

Research proposal

1. Title of the project

Novel techniques for nanotube separation and nanotube alignment as key point in high-performance CNT-TFT fabrication

2. Abstract

The study of carbon nanotube thin-film transistors generates significant research interest, particularly towards their applications for low-cost, scalable fabrication, large-area and high performance electronic devices. However, the promises of carbon nanotubes, which are high carrier mobility together with ambipolarity and high on/off ratio, still have not been achieved in thin films made of networks of SWNTs. In this project, we propose a method for efficient nanotubes separation and precise nanotubes alignment in the channel of the field effect transistor to enhance the performance of carbon nanotube thin film devices. The final aim is to approach in these networks the promising value of single strand carbon nanotube device. The challenges still open are: the big hysteresis of the electrical characteristics, the unstable ambipolarity. One of them, the high driving voltage in CNT-TFT, will be addressed by applying high-k dielectric top gate. We believe that our approach can show the great potential of CNT-networks TFTs for their applications in next-generation electronics.

3. Applicant

Vladimir J. Derenskyi
Prof. Dr. Maria Antonietta Loi

4. Key publications of the applicant

S.Bisri, J.Gao, V.Derenskyi, W.Gomulya, I.Iezhokin, M.A.Loï, "High Performance Ambipolar Random Network Field-Effect Transistor Carbon Nanotubes", *Submitted to Advanced Materials*

5. FOM research group

G-27
Group leader: M.A.Loï

6. Institute

Photophysics and OptoElectronics Group (POE)
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7. Duration of the project

4 years, starting from september 2012.

8. Personnel

The personnel working on this project are all part of the research group *Photophysics and OptoElectronics* of *The Zernike Institute for Advanced Materials*

Name	Task in project	Time
Prof. Dr. M.A. Loi	Supervision and management	5%
Dr. S.Z. Bisri	Supervision and management	10%
A. Kamp	Technical support	10%
V.J. Derenskyi	Experiment and analysis	100%

9. Cost estimates

9.1 Personnel positions

One 'onderzoeker in opleiding' position for four years

9.2 Running budget

15,000€ / year

9.3 Equipment

9.3.1 Available equipment

Ultrasonic Liquid Processor (Sonicator 3000)
Ultracentrifuge (Beckman Coulter Optima XE 90K)

UV/Vis/NIR Spectrophotometer (Lambda 900)
 Semiconductor Parameter Analyzer (Agilent E5270B)
 Oscilloscope (Agilent Technologies MSO 7054A)

9.3.2 Required equipment

Agilent 81150A 20 MHz Pulse Function Arbitrary Noise Generator and two probes to connect generator to the electrodes (for dielectrophoresis alignment of carbon nanotubes after deposition)

9.4 Other support

The project will be also supported by the available Facilities at The Zernike Institute for Advanced Materials, Rijksuniversiteit Groningen. An access to the cleanroom maintained by the (Bio)organic Materials and Devices group and access to the required equipment in the Zernike NanoLab Groningen, which is a part of NanoLabNL, will be provided.

9.5 Budget summary (in k€)

The expenses are summarized in the following table.

	2012	2013	2014	2015	2016	Total
PhD Student	1	1	1	1	1	
Postdoc	-	-	-	-	-	
Technician	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel Costs	13	38	43	46	32	172
Running Budget	7,5	15	15	15	7.5	60
Equipment	-	10	-	-	-	10
Total	20,5	63	58	61	39,5	242

All related consumables such a Si/SiO₂ wafers, carbon nanotubes, polymers, metal sources for contact evaporation, tips for micropipette, solvents (acetone, propanol, toluene etc.) and chemicals will be acquired from this budget. Most of equipments needed for this project are available in the laboratory and the cleanroom of the *P-OE* group and in the *Zernike Institute*. Function generator will be procured for experiment of dielectrophoresis alignment of carbon nanotubes.

10. Research programme

10.1 Introduction

Fast growth in semiconductor industry in the last few decades demands improvements of the performance of the electronic devices together with the miniaturization of their dimensions. Nevertheless, the active channel material for excellence Si has remained unchanged by far. The further advancement of conventional Si-technology is hampered by technological limits such as quantum tunneling, which reduces device thermal efficiency, and the complicated and expensive lithography processes required to further reduce the active channel size. These reasons forces us to explore better alternatives. One candidate to replace silicon is carbon nanotube (CNT). A single strand of semiconducting single-walled carbon nanotubes (sSWNTs) have demonstrated extraordinary high carrier mobility of up to $200\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [12] compared to $1400\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for Si. The band gaps of the sSWNTs are inversely proportional to the diameter with a typical value around 1 eV, which makes them perfect for transistor application. The presence of real band gap allows us to turn-off the device and makes high on/off ratio achievable, in comparison with the other nanocarbon candidate (i.e. graphene).

Today, two basic CNT-FET architectures exist: (a) CNT-FET based on single strand nanotube [13] and (b) random network CNT-FET. Single nanotube FET have an excellent performance – low operating voltage of 0.5 V, size less than 10 nm and carrier mobility of up to $150\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ but it is not suitable for large-scale manufacturing because the fabrication process includes few tricky steps such as single nanotube transfer onto the substrate and source/drain metallization using electron beam lithography in order to form transistor. Furthermore, high on-current levels are not easily accessible.

From the low-cost electronics viewpoint, CNT-network TFTs have great potential because of their solution-processability. However, their performance is significantly lower than Si-based or single nanotube based ones. Drastic reduction in carrier mobility comes from Schottky-barrier formed between semiconducting nanotube and metal contact and from charge trapping.

CNT-TFTs require high-purity nanotube dispersion acting as a channel. However, as-synthesized carbon nanotubes contains both metallic and semiconducting species that is why nanotubes separation before utilization for CNT-TFT fabrication is required. To date, two classes of separation techniques exists:

- Physical (Electrophoresis, Density Gradient Ultracentrifugation - DGU)
- Chemical (Chromatography, Selective Solubilisation)

Using DGU high purity left- or right-handed nanotube dispersion can be produced due to the difference in interaction between nanotube and the surfactant used. The disadvantage here is the long separation time (more than 20 hours for 1 batch) and the small yield (less than 1 ml). On the other hand, Electrophoresis and Chromatography are suitable for mass-production, but yield purity is lower compared to DGU. Therefore, in this research project, we propose to use the Selective Solubilisation method which has been initiated in our group.

Intrinsically, CNT-FETs show ambipolar behavior. Hole-carrier transport is allowed at negative gate bias and electron-carrier at positive gate bias. This novel ambipolar behavior was initially considered undesirable specially because accused to reduce the on-off ratio of the device, nevertheless, recent work shown that ability to control device polarity presents new opportunities. A good example of application of ambipolar field-

effect transistor is a light emitting FET or a CMOS-like inverter. However, under ambient condition electron conduction in CNTs is suppressed and hole conduction is improved. Absorption of moisture on the CNT surface extract electrons from CNTs and create holes in the CNTs. Ambipolarity can be recovered after annealing in vacuum or by using various doping strategies, which are, however, unpractical because of air instability [15].

Ambipolar random network CNT-FET were recently realized by our group [14]. The general structure of the device is shown on the Fig.1(b). The device with mobility of up to $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and on/off ratio up to 10^6 was fabricated by simply drop-casting the sSWNT dispersion in toluene on pre-patterned bottom-gate/bottom-contact substrates (An AFM image of the channel is shown on the Fig.1(a)). CoMoCAT nanotubes were used for the dispersion preparation. The choice of the polymer and CNT sample was governed by the conclusions in the recent paper of J.Gao et. al.[9] where the influence of the polymer side chain length towards nanotube selectivity have been discussed.

The obtained performance from the device that we had fabricated is still far from desired. It is also the challenge faced by the other research group worldwide. Therefore, here we propose the use of Selective Solubilization method for big-diameter SO (nanotubes produced by Laser Ablation technique) nanotubes.

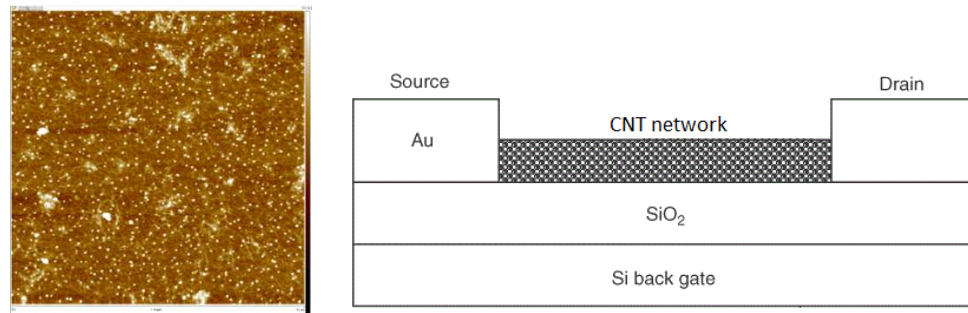


Fig.1 (a)AFM image of 10 layers deposited sSWNT film for device channel showing a dense, yet homogeneous random network (b) Structure of the CNT-TFT

10.2 Aims, Purposes and Research Questions

The proposed research aims at fabrication of CNT-TFT that can act as the most important candidate for application in modern electronics integration. The requirements for the device that intended to be achieved are stable ambipolar transport characteristics, low hysteresis, low driving voltage, carrier mobility for both hole and electron ($>1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) as well as high on/off ratio ($>10^6$).

Therefore, the project will address the following fundamental questions:

1. What are the influences of the side chain length of the polymer towards the selectivity? Is it possible to vary the length of the polymer side chain in order to separate nanotubes with specific diameter and chirality?
2. Is it possible to achieve 100% single-chirality nanotubes?
3. What is the best way to efficiently align nanotubes in a channel, so that the device performance can be significantly improved?
4. How to maintain ambipolar transport, lower driving voltage and suppress the hysteresis in the device transport characteristics?

To answer those questions, following research lines should be realized:

1. The investigation of the ability of conjugated polymer derivatives to selectively disperse sSWNTs from different nanotube sources.
2. The search of efficient way to align nanotubes, by utilizing simple dielectrophoresis technique, and SAM-assisted deposition technique (Host-Guest Molecular Printboard System).
3. Large-scale device fabrication by Langmuir-Blodgett method with aligned nanotubes.
4. Application of the high-k dielectric in combination with top-gate architecture to lower driving voltage and to suppress hysteresis

10.3 Research methods

Selective dispersion of nanotubes

We will start from the investigation of the nanotubes selectivity by conjugated polymers. At first, the ability of polyfluorene and polythiophene derivatives to select nanotubes with different diameter will be examined. We will use three types of nanotubes in our experiments: SO nanotubes – big diameter species produced by laser ablation; HiPCO and CoMoCAT nanotubes – small diameter species produced by chemical vapor deposition (CVD).

To date, only HiPCO (High Pressure Carbon Monoxide) and CoMoCAT nanotubes with diameter distribution about 0.8-1.2 nm were used as starting material for polymer-assisted separation [10, 14]. Here we propose the usage of SO nanotubes produced by Laser Ablation. This method produces carbon nanotubes with a controllable diameter in the range between 1.0 and 1.6 nm, determined by the reaction temperature. Large diameter CNTs are expected to exhibit higher carrier density accumulation and higher carrier mobility compared to small diameter species. However, the separation of this kind of nanotubes remains a big challenge.

The first step in the proposed project is the nanotubes separation. In our research project, we will utilize noncovalent functionalization through polymer wrapping which allow nanotubes dispersion. The polymer is mixed with commercially available nanotubes in organic solvent, resulting in differentiation between metallic and semiconducting tubes. The interaction between π -conjugated polymer and nanotube occurs via $\pi - \pi$ stacking [20]. The selectivity will strongly depend on the solvent used and the side chain length of the polymer. Recently, a detailed calculation and simulation have been carried in collaboration with our group. Results showed that the stable dispersion can be achieved using PFO with octyl side chain and HiPCO or CoMoCAT nanotubes[9]. Smaller side chain have to compete with backbone-backbone interaction, while longer side chains can bend and more subjected to disorder effect. Up to date, only sSWNT dispersion using HiPCO (with rr-P3ATs)[10] and CoMoCAT (with PFO) nanotubes have been realized. We will start with the polyfluorene (Fig.2(a)) and polythiophene (Fig.2(b)) derivatives because of the success in separating small diameter nanotubes. We will adapt these polymers to separate the big nanotubes (SO).

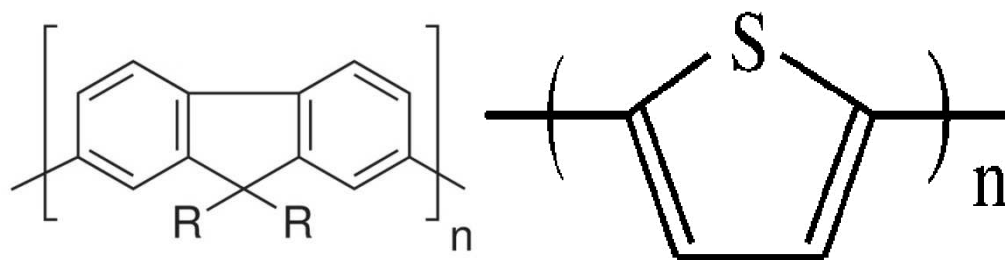


Fig.2 (a) Polyfluorene, R represents side chain (b) Polythiophene

In order to study polymer selectivity towards different chirality nanotubes, we will use various polymer and optimize the mixing (sonication) as well as the cleaning processes. Subsequently, the absorption spectra of the obtained dispersion will be measured. The type of nanotubes prevailing in the dispersion can be precisely identified from the absorption peaks present in the spectra. All polymers utilized in our project will be synthesized by our collaborators from the group of Prof. Dr. Ullrich Scherf from the University Wuppertal, Germany.

CNT film alignment

After successful s-SWNT dispersion preparation, we will deposit them on top of SiO₂/Si or flexible substrate to fabricate FET. In this project we will mostly focus on the Langmuir-Blodgett deposition and SAM-assisted deposition (including molecular prinboards). However, the simplest fabrication technique, which is drop casting, together with dielectrophoresis alignment, will be used at the beginning to test the prepared nanotube dispersion.

Dielectrophoresis

When dielectric particles are exposed to a non-uniform electric field, charges move away from their initial balanced positions. The charge redistribution creates electric dipole moments that force the nanotube to rotate and position along the electric field lines. Therefore, the polarized nanotubes are subjected to a net force and can be aligned to follow the electric field direction (Fig.3) if they are free to move in a medium. The dielectrophoresis of CNTs is affected by many factors including the dimension of the nanotubes, the properties of the medium and the strength of the electric field. We will optimize the process by adjusting a number of parameters: bias voltage, frequency, deposition time, width of the electrodes and nanotube solution concentration, to control the deposition and alignment of the nanotubes.

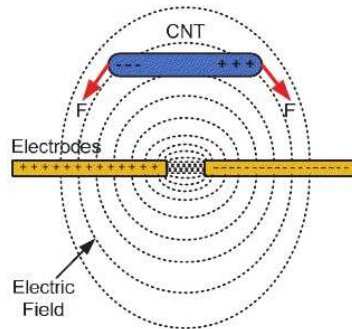


Fig.3 Principle of dielectrophoresis deposition and alignment of a carbon nanotube

SAM-assisted deposition

In the subsequent phase of our research we want to utilize SAM-assisted nanotube deposition with an aim to fabricate ordered channel for FET. SAMs molecule consists of a head group, tail (spacer) and functional end group (Fig. 4(b)).

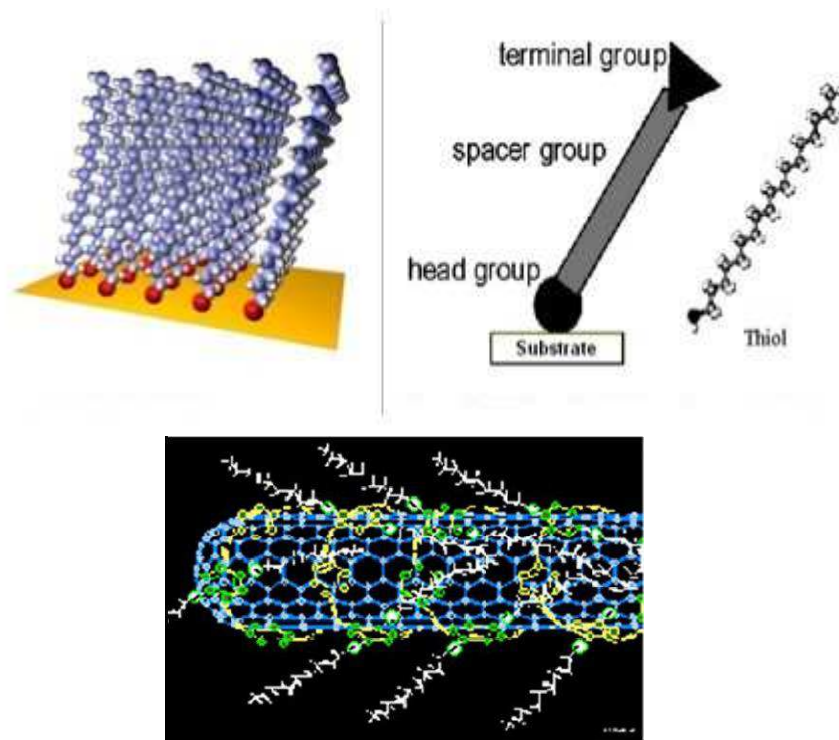


Fig.4 (a) Self assembled monolayer, (b) General structure of a SAMs molecule, (c) Nanotube wrapped with functionalized polymer

SAMs are created by the chemisorption of “head groups” followed by a slow organization of “tail groups” (Fig.4(a)). In our case, we will use a head group with the strong affinity towards SiO_2 , in order to form monolayer in the channel between electrodes. Terminal group will consist of polymer wrapped around semiconducting nanotube (Fig.4(c)). To realize the proposed structure, functionalization of polymer side chains using appropriate head group (e.g. hydroxyl group) will be attempted.

Another possibility to form well-aligned nanotube film is by using Host-Guest Molecular Printboard System [21]. The use of supramolecular interaction for the immobilization of carbon nanotubes at surface has been a relatively unexplored research topic in the field of supramolecular chemistry.

Molecular printboards are self-assembled monolayers of receptor molecules on a flat surface. The regular molecular assemblies offer anchoring points for individual molecules that are immobilized by supramolecular host-guest interactions. In this project we propose to use β -cyclodextrin (CD)[16] host-guest interactions for the immobilization of guest molecules, that is, the interactions between CD-host self-assembled monolayers and polymer wrapped carbon nanotubes modified with multiple hydrophobic guest moieties.

The usage of SAMs assisted deposition can also be beneficiary to control the threshold voltage of the fabricated devices by selecting the proper combination of the SAM molecules.

In order to apply these techniques, nontrivial conjugated polymer functionalization will be done. This part of research project will be carried in close collaboration with the group of Prof. Dr. Ullrich Scherf from the University Wuppertal, where they will modify the polymers with special end-group moieties..

Langmuir-Blodgett method

Drop casting deposition technique is time consuming and allows only one-by-one device fabrication, that is out of practical use. In Langmuir-Blodgett (LB) method the whole substrate can be covered at a time thus allowing large-scale device fabrication, that is one out of the main research lines of proposed project. LB method allows the control of the layer structure down to the molecular level [11]. In order to form a Langmuir monolayer, it is necessary for a dispersion to be water insoluble and soluble in organic solvent. LB compatible materials consist of two parts, a head and a tail. The head part is a hydrophilic chemical group. On the other hand, the tail part is hydrophobic, usually consisting of a long carbon chain. The monolayer is formed by spreading the organic molecules on the water subphase. Monolayer can be transferred to a substrate by dipping the substrate through monolayer (Fig.5(a)). The monolayer can be kept uniform by controlling the density of the Langmuir film during deposition.

This part of the project requires following steps: (a) synthesis of an amphiphilic (possessing both hydrophilic and hydrophobic properties) polymer with ability to selectively disperse nanotubes; (b) sSWNTs dispersion preparation to become Langmuir film; and (c) LB film deposition.

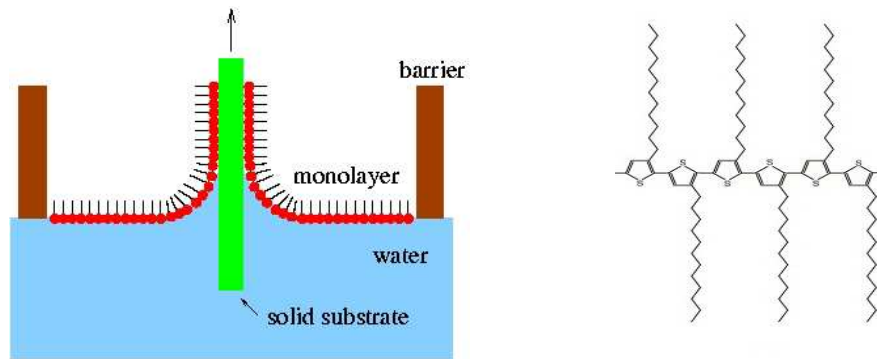


Fig.5 (a) Process of monolayer formation on a substrate (b) Poly(3-dodecylthiophene) (rr-P3DDT)

Polythiophene is believed to be a good candidate for this purpose. Selective properties of the polythiophene derivatives were recently confirmed [10] by the usage of regioregular poly(3-dodecylthiophene) (rr-P3DDT) (Fig.5(b)) to disperse HiPCO nanotubes. This polymer consists of hydrophobic side chains and hydrophobic backbone. Therefore, we can just functionalize it with hydrophilic side chain in order to utilize for LB method. Polymer synthesis will be performed by the group of Prof. Dr. Ullrich Scherf from the University Wuppertal.

LB film deposition will be done in the group of *Surfaces and Thin Films* (leader prof. Dr. P. (Petra) Rudolf) where a dedicated equipment for this purpose is available.

Novel gating

In order to overcome the problem of high driving voltage and big hysteresis in bottom-gated CNT-TFT, top-gate architecture with high- k dielectric (Fig.6)(ZrO_2 , TiO_2 , etc)[19], ionic liquids[17], and polyelectrolytes [18] - can be utilized.

The advantages of the high- k dielectric structures are the low operating voltage due to the capacitance increased by a factor of k (relative dielectric constant). On the other hand, the top-gate architecture can stabilize the electrical characteristics of CNTs against environmental variations, thus suppress the origin of hysteresis trapping.

Top gate high- k dielectric fabrication will be performed by using electron beam evaporation which is available in the NanoLab Groningen. On the other hand, the utilization of ionic liquid gate and polyelectrolyte gate will be performed in the same N_2 glovebox where the nanotube dispersion is drop casted.

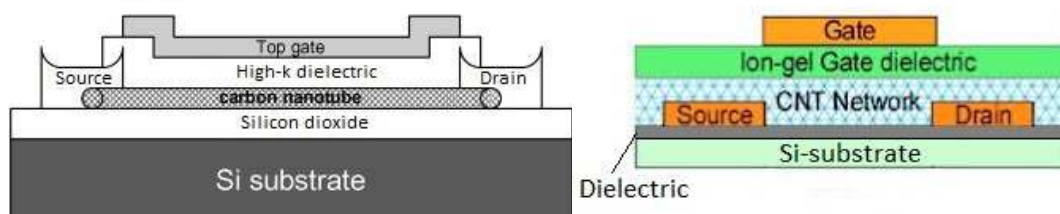


Fig.6 Cross-sectional view of a top-gate CNT-TFT with (a) high- k dielectric (b) ion-gel dielectric

10.4 Research plan

The project will take 48 months in total. A time schedule is given below:

September 2012 – August 2013	Investigation of the polymers selectivity towards SO SWNTs. Preparation of high-purity sSWNT dispersion. FET fabrication using simple drop-casting technique and DEP nanotube alignment.
September 2013 – August 2014	Collaboration with the group of the Prof. Dr. Ullrich Scherf from the University Wuppertal in order to synthesize and functionalize required polymers. FET fabrication with a SAM-assisted deposition technique and Host-Guest Molecular Printboards System.
September 2014 – August 2015	Polymer functionalization in order to allow Langmuir-Blodgett deposition. Device fabrication with the Langmuir-Blodgett deposition technique. Device characterization.
September 2015 – August 2016	Experiments with novel gating to lower driving voltage and suppress hysteresis. Ambipolar CMOS inverter fabrication as demonstration of the high performance nanotube TFT application. PhD thesis writing.

11. Infrastructure

The Zernike Institute for Advanced Materials provides a variety of processing and measuring facilities. For our research, we will use the next equipment:

- Ultrasonic Liquid Processor and Ultracentrifuge for SWNT dispersion preparation. This equipment is available in the chemistry lab of the *Photophysics and OptoElectronics* group.
- Semiconductor Parameter Analyzer and probes for electrical characterization are available in the *Photophysics and OptoElectronics* group.
- UV/Vis/NIR Spectrophotometer for dispersion characterization is available at the Zernike Institute for Advanced Materials, which is maintained in the Optical Science Center. However, there is a plan to buy a new and better in-house UV/Vis/NIR Spectrophotometer that is more suitable for carbon nanotube research project by *Photophysics and OptoElectronics* group.
- Glovebox and spin coater required for device fabrication are available in the cleanroom maintained by the *Chemistry of (Bio)Organic Materials and Devices* group (leader prof. dr. J.C. (Kees) Hummelen).

- An Atomic Force Microscope (AFM) to study the quality of the CNT network – is available at *Molecular Electronics Cluster*.
- Equipments required for LB deposition is available in the group of *Surfaces and Thin Films* (leader prof. Dr. P. (Petra) Rudolf).
- Equipments required for high-*k* dielectric deposition, which is the electron beam evaporater, is available at the NanoLab Groningen.

12. Application perspective in industry, other disciplines or society

The study of random-network CNT-TFT obviously can make a great contribution to the field of next-generation electronics. The scalability of the separation and deposition techniques proposed in this project allows integration of large number of devices on a single chip. Another potential application for ambipolar CNT-TFT is the usage as light source. In order to tune their electronic structure, molecule encapsulation into the nanotube can be performed to form peapods.

Carbon nanotubes are considered to be an excellent candidate for chemical and biological sensors, however the production of pure and uncontaminated nanotubes for high-performance sensor is very costly. An ability to separate single-chirality species will solve this problem and will make a huge impact in future sensors industry.

Knowledge obtained during the first part of this research project – nanotubes separation – can also be used for metallic nanotubes separation. Metallic carbon nanotubes outreaches ITO performance and are considered to be a good candidate to replace it in the industry of flexible, transparent and stretchable electronics.

13. References

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