Boer, et al, *Langmuir* **20** (2004) 1539
- [16] A. Rakitin et al, *Physical Review Letters* **86** (2001) 3670
- [17] A.J. Storm et al, *Applied Physics Letters* **79** (2001) 3881
- [18] D. Wei et al, *Nano Letters*, **XX** (XXXX) A
- [19] H-Y. Lee et al, *Applied Physics Letters* **80** (2002) 1670
- [20] S. Roche, *Physical Review Letters* **91** (2003) 108101