Toptalent

Application form (closing date 8 January 2008)

Complete this form in English or Dutch

Den Haag, August 2007 (versie 273/1/2008 / aantal pagina's 12)
Nederlandse Organisatie voor Wetenschappelijk Onderzoek

1 Basic details

1.1 Details of applicant

- Title(s), initial(s), First name: Alina Veligura
- Male/female: Female
- Address for correspondence: Duindoornstraat 455
  9741 PT, Groningen
- Telephone: 0644683293
- E-mail: a.veligura@student.rug.nl
- Website (optional):

1.2 Details of intended supervisor

Note! Separate letter of recommendation is required!

- Title(s), initial(s), First name, surname: Prof. dr. ir. Bart J. van Wees
- Address for correspondence: Physics of Nanodevices
  Zernike Institute for Advanced Materials
  University of Groningen
  Nijenborgh 4
  NL 9747 AG Groningen
  The Netherlands
- Telefoon (vast/mobiel):
- Telephone: +31 50 363 4933/4974
- E-mail: b.j.van.wees@rug.nl
- Website (optional): http://nanodevices.fmns.rug.nl/

1.3 Host institution

Rijksuniversiteit Groningen (RUG)

2 Research proposal

2.1 Research field

Sciences / technology

2.2 Title of research proposal

Studying molecular switches with graphene-based devices

2.3 Summary of research proposal

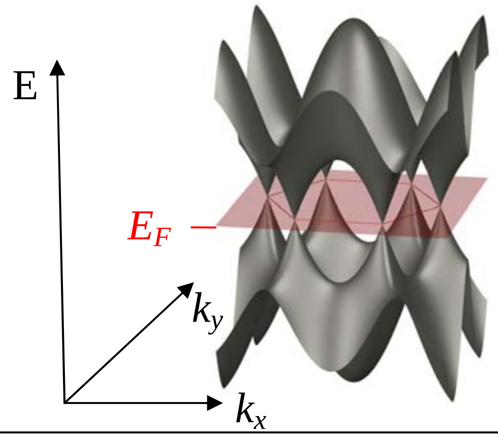
We will use a recent discovery that the conductance of graphene can be manipulated by molecules assembled on its surface. We propose to build graphene-based devices which will allow us to study photo-/thermochromic switches down to the ultimate single-molecule level.

2.4 Brief description of research proposal

2.4.1 Introduction

Graphene, as a single planar sheet of sp^2-bonded carbon atoms, tightly packed in a honeycomb crystal lattice, theoretically was described already 60 years ago [1]. But only in 2004 a stable 2D sheet of carbon atoms was isolated (A.Geim *et al.*) by using the technique of micromechanical cleavage [2]. Graphene's unique properties arise from the collective behavior of its charge-carrying fermions. The interaction between fermions and the honeycomb lattice causes electrons effectively to obey the relativistic Dirac equation. As a consequence, these are distributed in a conical spectrum. Both the electrons and holes could be considered as massless particles inside zero band gap graphene [3]. Their states are interconnected, and coexist together at the zero energy level called Dirac point (Box 1).

Box 1. A band-structure picture of graphene: energy versus particle momentum.



The situation when the Fermi level coincides with Dirac point (intersection of electron and hole states) is depicted. The Fermi energy position can be tuned upwards (downwards) by inducing electrons (holes) in the system, for example, by an electrostatic gate electrode.

Graphene-based electrical sensors have the potential to revolutionize gas sensors. Very recent research [3] show that an advantage of graphene comes from the specific properties: it is a 2D material, unlike 3D ones it offers its whole volume to the surface adsorbates; it has low Johnson noise even in the limit of few charge carriers; graphene allows four-probe measurements on a single-crystal device with electrical contacts that are Ohmic and have low resistance.

The change in conductivity of a graphene-based device under molecular exposure raises a fundamental question: what is the mechanism behind this change? The results reported on graphene-based sensors are so far quite contradictory; they show the observation of change in either the mobility μ [4] or the density of charge carriers [3]. Change in mobility confirms the theoretical description of charge impurities being the scatterers that currently limit μ in graphene device [5,6]. From another point of view, there are published results which show μ unchanged during the exposure period [3,7]. These results clearly raise doubts about the role of charge impurities in the scattering processes. One of the possible explanations may be in considering the presence of few-nm-thick layer of adsorbed water [8], providing sufficient dielectric screening to suppress scattering on charged impurities.

Here we will propose **a novel experimental way of studying the mechanism by which adsorbates change the transport properties of graphene.**

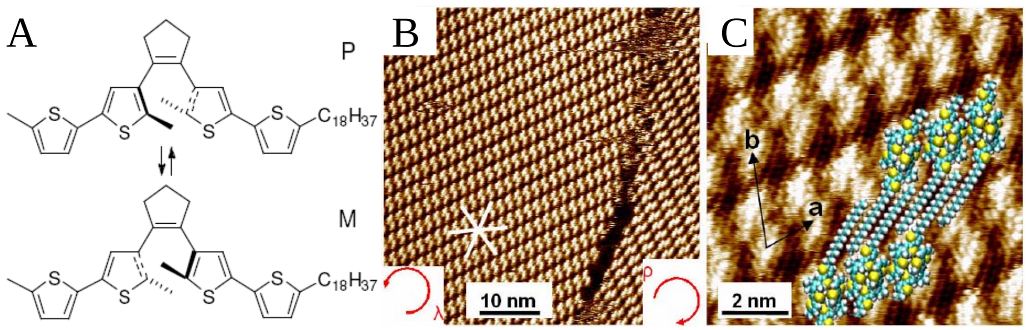
Further along the course of the proposed research, we plan to **develop graphene-based devices as sensors for the behavior of molecular switches on the carbon lattice surface.**

Molecular switches are a class of organic molecules on which reversible modulations of physical properties may be performed by using an external trigger: light [9], an electrical field [10], temperature [11], etc. The switching effect is based on the reorganization of the π-conjugated backbone of the molecule (Box 2) that consequently leads to a change in the physical properties like absorption and luminescence spectra or electrical conductivity.

There are known single-molecule techniques such as optical ones (Single Molecule Spectroscopy: SMS) [12] and charge transport based studies (Scanning Tunneling Microscopy: STM). Each of the techniques gives only partial information about molecule: SMS studies only optical transitions in electronic structure; while STM determines the occupied and unoccupied molecular states of solely ordered systems. Here we would like to offer new single-molecule technique that allows one to study response from few or even single molecules [3] by sending a current through the graphene.

2D flakes of graphene in the state of metallic conductivity provide a strong tool for studying monolayers of molecular switches. Among suitable molecules, those showing strong interaction with graphene (for example, species with alkane tails) will be our first candidates. In the group of Synthetic Organic Chemistry (Zernike Institute for Advanced Materials) a self-assembled layer of diarylethene (Box 2) on graphite surface has been already prepared and studied [13].

Box 2. Self-assembled thermal switches on graphite.



A) Schematic representation of the thermal interconversion occurring between P and M conformers of diarylethene in solution; **B)** Domains formed by diarylethene-based dimmers; **C)** High resolution STM image and proposed packing model obtained by force-field calculations [13].
The orientations of the main crystallographic axes of graphite are schematically represented by white lines.

The conical band structure of graphene, in particular the coexistence of both electron and hole states in the vicinity of the Dirac point, makes graphene one of the most attractive material for studying molecular switching processes in the monolayers. The changes in the physical properties of switches, in particular charge or its distribution (electric dipole moment), accompanied by reorganization of their molecular structure can be detected by graphene-based sensor with high accuracy. A Hall bar geometry could provide a sensitivity high enough to detect one electron charge transfer from the molecule to the graphene surface.

The main question for an assembly of switches is the preservation of their switching properties and changes in switching dynamics on the surface. Therefore we will explore two lines within the project:

A) examination of switching conditions of molecules assembled on graphene;
B) studying of their switching dynamics.

We also plan to preserve photo-, thermochromic properties of switches by synthetic modification of the molecules before assembling them on graphene.

2.4.2 Research question(s)

- What is the optimum design for graphene-based sensor to achieve single-molecule detection?
- How can the transport processes in graphene be controlled by molecular adsorbates?
- How to perform sensitive measurements of the electrical properties of monolayers with incorporated molecular switches via graphene-based sensors?

2.4.3 Method / Approach

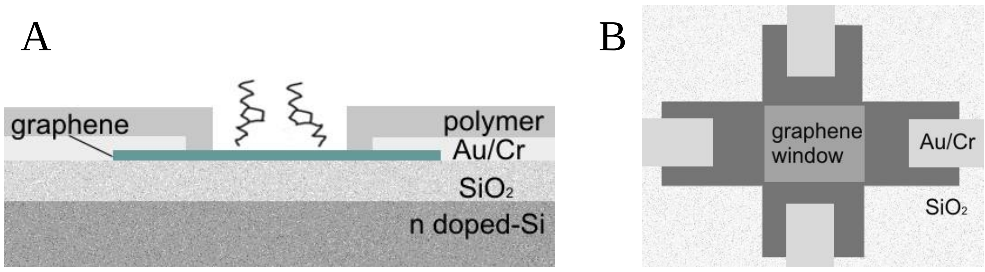
My PhD Project will be a continuation and broadening for my current Master Project in the research group Physics of Nanodevices at Zernike Institute for Advanced Materials. We have already developed a technique to fabricate well defined single layer graphene flakes of different sizes. With the combination of electron beam lithography, liftoff techniques and oxygen plasma etching the graphene-based devices of any necessary shape and dimension can be constructed. The group achieved a breakthrough in the field of spintronics in graphene by fabricating mesoscopic spin valve devices and injecting spin current into a single graphene layer. These results have been recently published in *Nature* [14]. Having all these techniques available we are in a good position to start a new direction of graphene-based sensors.

During the sample preparation, the cleaning procedure becomes a crucial step if the purpose is single-molecule detection. Realizing this necessity, we already developed the recipe for obtaining a well cleaned graphene-based device [15].

Expected results, according to the raised questions, are:

- **Single-molecule detection.**
  We plan to build a graphene-based sensor using the techniques available in our group.

Box 3. Schematic picture of a Hall sensor based on graphene.



A) Side view; **B)** Top view.
n doped-Si is used as a gate insulated by SiO_2 layer. The contacts are Au/Cr covered with polymer. The "window" is an opened area for exposing a part of graphene to the relevant molecules. A magnetic field is applied perpendicular to the surface.

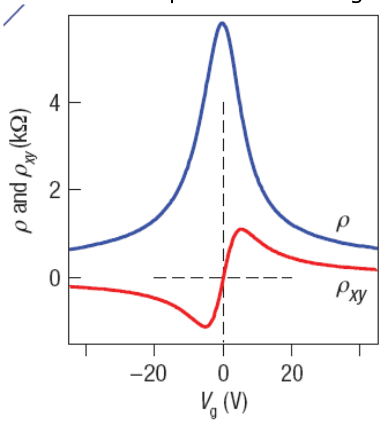
The Hall bar geometry (Box 3) of electrical contacts allows achieving the highest sensitivity towards adsorption of molecules. The design idea of the device consists of a "window" that opens a part of the graphene flake for exposure to molecules, and the system of electrical contacts isolated from each other and the molecules.

There are two possible regimes of operating the device:

1) registration of changes in the longitudinal resistivity ρ with a gate voltage set to a distance about 10 V from the Dirac point (where the carrier density n ≅ $1.2 \cdot 10^{12}$ cm^{-2} is already high);
2) registration of changes in the direction of Hall resistivity ρ_{xy} at gate voltages in the vicinity of the Dirac point (at of about ±100 mV). See Box 4.

Here the carrier density may be tuned either by gate voltage or by the presence of the molecules on top of graphene. While the first regime allows the detecting linear changes of resistivity with increase of the number of adsorbated molecules, the second regime gives the highest efficiency of detecting because of the steep response of ρ_{xy} on any adsorption event.

Box 4. The dependence of longitudinal ρ and Hall ρ_{xy} resistivities on gate voltage [3].



The longitudinal resistivity ρ reaches its maximum value at the Dirac point. Away from Dirac point the dependence on gate voltage can be considered as linear.
The Hall resistivity ρ_{xy} has two maxima. The positive (negative) sign of the maximum indicates electron (hole) doping. In the vicinity of the Dirac point, ρ_{xy} has the steepest slope.

- **Mechanisms of the electrical transport.**

To verify the theoretically described mechanism of charge carrier transport in presence of charge impurities in graphene we are going to use free hanging membranes of graphene, fabricated via lift-off technique. This technique was recently tested in our group. It allows making the membranes between electrodes, which excludes the influence from impurities on silicon substrate. Thus changes in the device conductivity in molecular environment will be caused only by the impurities due the adsorption of the molecules.

Another method that we plan to use to determine the role of adsorbated molecules in carrier scattering processes is Raman spectroscopy. Recent results [16] show that Raman spectra (in the regions of wave numbers around 1560 cm^{-1} and 2700 cm^{-1}) on graphene flake give information about the type and density of charged impurities present in single layer. Thus the question whether given adsorbed molecules act as charge impurities or not may be answered after careful Raman spectra analysis.

- **Molecular switches study.**

A next step of our research is studying diluted monolayers of molecular switches assembled on graphene. We plan to use UV, visible light and temperature switchable molecules. Two types of monolayers will be studied: self-assembled (molecules physisorbed on the surface) and covalently attached (by chemical modification of graphene).

Depending on changes in molecular structure the charge carriers of different types can be induced in graphene. For those molecules, that undergo charge transfer during the switching process, the outcome of the experiments shall yield changes either in electrical mobility μ or charge carrier density n. Along this line we will:

A) use graphene as a sensor for monitoring the assembly process of the molecules in the layer;
B) use graphene as a sensor for monitoring physical changes (dynamics) in the molecular layer.

In private communications with others groups of the Zernike Institute for Advanced Materials we have already discussed the possibilities to study also electronic density redistribution (electrical dipole moments) of molecules by capacitive interaction with graphene.

2.4.4 Innovation

The idea of studying organic molecules via conductance changes induced by the molecules' presence on the graphene surface is new. Our assumptions and plans are based on the recent discovery that the graphene conductance can be modulated by molecules assembled on graphene.

In the course of the project we plan to use the developed design of graphene sensors in liquid environment that is sometimes a crucial condition for the class of complicated molecules such as switches or motors. Our collaboration with group of Synthetic Organic Chemistry at Zernike Institute for Advanced Materials (Prof. B.L. Feringa) provides us with a variety of interesting molecular switches to study their behavior. Within the current project we will be also consulting with surface physics specialists in the Zernike Institute (Prof. P. Rudolf).

With our method and specific sensor design we expect to achieve a level of single-molecule detection. Moreover, the proposed experiments allow characterizing the processes of charge transport and the influence of the adsorbed molecules.

2.4.5 Relevance for science, technology or society

Graphene as a 2D sheet of carbon atoms has a big potential for practical applications in electronics. The possible application of graphene-based device as a sensor of molecular switches behavior is completely new idea. We are confident that the proposed technique of single-molecule study will innovate the material research on the molecular level and will find its place in future industrial applications. The sensitivity of graphene to ions close to its surface in liquid environment could potentially make graphene an alternative for the electrodes used in cyclic voltammetry (electrochemistry) measurements. Moreover, so far the mechanisms of charge transport in graphene are not fully understood. Our research is focused on this issue too.

2.4.6 Literature references

1. P.R. Wallace, The band theory of graphite, *Phys. Rev.* **71** (9), 622-634 (1947).
2. K.S. Novoselov *et al.*, *Science* **306**, 666 (2004).
3. F.Schedin *et al.*, *Nat. Mat.* **6**, 652-655 (2007).
4. E. H. Hwang, S. Adam, S. Das Sarma, *cond-mat/0610834v1*, 30 Oct 2006.
5. T. Ando, *Jor. Phys. Soc. Japan* **75 (7)**, 074716 (2006).
6. E.H. Hwang, S. Adam, S. Das Sarma, *Phys. Rev. Letters*, **98**, 186806 (2007).
7. T.O. Wehling *et al.*, *cond-mat/07103390v1*, 15 Mar 2007.
8. Soghtao Wo *et al.*, *Jor. Appl. Phys*. **100**, 093504 (2006).
9. A.C. Whalley *et al.*, *J. Am. Chem.Soc.* **129**, 12590 (2007).
10. J. Areephong, W.R. Browne, N. Katsonis and B.L. Feringa, *Chem. Commun.* 3930-3932 (2006).
11. D. Dulic, T. Kudernac, A. Puzys, B.L. Feringa and B. J. van Wees, *Adv. Mater.* **19**, 2898-2902 (2007).
12. J.K. Gimzewski and C. Joachim, *Science* **283**, 1683-1688 (1999).
13. N. Katsonis *et al.*, *J. Am. Chem.Soc.* submitted (2007).
14. N. Tombros, C. Jozsa, M. Popiniciuc, H.T. Jonkman, and B.J. van Wees, *Nature* **488**, 571 (2007).
15. A. Veligura, C. Jozsa, N. Tombros, and B.J. van Wees, *Appl. Phys. Lett*, in preparation (2007).
16. C. Casiraghi *et al.*, *cond-mat/07092566v1*, 17 Sep 2007.

The total number of words: 1994.

2.4.7 Plan of work

Briefly indicate for each calendar year which activities are planned

Year	Research activities
2008	Construction of graphene-based devices, checking sensitivity to gases (NH_3, NH_2, etc.)
2009	Preparation of free hanging graphene membranes, electrical transport measurements in presence of molecules, assembling of molecular switches on the graphene surface
2010	Raman spectroscopy measurements, studying of molecular switches layers on graphene
2011	Synthetic modification of the switches, achieving of single-molecule sensitivity
2012	Studying of changes in molecular dipole moments, PhD thesis writing

3 Cost estimates

8a. Budget

Costs	2008	2009	2010	2011	2012	Total
Staff (in k€)	0	0	0	0	0	0
Applicant	8.000	35.000	40.000	44.000	49.000	176.000
Non staff (in k€)	0	0	0	0	0	0
Benchfee (standard)	0	0	0	0	0	0
Equipment	5.000	5.000	5.000	5.000	5.000	25.000
Consumables	0	0	0	0	0	
Travel	0	1.000	1.000	1.000	1.000	4.000
Other	0	1.000	1.000	1.000	1.000	4.000
TOTAL	13.000	42.000	47.000	51.000	56.000	209.000

3.1 Costs exceeding the grant

The maximum amount of the grant is 180 k€. Costs exceeding the maximum grant must be met by the university.
University guarantees to meet additional costs and to provide support services and supervision.
Select:
- Yes

3.2 Other Grants

- Have any other grants for this project or for the applicant been requested either from NWO or from any other institution?

Select:
- No

4 Curriculum Vitae

4.1 Personal details

Applicant

-Title(s), initial(s), first name:	Alina
-Surname:	Veligura
-Nationality:	Ukrainian
-Date of birth:	20.09.1983
-Country and place of birth:	Ukraine, Kiev

Parents

-Country of birth father:	Ukraine
-Country of birth mother:	Ukraine

4.2 Secondary education

School type: high school # 134 named after Yuriy Gagarin
City and country: Ukraine, Kiev
Period: 1998-2000
Graduation date: 20 June, 2000. Cum laude certificate.

4.3 Bachelor's degree

University/College of Higher Education: National Taras Shevchenko University of Kiev
Faculty/discipline: Medical Radiophysics Department
City and country: Kiev, Ukraine
Period: 2000-2004
Date Bachelor’s degree: 28 June, 2004
Grade average: cum laude diploma.

4.4 Research master's

University: Rijksuniversiteit Groningen, Zernike Institute for Advanced Materials
Faculty/discipline: Mathematics and Natural Sciences/ Physics of Nanodevices
City and country: Groningen, the Netherlands
Period: 2006-2008
Expected date Master’s degree: 15 June, 2008
Grade average (so far): 7.8, Top Master Programme in Nanoscience
Title Master’s thesis (if applicable): Graphene-based device preparation for molecular detection
Grade for thesis (if applicable):

4.5 Motivation for application

This grant will allow me to expand my knowledge in material (nano)science; in particular, the combination of graphene with molecular switches leads to an interesting overlap of material science with molecular science. I’m confident in my ability (two MSc’s: physics and nanoscience/chemistry) to realize the ideas described in this proposal, and make a contribution to this blooming field of research. Moreover, the proposal can raise/answer questions in many research directions, which may become separate investigations in my post doctoral career.

4.6 Current work experience (if applicable)

4.7 Previous relevant work experience (if applicable)

The Scientific and Training center "Physical and Chemical Material Science" of National Taras Shevchenko University of Kiev and NAS of Ukraine:

- Laboratory assistant, April 2002 – November 2003, 10 h/week;
- Junior Scientific Researcher, December 2003 –June 2006, 14 h/week.

4.8 International activities (if applicable)

- International collaboration with Prof Dr. rer. nat. habil. Peter Scharff's research group, Chemistry Department, Institute of Physics, Technische Univerität Ilmenau, Germany: 2002-2006. Prof. Sharff's group was doing synthesis of organic molecules and our group was working on molecules characterizations.
- Scientific research visits to Technische Univerität Ilmenau in 2002, 2003, 2004, 2005.

4.9 Other academic activities (if applicable)

- Staff member of organizing NATO ARW / Summer School "Frontiers in molecular-scale science and technology of nanocarbon, nanosilicon and biopolymer integrated nanosystems", Ilmenau (Germany), 12-16 July, 2003.
- A member of organizing committee of Top Master's Nanosymposium "Aiming at life" 9^{th} of June 2007, Zernike institute for Advanced materials, Groningen, the Netherlands.

4.10 Research grants and prizes (if applicable)

1. Scholar of DAAD program Studienpraktikum einer Gruppe aus der Ukraine (10.08. 02 - 18.08.02), in TU Ilmenau, Germany - Grant DAAD Zeichen: **222-stpa-III-3-02-ukr.**
8 days research visit to Technical University of Ilmenau for the group of 12 students. All costs were taken by DAAD organization.
2. Scholar of DAAD program Study Visit in German Universities, Institutes (1.05.04 – 11.05.04) – Grant DAAD Zeichen: **222-in-19-II-04-ukr-uk.**
10 days introduction-visit to German universities: Aachen University of Applied Sciences, Research Centre Jülich, Munster University, Technical University of Ilmenau, Drezden Technical University for the group of 10 students. All costs were taken by DAAD organization.
3. Scholar of DAAD Leonhard–Euler–Stipendienprogramm 2004/2005 – Grant DAAD (Zuwendungsvertrag **A04/00952**).
Personal scholarship for one year, with one month scientific practice in Technical University of Ilmenau. Around 2000 € per year (amount changes from time to time).
4. European Materials Research Society, **Young Scientist Award,** EMRS Spring Meeting 2005. Amount - 100 €.
5. Top Master Programme in Nanoscience 2006/2008, Zernike institute for Advanced materials.
Two-year international English-language Master's degree programme, open to excellent students and granted with scholarship. Around 9000 € per year.

4.11 Gaps / other relevant information (if applicable)

My Top Master research in the University of Groningen is my second high education.
The interest of my research required knowledge in chemistry and modern techniques of material investigations. Therefore I took a decision to continue my study and applied for

the Top Master Programme in Nanoscience that offered me an opportunity to get new knowledge and improve my skills in making research. My first research Master Degree I got in Ukraine (2004-2006) with a cum laude diploma.

Master's degree

University/College of Higher Education: National Taras Shevchenko University of Kiev
Faculty/discipline: Medical Radiophysics Department
City and country: Kiev, Ukraine
Period: 2004-2006
Title Master's thesis (if applicable): ss-DNA induced assembly of modified golden nanoparticles: optilcal properties, structure and application
Date Master's degree: 20 June, 2006
Grade average: cum laude diploma.

4.12 List of publications (if applicable)

1. Oleg I. Lysko, **Alina V. Veligura**, Vitaliy A. Dubok, Aleksandr D. Gorchinskiy, Yuriy I. Prylutskyy, Svitlana V. Prylutska, Eugenia V. Buzaneva, Peter Scharff, Katrin Risch, Physical and biophysical study of interaction calcium hydroxyapatite with C_{60} clusters in water solution and with DNA/gold and DNA/gold/C_{60} hydrogels, *Bulletin of the University of Kiev a Series: Physics&Mathematics* **(3)** pp 323-334 (2002).
2. **Alina V. Veligura**, Aleksandr D. Gorchinskiy, The changes in the conductivity of polymerized DNA and DNA/nanosilica complex induced by the UV irradiation, *Bulletin of the University of Kiev a Series: Physics&Mathematics* **(4)** pp 313-318 (2003).
3. E. Buzaneva, A. Gorchinskiy, O. Ivanyuta, **A. Veligura,** D. Zherebetskyy**,** O. Lysko, D. Kolomiyets, O. Vysokolyan, I. Lysko, P. Scharff, K. Risch, C. Tsamis, A. Nassiopoulou, Design and study of DNA/nanocarbon and macrocyclic metal complex/C_{60} nanostructures, *Frontiers of multifunctional integrated nanosystems*, *NATO Science Series*, *II-Mathematics*, *Physics and Chemistry*–**v. 64**, pp. 251-276 (2004).
4. **Alina Veligura**, Michael Koehler, Wolfgang Fritzsche, Peter Lytvyn, Alexandr Gorchinskyy, Eugenia Buzaneva, Uv induced ds(ss)-DNA damage: optical and electrical recognition**,** *Meeting abstract***,** *BMC Plant Biology 2005*, **5** (Suppl 1):S32 (31 May 2005).
5. Veligura A., et al., UV-Induced DS(SS) - DNA Damage: Optical and Electrical Recognition, *Cell Biology and Instrumentation: UV Radiation*, *Nitric Oxide and Cell Death in Plants*, *NATO Science Series*, *I- Life and Behavior Sciences* - **v. 371**, pp.109-128 (2006).
6. N. Tombros, S. Tanabe, **A. Veligura**, C. Jozsa, M. Popinciuc, H.T. Jonkman and B.J. van Wees, Anisotropic spin relaxation in graphene spin valves, *Phys. Rev. Lett.*, submitted (2007).
7. **A. Veligura**, C. Jozsa, N. Tombros, and B.J. van Wees, Graphene cleaning by baking in Ar/H_2 atmosphere, *Appl. Phys. Lett.* in preparation (2007).

Statement

I hereby declare that the present form has been completed truthfully

Place: Groningen

Date: 20.12.2007

Signature of applicant: Alina Veligura

Signature of university representative:
dr. S.K. Kuipers
voorzitter College van Bestuur

b.a.