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PARNASS

Parallel Nanoassembling Directed by Short-range Field Forces

STRP

SIXTH FRAMEWORK PROGRAMME

PRIORITY 3 - NMP

Nanotechnologies and Nanosciences, Knowledge-based Multifunctional Materials and New Production Processes and Devices

Publishable Final Activity Report

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Project coordinator name: U. Schmucker

Project coordinator organization name: Fraunhofer IFF

The PARNASS project was funded under the sixth framework programme to bridge the gap between nanoscience and technology by taking recent advances in the underlying nanoscale physics and chemistry and transferring them to the real world of manufacturing engineering and mass production.

Project Objectives

The synergy of advanced technologies on the nanometer scale and the exploitation of new physics are opening a broad range of revolutionary opportunities for virtually every sector of industry and every realm of day-to-day life. One example of such synergy is the integration of new functionalities in conventional and new components and materials in silicon-based hybrid microsystems that incorporate the unique properties of nanoscale sensing or actuation with the functionality of silicon microelectronic circuits. The nanocomponents and microelectronic components in such a hybrid systems are first fabricated as separate units and then bonded together, thus making it possible to overcome limitations on design, fabrication and function inherent in monolithic integration.

Along with its clear advantages of greater flexibility of design and ability to produce materials and structures that monolithic fabrication cannot, the hybrid approach entails a physical and engineering challenge, namely extremely high positioning precision over a large area during component assembly. The primary objective of this project is to master this challenge by applying a radically innovative approach from which the project derives its name: Parallel nanoassembly directed by short-range field forces (PARNASS). Ultimately, nanoengineered force fields shall support nanoscale assembly tasks much like robotic manipulators in macroscopic assembly tasks.

The hybrid systems envisioned shall constitute a sort of integrated system composed of dissimilar components that may, for example, be used as sensory devices that take advantage of the properties of different materials, components or processes. To enhance the chances of success and maximize its impact, the project was organized as a set of interrelated multidisciplinary tasks. Each task relates to some specific aspect of pertinent materials, components and processes and each task has its own practical significance. Collectively, all the tasks established the basis for achieving the stated objectives:

- To obtain a deeper phenomenological understanding of nanoscale forces and apply this understanding to design optimal nanostructures for nanoparticle trapping and alignment,
- To design and construct an automated analyzer for the production and analysis of nanostructures and
- To develop and prototype a proof-of-concept hybrid device.

The theoretical and experimental studies in the project geared toward acquiring detailed qualitative and quantitative knowledge of the forces and determining the geometry and material of nanostructures in order to be able to produce the optimal nanoengineered forces to trap and align hybrid nanocomponents, e.g. carbon nanotubes or quantum nanowires.

Another project deliverable, the automated analyzer was constructed to support the design of nanostructures and enable the production and analysis of both nanostructures and the force fields they produce. The analyzer was designed and constructed as a type of nanoengineering cell. In conjunction with in situ nanopatterning capabilities, it facilitates on-the-fly pattern modification, pattern characterization and mapping of force fields produced by the patterns. The analyzer is expected to have an impact beyond the confines of the project, e.g., as a nanoengineering option in integrated SPM/SEM/FIB devices. There is no analogous device on the global market.

Another objective of the project, the prototyped proof-of-concept hybrid device consists of nanoelectronic sensory devices that employ carbon nanotubes as their core sensing component integrated in a signal processing microelectronic circuit. The devices are able to selectively detect different target analytes in different media with high sensitivity.

Technological Issues

Nanoscale structures and components are usually either fabricated by chemical processes, e.g. gas phase deposition, by ion or electron beam patterning or by systematic manipulation of individual objects with scanning probe microscopes. Chemical processes are well suited and even advantageous for many applications, e.g. nanoscale coating. However, since these processes produce products that always exhibit a stochastic distribution, they cannot be used to fabricate more complex structures consisting of several component or materials in a functional arrangement. Ion or electron beam patterning and the manipulation of individual nanoobjects with scanning probe microscopes can to a certain extent but a serial approach is highly ineffective and relatively unsuited for purposes of manufacturing.

Just as clamps, springs and robotic manipulators are effectively employed for macroscopic assembly tasks, forces that acting on a scale of a few nanometers can, in principle, be taken advantage of to support assembly operations. On a scale of up to approximately 100 nm, electromagnetic fields and thermodynamic effects cause different types of forces to act between objects of the same order of magnitude. The ranges and effects of these forces differ from the known macroscopic effects fundamentally and their nature and interaction have scarcely been researched. Applying these forces to assembly operations requires fundamentally and thoroughly understanding their mechanisms. One of this project's objectives was to clarify how the skilful selection, chemical modification and mechanical structuring of nanoparticles and substrates can facilitate a kind of self-organizing assembly process.

Thus, the project explicitly concentrated on a specific kind of self-assembly, i.e. self-controlled construction processes. Self-assembly at nanoscale is driven by forces that bind nanoobjects to each other, to surfaces and to other nearby structures. These include familiar electrostatic and magnetic forces as well as Casimir forces and closely related van der Waals forces. Work in the project focused on better understanding the nature of Casimir forces together with van der Waals forces. Detailed understanding of nanoscale assembly must be based on sound knowledge of the forces acting on nanoscale objects. This is the fundamental scientific goal of the project, which combines theoretical investigations with sophisticated physical experiments and engineering to create and characterize self-assembled nanostructures.

Tasks in Theoretical Physics

The main task of theoretical physics in the project was to deepen the understanding of the forces acting at nanoscale with the goal of delivering consistent theoretical analysis and experimental data. There is general interest in these forces because they are increasing being applied in fields ranging from cosmology to nanotechnology. These forces are directly related to both physics that limits the existence of extra dimensions and forces following from new physics such non-Newtonian forces at small separations.

The nature of the underlying physics changes dramatically at scales of a few hundred nanometers and below. The laws of classical physics and methods based on them are no longer applicable since quantum and size effects become increasingly important and even dominant in some cases. At nanoscale, van der Waals and Casimir forces are dominating. These forces usually manifest themselves as attractive forces and, in some instances, act as undesired forces that cause moving parts in micro-electro-mechanical systems to “stick”. On the other hand, these forces may also be repulsive, providing a much discussed possibility to prevent unwanted “sticking” or even decrease friction at nanoscale.

Since the forces under investigation may be described differently, the task of theoretical physics was quite demanding. In principle at least, forces acting between microscopic bodies may be described from the vantage of vacuum energy in quantum field theory. Alternatively, the forces may be regarded as dispersion forces derived from classical electrodynamics. Therefore, a wide range of methods of description exists, ranging from first principle calculations to purely phenomenological approaches.

The state-of-art at the start of the project was characterized by a good understanding of the forces at large distances over several hundred nanometers. Experiments on Casimir force measurements at these distances correlated to theoretical calculations within 1%. However, this is far from the distance range relevant to the problem. Significantly less was known about these forces at scales of a few tens of nanometers or closer. Moreover, the relation between different theoretical approaches was relatively unclear.

Some researchers consider these forces to be a pure effect of surface plasmons while others take the entire spectrum into account. Since single walled carbon nanotubes were the primary candidate for the hybrid sensory device investigated in this project, this question was a particular concern. For single walled nano tubes the commonly used approach to consider as a hollow dielectric cylinder failed. A more realistic plasma shell model was considered instead. New results were obtained for the geometry dependence of the forces.

Casimir and van der Waals forces are a rapidly developing field of theoretical physics that started with the broad introduction of atomic force microscopes (AFM). Interest in the Casimir effect has exploded in recent years. As a result, significant advances have been made in both theoretical and applied research related to Casimir and van der Waals forces. A new approach based on functional determinant representation has made calculating the forces between arbitrarily shaped bodies more reliable and significantly easier.

Theoretical investigations in this project primarily focused on improving approaches and their relation with more phenomenological and applied approaches. The starting point was an idealized model of interaction between two parallel and ideally reflecting surfaces where the Casimir force is well known, well understood theoretically and solidly verified experimentally. However, this idealized form is only applicable at much larger distances than were relevant to the project. At shorter distances, the force depends on intrinsic properties of the interacting bodies. Therefore, two complementary models were examined, a dielectric medium model and a plasma shell model. The latter is intended to describe a carbon sheet that resembles a single wall carbon nanotube. Both models were proven to deliver adequate results for small separation and even direct contact.

Another direction of research addresses the dependence on the geometry of the interacting bodies. Apart from plane parallel geometry (and some more simple geometries), no general method to calculate the forces has been available mainly because of the presence of so-called “ultraviolet divergences”, the elimination of which made direct numerical approaches useless. Several approximate schemes of quite limited applicability were the only alternative. The most important are the “proximity force approximation”, which is only applicable to small deviations from plane geometry, and the “pairwise summation method”, which is only applicable to dilute media. Significant progress was made in this field in early 2006 when the aforementioned method was devised. The interaction energy is represented by a functional determinant free of the mentioned “ultraviolet divergences” and, thus, in principle, open to direct numerical evaluation. This project applied this method to obtain analytic corrections necessary for experiments and was first to obtain analytic corrections beyond the proximity force approximation. Together, these developments represented a breakthrough in the theory of the Casmir and van der Waals forces.

Establishing a relationship between calculations and experiments was a significant challenge. The difficulties are theoretical and practical. In the theoretical realm and in addition to the aforementioned problems, a number of additional factors become important at small separation. Especially under ambient conditions, these are primarily specific surface properties that may vary strongly even from sample to sample. In addition one is faced with water layers, surfactants and so on which may obscure the results. In the experimental realm, the direct measurement of forces between nanoobjects is extremely difficult.

One common technique is imaging the surface and moving objects on it with an AFM. Since quantitative results of forces are not easily obtained with an AFM, a new method was developed. It was called *method of the most bent state*. It makes use of the balance between static friction forces and the elastic restoring force of a bent nanowire. The idea behind this method is quite simple, however the experimental results obtained allowed even for quantitative estimations on the pinning forces, more exactly on the shear stress acting between a nanowire and the substrate. The interplay between pinning forces and intrinsic properties such as elasticity determines the domain of parameters that defines requisite conditions for the self-assembly of nanoobjects.

The knowledge acquired within this project shall also facilitate progress towards stronger constraints on hypothetical fundamental interactions. These conatraints can be obtained from the precision Casimir force measurements and are of big interest for fundamental physics.

The results of the work in theoretical physics in the project were published in eight papers in leading international research journals (which had received seventy-one citations according to the ISI-Web of Knowledge by the time this report was compiled), and were presented at a total of sixteen seminars, workshops and conferences. At least one more publication is being prepared.

Forty-two citations of one paper on the work in this project published in June 2006 are evidence of the far-reaching impact of the results from the PARNASS project.

Tasks in Experimental Investigation

The experimental investigation was intended to acquire a quantitative knowledge of the forces acting on nanoparticles and their response to these forces. The work consisted of three steps. First, techniques to prepare suitable substrate on which nanoparticles can be deposited were developed. Second, qualitative knowledge of the forces on the nanoparticles was acquired. Finally, this qualitative knowledge was built upon to derive a quantitative model capable of describing and predicting the behavior of nanoparticles when acted on by a design's force fields.

One important class of nanoparticles studied was semiconductor nanowires, i.e. long, thin rods of materials such as InAs that are typically a few tens of nanometers in diameter and several microns in length. Lund and Halmstad Universities have the capability to grow extremely high quality nanowires with a good degree of uniformity. A mix of growth techniques makes it possible to investigate a variety of semiconductor materials as well as more complex heterostructures and three-dimensional nanoparticles such as branched nanotrees and core-shell nanowires. A range of methods, including high-resolution electron microscopy, scanning electron microscopy and various probe microscopy techniques are employed to characterize the basic structures and materials.

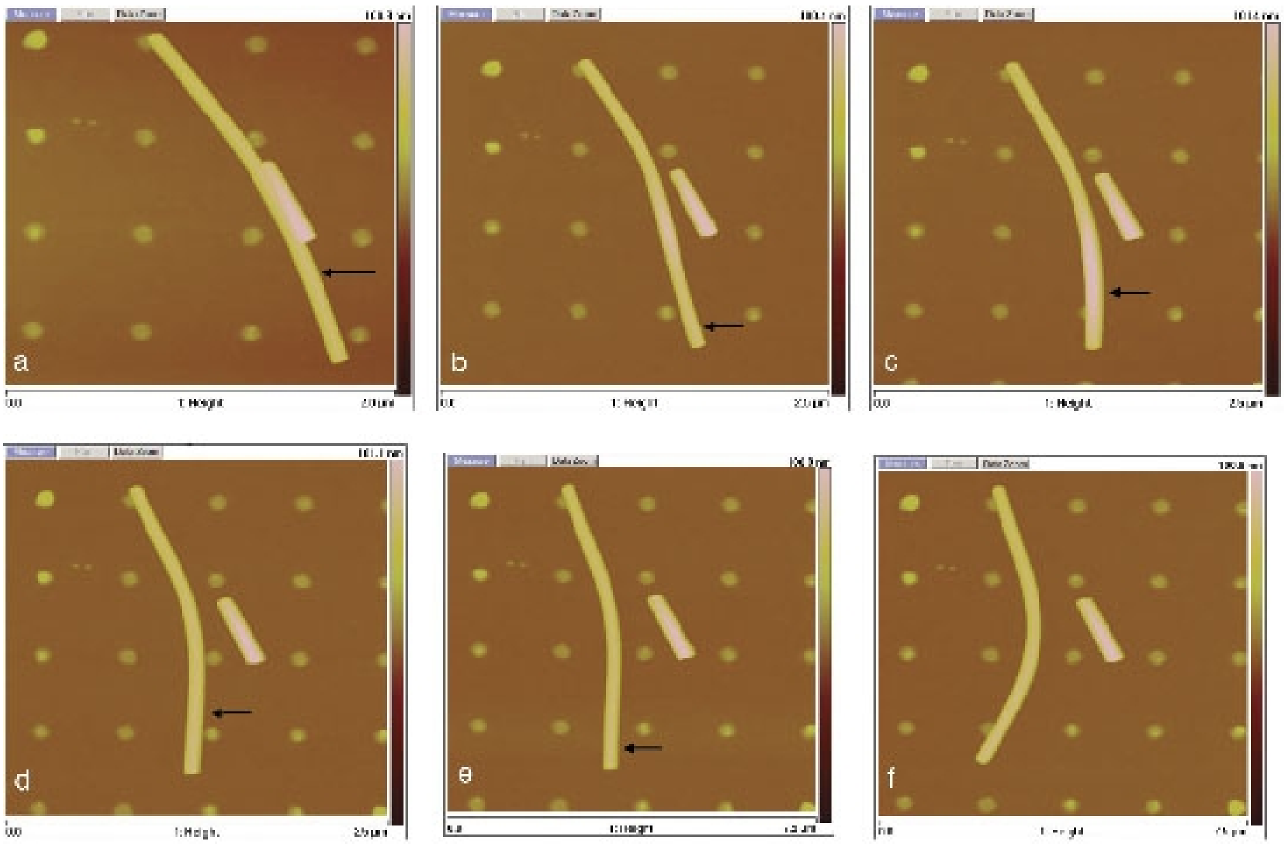


Figure 1. Demonstration of current capabilities AFM manipulation of an InAs nanowire. The images a)-f) show how both ends of the nanowire can be bent to form a curve. The wire snaps in the final step. The arrows indicate where and how the wire was manipulated to arrive at the next step pictured. Several intermediate steps have been omitted for the sake of brevity. This nanowire had an average diameter of 54 nm and was 4 microns long.

A second class of nanoparticles studied was single-wall carbon nanotubes, which are considerably thinner than nanowires and can be as small as one nanometer in diameter. Produced at the Universitat Rovira I Vigili in Tarragona, the nanotubes are purified in a complex series of steps and finally suspended in a carrier solvent. They can then be deposited on a suitable substrate and the solvent removed or allowed to evaporate.

Direct manipulation with the tip from an atomic force microscope was the technique applied most to acquire qualitative knowledge of the nanoparticles' reaction to forces. Direct manipulation can push nanowires and nanotubes laterally on a substrate surface with a high degree of control and can bend them into non-equilibrium shapes or push them so that they interact with one other or objects placed on the surface.

Figure 1 illustrates a complex nanowire manipulation experiment. In the course of the experiment, the nanowire was progressively bent into an ever tighter curve by a sequence of pushes until it finally snapped. Figure 2 presents a more complicated experiment in which a substrate surface covered with an array of gold was used. Two touching nanowires were separated and the longer of the pair was then pushed over the top of two gold dots and bent into a curve, each end eventually touching one gold dot.

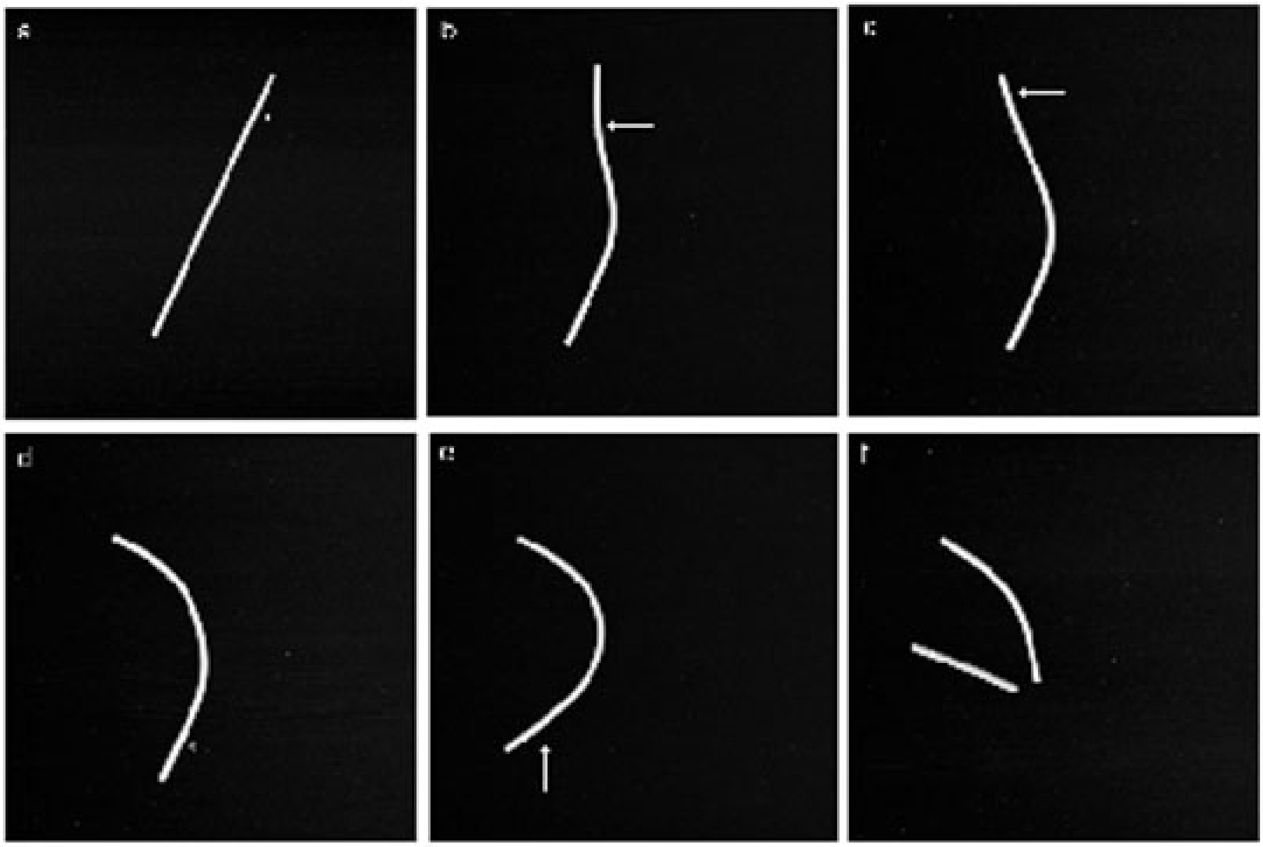


Figure 2. Pushing a long InAs nanowire away from a shorter section of wire to which it became attached during deposition. Afterward it is moved laterally, smoothly passing over the top of two gold dots in the marker array. It comes to rest against a gold dot and does not bend further.

A measure of the deficiency of knowledge about the mechanical properties of semiconductor nanowires is the continued uncertainty whether macroscopic models of elasticity are appropriate at this length scale. Obviously this question needs to be answered before it will be possible to infer the forces acting on wires by analyzing their movement or of the shapes they assume. Therefore, one fundamental task of these investigations was to characterize the wires' elastic behavior as a function of their size, shape and processing history.

Studying the interplay of friction with the substrate surface and elastic forces in the wire has been particularly fruitful. The measured shape of the wire can be used to quantify information on the forces acting on it. Classical elasticity theory directly relates the stress in a distorted wire to its curvature. A key insight is that the intensity of the friction between a wire and its substrate determines the maximum curvature the wire can assume. If friction is weak, a tightly curved wire will simply straighten to relieve the elastic stress. The higher the friction, the more tightly a wire can be bent. The curvature of any wire can be measured directly from AFM images of it, which can then be used to calculate the strain. Assuming the Young's modulus of the wire is the same as in bulk InAs makes it possible to directly derive numerical values for the shear stress and the coefficient of friction.

Just as the elastic properties, the applicability of existing models of friction to nanowires sliding on a planar surface was not at all clear at the outset of the project. The contact between the wire and the substrate perpendicular to the wire axis only covers a few tens of nanometers. However, the contact along the wire axis extends a few microns. Therefore, much effort to quantify the variation of nanowire friction with the nanowire diameter and on surface with various properties. This made it possible to investigate the influence (if any) of an adsorbed water layer on the substrate and to map the range of friction forces experienced by the nanowires.

Figure 3 visualizes the general form of the friction behavior of the InAs nanowires. Values for both sliding friction and static friction were extractable from the measurements. The sliding and static friction of large diameter wires clear differs by two or even three orders of magnitude. Wires below around 40 nm in diameter the sliding friction values jump upwards to mix with those for static friction. The authors interpret this as a transition from pure sliding to a jerky stick-slip motion similar to the motion responsible for screeching tires in the macroscopic world.

The plot in Figure 3 makes one thing is immediately evident: Self-assembly involving lateral movement across the surface will only be possible with low friction values associated with true sliding motion. It follows that, for any given substrate, there is a size of nanoparticle below which friction will prevent any lateral movement and hence self-assembly. Therefore, the applied studies in the project concentrated on identifying optimal trapping and alignment strategies on the lowest friction surface analyzed, i.e. silanized silicon dioxide.

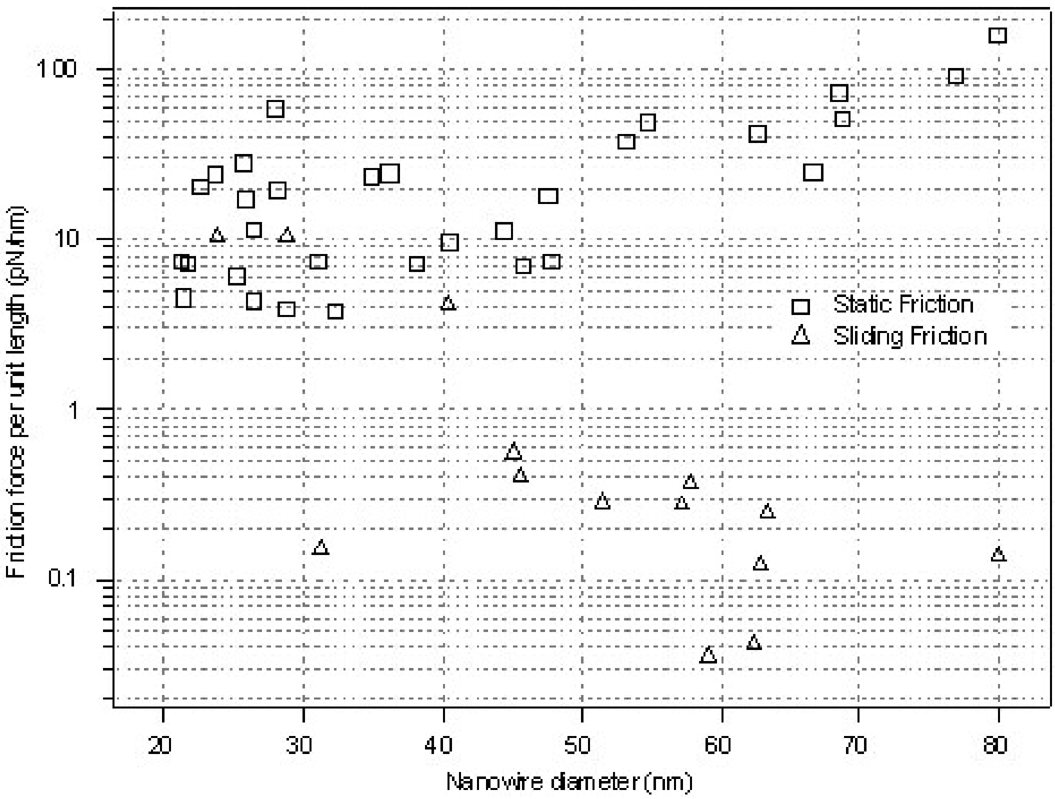


Figure 3 Friction force per unit length over NW diameter for InAs NWs deposited on a Si3N4 substrate.

The silanization of silicon dioxide entails coating the oxide with a single layer of organic molecules. The molecules in a silanized layer stand upright like the bristles on a brush and form a layer with a thickness corresponding to the length of the molecule. In the case presented here, the chains were thirteen carbon atoms long, each carbon atom in the chain being connected to two fluorine atoms in addition to its neighbors in the chain.

As would be expected from relatives of Teflon, fluorinated silane layers exhibited very low coefficients of friction in macroscopic measurements. In the project's experiments, the silanized surfaces indeed had the lowest values for sliding friction. However, the values for static friction did not differ much from those measured on other substrates. From the perspective of application, this is a decided advantage. Once a nanoparticle has stopped moving, it will stay put, held in place by the significantly higher value of sliding friction.

The experiments conducted in the project applied the quantitative knowledge of friction acquired to the nanoscale to perform directed self-assembly in which nanowires move to their intended positions without individual manipulation.The experiments have delivered quite promising results and will be continued beyond the conclusion of the PARNASS project.

Nanoanalyzer

One stated objective of the project was the design and construction of an automated analyzer to investigate that fundamental forces acting between nanoparticles and surfaces as well as between the nanoparticles themselves.

A high resolution electron beam lithography and nanoengineering workstation *e_LiNE*^{TM} manufactured by Raith GmbH (see Fig. 4) was selected as the host system for the automated nanoanalyzer. The system is equipped with a thermal-assisted field emission gun that keeps beam size below 2 nm @ 20keV as well as an interferometer stage with active piezoelectric leveling and a closed loop positioning system, which enables navigating a surface under scanning electron microscope (SEM) control with an accuracy of a few nm in the range of 100x100x30 mm. Resting atop an integrated vibration isolation system, the analyzer allows ultraprecise sample positioning in relation to the electron beam or SPM tool.

Fig. 4. The e_LiNE^{TM} *ultra high resolution electron beam lithography and nanoengineering workstation*

Driven by strong market demands for inexpensive and reliable equipment with moderate maintenance costs that does not require highly skilled operators, two versions of the analyzer setup were developed. A simple and less expensive solution entails mounting the AFM “as built” onto a dedicated sample holder of the *e_LiNE* system. Apart from a lower price, the advantage of this solution is its high flexibility in terms of assembling and desassembling the system. Furthermore, this setup allows the use of different nanoengineering options in the same *e_LiNE* system.

A more sophisticated approach involves mechanically decoupling the analyzer head from the AFM’s scanner. The analyzer head is placed on a firm bridge mounted on the supporting arms of the interferometer stage of the *e_LiNE* system. The sample is placed on the xyz scanner of the nano force analyzer, which is mounted in turn on the interferometer stage. The advantage of this setup is the sample stage’s wide range of lateral travel. Consequently, not only small samples but also wafers of up to 4” can be investigated simultaneously with SEM and AFM. This setup also facilitates a more reliable compensation of mechanical drift between nanoforce probes and samples.

Thus, both variants of the nano force analyzer are based on a combination of well established techniques of scanning probe microscopy (SPM) and scanning electron microscopy. Therefore, the device can be employed for a variety of applications:

- Force measurements: These include measurements of the interaction forces between nanoparticles and the supporting substrate as well as the interaction forces between the nanoparticles themselves.
- Geometry measurements: Surface imaging and extended metrology can be employed to investigate the physical dimensions of nanoparticles.

- Nanofabrication facility: The analyzer also provides the capability to fabricate and modify nanostructures. The SPM tip may be utilized for tooling or as a nanomanipulator.

The combination of two such commonly employed techniques as SPM and SEM or focused ion beam (FIB) opens a wide range of possibilities. The integration of SPM/SEM/FIB in a single device constitutes more than a mere combination of complementary microscopy techniques. SPM probes be can used not only as sensors but also as cutters, task tools or end effectors to finish surfaces. They can also be used to manipulate individual nanoscale objects and assemble them in required configurations. Generally, such an integrated device could be used to take ultraprecise measurements of forces acting on nanoscale and may have much broader application for the design, production and analysis of nanostructured surfaces.

Unfortunately, no universal “all-purpose probes” exist, which are optimal for every type of force measurement or mapping and suitable for every SPM mode. Therefore, switching from one mode or one tip geometry to another requires changing the probe. Usually, an operator can do this easily by manually replacing the old probe with a new one, accurately attaching it to its original position and properly aligning it.

However, even under standard ambient conditions, this procedure has several disadvantages, above all the amount of time involved. The procedure becomes even more time consuming when applied under specific ambient conditions such as vacuums or low temperatures. Moreover, since the target area for the placement of the probe stylus or end effector is less than a few tenths of a nanometer. Thus, probe alignment requires precision that even exceeds the abilities of highly skilled technicians with extremely steady hands. This problem is well-known and semi-automatic or automatic systems have generally solved it with automatic probe exchange and alignment.

Nevertheless, these systems also have a distinct disadvantage. They more closely resemble a miniaturization than a real dedicated nanoscale approach. When they borrow a serial or distributed structure from macromachines, they inherit some critical features for nanoscale applications. They are usually bulky and have a relatively large mechanical loop, i.e. inertial, thermal and mechanical displacements are cumulative in these systems and uncontrollably affect the accuracy of probe positioning.

These systems usually include a handling system that operates in conjunction with tool magazines and corresponding pick-transport-place cycles or include rotating carousel-like probe carriers supported by bearings locked in position by click balls or springs. The first systems experience an irreproducible event, namely the probe’s chaotic jump into final mechanical contact. This randomly offsets probe placement. A second similarly uncontrolled displacement generates a collective clamping action among members and inherent bearing backlash. This suggests any design of a changer tailored to nanoscale operation must be adapted to circumvent the adverse effects of such irreproducible events

Even when combined with high-precision translation stages, the net accuracy of macrosystems is usually limited to a range of around a few micrometers. While this may suffice to align a probe relatively with an AFM laser detector system, it definitely falls short of the accuracy required for nanoscale precision. Moreover, to satisfy the requirements of the aforementioned application, a changer must be able to repeatedly change a limited number of force sensing probes or processing tools rather than a large number of probes when they become damaged, contaminated or dull as in automated AFM operation in the semiconductor industry.

The main purpose of the changer is to position a requisite tool and its sensing or effecting element where desired and, when necessary, replace it automatically with another tool with the requisite alignment accuracy and repeatability. A “tool” is any device that characterizes or modifies surfaces or even manipulates nanoparticles.

The use of modern SEM or FIB microscopes as hosting systems presents a major problem. Their vacuum chambers furnish virtually no free space because they are typically already equipped with a number of densely packed modules and units, e.g. integrated gas injectors for beam-induced deposition and etching, X-ray analyzers and other analytical detectors. Additional space is unavailable for manipulators or feed mechanisms with magazines for task tools exchange or processing tools commonly used in automated macromachines.

The research in this project determined that an automatic tool changer resembling a turntable solves this problem optimally. Such a changer has the task tools or processing tools (probes or grippers) or their holders mounted on a rotary support with a fulcrum offset relative to the optical axis of the SEM. This solution has two major advantages:

- Compact design: A smaller mechanical loop eliminates external low frequency mechanical noise and lessens the amount of thermal drift.
- Existence of a geometric locus curve: The SEM can be focused and a force probe consistently placed on the geometric locus curve, thus ensuring the requisite accuracy when replacement tools are positioned and aligned. Tools must only be positioned and aligned so that their sensing or effecting sections touch on the locus curve.

The main challenges when designing this automatic turntable tool changer were:

- Devising and engineering appropriate kinematics and a self-seating tool holder design;
- Designing an appropriate self-seating rotary support including the means to align and adjust it and
- Fabricating all parts to conform with ambient conditions and electromagnetic considerations in order to prevent SEM image disturbances and vacuum deterioration.

While the changer must be able to exchange several different force sensing probes or processing tools repeatedly, the analyzer must additionally be able to measure the interaction forces to manipulate, form and fabricate nanoobjects and nanostructures in real time as well as to control and visualize them. This necessitates automation methods and configurations that facilitate high throughput creation and characterization of these structures.

Nanocis Imaging's *MultiView 1000*™ SPM system constitutes the core of the analyzer. This SPM's unique design leaves an unobstructed optical path between the SEM gun and a sample so that the sample may be simultaneously studied and processed with SPM and SEM. The changer is engineered and mounted on the SPM's head to provide an unobstructed optical path and eliminate any effects of changer operation that might adversely affect SPM and SEM performance.

The system is modularized for optimum flexibility. Both the SPM and automatic tool changer are detachable, facilitating integration of the analyzer in other systems. The structure of the changer consists of a stationary support platform fastened to the SPM head and a rotary movable turntable kinematically mounted on the stationary support and linked to the displacement driver comprised of an oscillating piezomotor with a special driving gear.

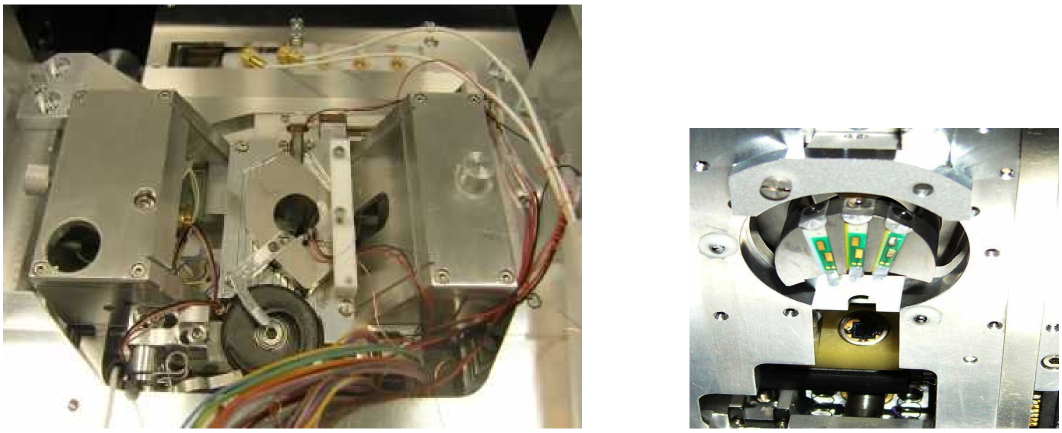


Figure 5. Tool changer mounted on the analyzer head. Left: View of the assembled parts from above. Right: View of the analyzer head with three cantilevers mounted on PCB boards from below.

The changer's design represents a novel approach to kinematically mounting precision SPM components. It is based on a configuration that allows transforming a six point kinematic mount with a single stand into a kinematic mount with interchangeable stands having circularly arced pathes. The changer incorporates the accuracy of a six point kinematic mounting in a rotary indexing machine with a turntable with attached SPM probes or tools. This design reliably moves a turntable from one predetermined (indexed) position to another predetermined (indexed) position relative to the SPM head to reposition SPM probes or tools quickly, easily and accurately. A distinct advantage of this type of kinematic mount is its applicability not only to position parts precisely and reproducibly but also to support a turntable since the three point contact can function as ball-and-socket attachment that defines a pivot point for the turntable.

The support platform is designed for unobstructed operation of the SPM scanner or translation stage and optical or SEM observation of either a tool or sample or both. The six point contact zones on the support platform are configured and designed so that each tool holder's location and angular position relative to a sample is essentially the same as each of the kinematically mounted carrier's preceding and succeeding positions.

The changer incorporates a number of additional alignment systems to enhance accuracy and reproducibility. The tool holders or probe supports also kinematically mounted on the back of the turntable and placed in specially machined holder slots. Thus, the turntable constitutes a kind of a magazine that accommodates and stores tools attached to tool holders.

The tool holder is a plate precision laser machined to dovetail on each side. The slots are appropriately shaped to accommodate the plate and precisely machined to dovetail with the plate. This quick-snap self-seating mechanism creates a specific kinematic mount. Two special elastic elements integrated in the self-seating mechanism compensate for potential cumulative machining tolerances and join the plate securely to the slot

Each slot additionally has a finely pitched ball-tipped screw to mechanically adjust a plate's exact position in a slot. The ball-tipped screw establishes single-point contact with the edge of a holder plate. The configuration of the single-point contact and elastic elements determine the tool holder's position and orientation relative to the slot and the kinematic mount's closed mechanical loop.

This additional mechanical adjustment is employed to pre-align tool holders outside the vacuum chamber before mounting the changer on the SPM. Final fine alignment is performed inside the SEM chamber where two additional piezoactuators integrated in the turntable shift the probes laterally. The SEM continuously monitors this final alignment.

The prototype changer was engineered, built and tested with emphasis on its accuracy and repeatability. The full cycle to replace two neighboring tools takes 5-10 sec. Replacement of the most distant tools (four sequential replacements) takes 80-90 sec. The calibration grade measurements of the relative positioning accuracy between two subsequent tool replacements for arbitrarily mounted non-aligned tools shows the net accuracy is better than 10 micrometers. The relative positioning accuracy between two tools pre-aligned with additional mechanical adjustments integrated into the tool holder is better than 1.0 micrometer. The final fine alignment, which is carried out in-situ inside the SEM chamber by use of two integrated piezoactuators enables the highest achieved accuracy better than 20 nanometers.

Proof-of-Concept Sensory Device

Carbon Nanotubes

Formed from pure carbon bonds, a carbon nanotube can be described as monolayer sheets of graphene atoms arranged in a hexagonal grid pattern that have been rolled into a tube. A carbon nanotube can have a single wall (SWNT) or tubes of various diameters within tubes as in the case of multi-walled nanotubes (MWNT). The graphene grid structure may either align with or twist relative to the tube axis. This variation in grid alignment and the tube diameter determine the electrical properties of the various types of tubes. The most fundamental property is a tube's behavior as a metal or a semiconductor.

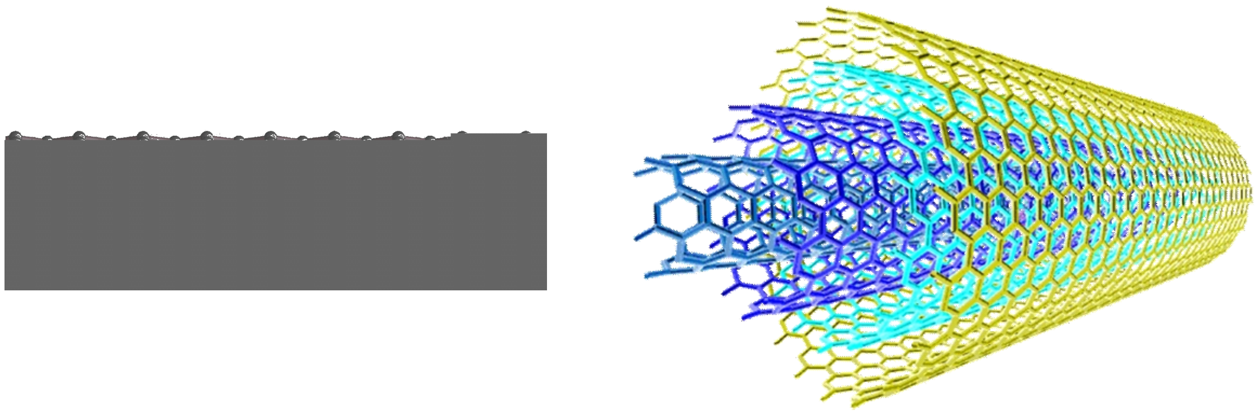


Figure 6. An SWNT (left) and an MWNT (right)

Two-thirds of the nanotubes in synthesized SWNT are semiconducting and one third are metallic. URV synthesizes SWNTby the chemical vapor deposition (CVD) based on the decomposition of a carbon-containing gas above a transition metal to grow nanotubes in a chemical vapor deposition reactor. Figure 7 presents a schematic of the process.

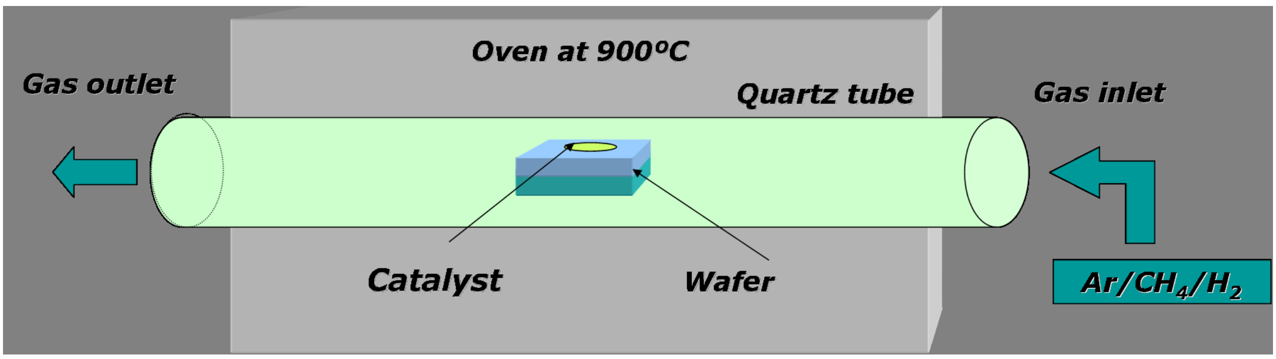
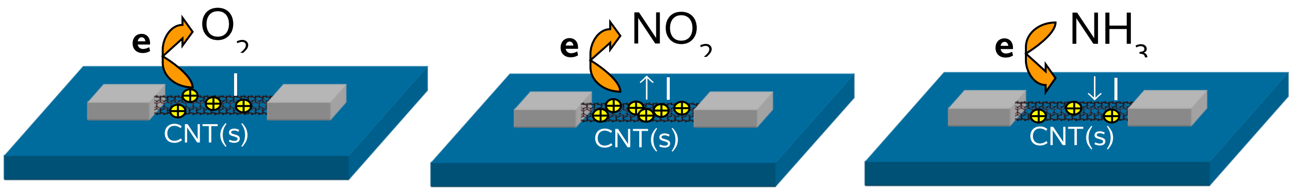


Figure 7. CVD synthesis of CNTs

Chemical vapor deposition deposits carbon atoms atop heated catalyst material (usually iron nitrate). URV uses methane as the carbon source to grow SWNT at 900° C.

Carbon Nanotubes for Sensory Devices

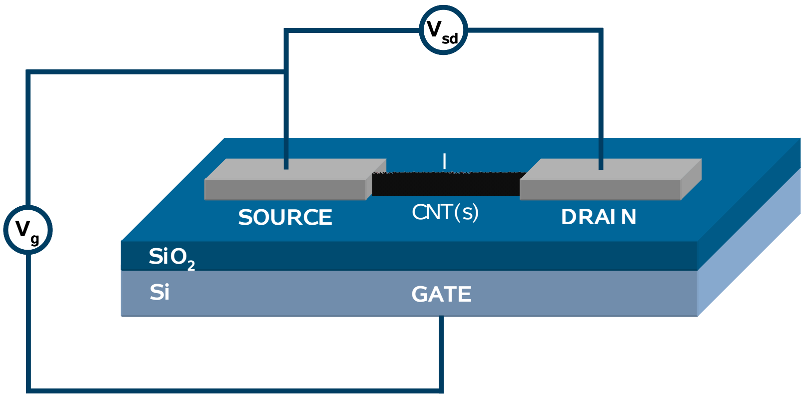
Semiconducting carbon nanotubes are extremely sensitive to their environment. Since carbon nanotubes are surrounded by a cloud of π-electrons, species in the environment can donate or withdraw electrons (thus changing the measurable electrical current passing through the carbon nanotube). A carbon nanotube in air is referred to as a *p*-type semiconductor because O_2 absorbs these π-electrons and the current through the carbon nanotube is caused by positive holes. If NO_2 were introduced instead of O_2, the current intensity would increase because NO_2 has a higher electron affinity than O_2 and, thus, the number of positive holes would increase. If NH_3 were introduced, the current intensity would decrease because NH_3 adds electrons to the cloud of π-electrons and, thus, the number of positive holes would decrease:



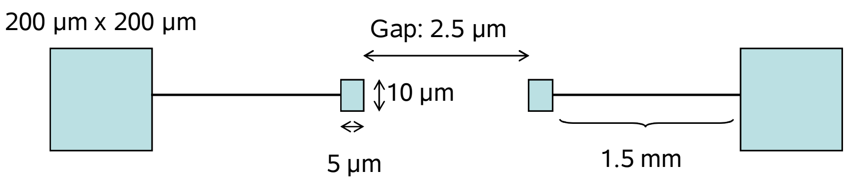
Thus, supplemented with some additional improvements in order to make them selective to the different analytes of interest carbon nanotubes can be advantageously utilized as a core of sensory devices.

Sensory Device Design

The sensory device is a carbon nanotube field effect transistor (CNTFET):



Carbon nanotubes constitute the semiconductor channel bridging two slightly separated metal electrodes above a silicon surface coated with SiO_2. Applying an electric field to the silicon wafer through the gate electrode makes it possible to switch the flow of the current across a nanotube on and off by controlling the movement of charge carriers onto it, thus switching the nanotube from a conducting to an insulating state. The CNTFET was constructed above Si/SiO_2 substrates (a 500 nm layer of silicon dioxide thermally grown on heavily n-type doped silicon substrates). The schematic and dimensions of the source and drain electrodes are:



Source and drain electrodes (10x5 μm) were patterned by using optical lithography (200nm thick Ti and 500nm thick Au, respectively). The gap distance between the electrodes was 2.5 μm. The Si substrate was used as the gate electrode.

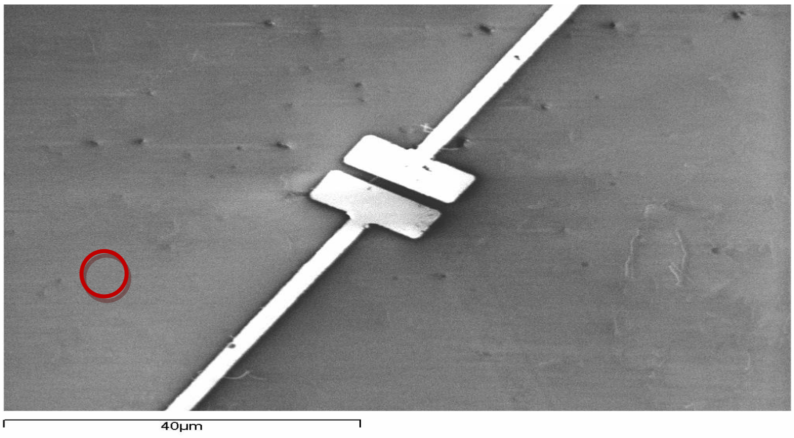


Figure 8. ESEM image of a CNTFET device. The red circle indicates the location of the CNT.

The sensory device was functionalized to selectively detect two target analytes: Human immunoglobulin G (HIgG) in solution, and SO_2 in air.

<u>Selective Detection of HIgG in Solution.</u>

Figure 9 presents the process followed to selectively functionalize CTNs to selectively detect HIgG. Tween 20 is a surfactant that irreversibly binds to the side walls of SWCNTs through hydrophobic interactions. Tween 20 will fill the gaps left between adsorbed anti-HIgG molecules to prevent the non-specific binding of other proteins.

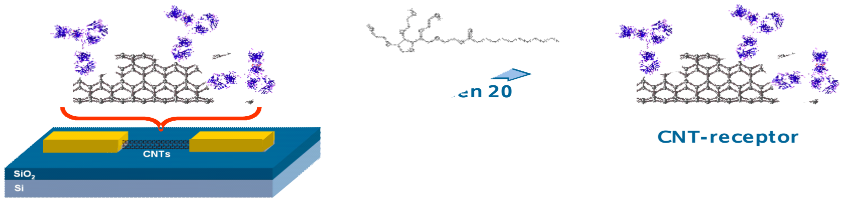


Figure 9. Functionalization of CNTs to selectively detect HIgG

Figure 10 plots the electrical current value over time at specific gate and source-drain voltages (V_g = -4 V, V_{sd} = 0.25 V) when increasing amounts of HIgG are added. The results in Figure 3 indicate that the electrical current starts to decrease within 60 seconds after each addition of HIgG (total concentration values from 1.25 mg/L up to 8.75 mg/L, i.e. from 8 nM up to 56 nM) and the signal stabilizes around 10 minutes after each addition. The inset plots the relationship between instrument response and HIgG concentration. This device exhibited a sensitivity of -1.5 nA/(mg/L). The minimum HIgG concentration detectable with the CNTFET device so far has been 0.5 mg/L. Although the change in the electrical current takes place within a few minutes, the system was left undisturbed between each addition for about five minutes so that the signal could stabilize.

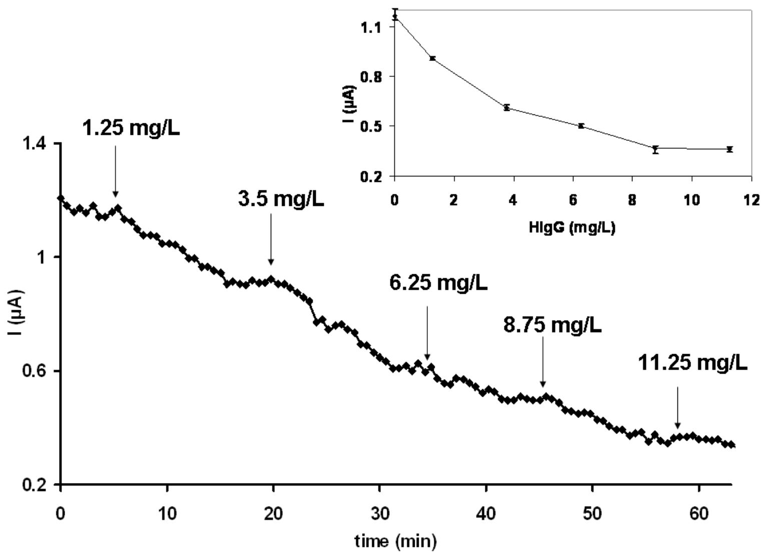


Figure 10. Time dependence of the source-drain current, I (at V_g = -4 V and V_{sd} = 0.25 V), for increasing concentrations of HIgG. Arrows indicate the addition points of HIgG and the total concentration in the cell.

Selective Detection of SO_2 in Air

Following Figure depicts the functionalization process:

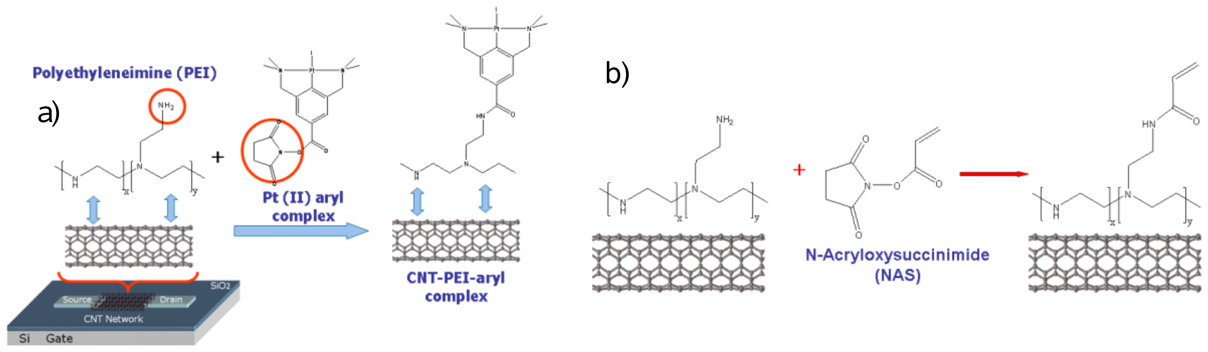


Figure 11. a) Functionalization process of CNTs with PEI and the Pt (II) complex. b) Reaction of the remaining free amino groups of PEI with the blocking molecule NAS.

This design attaches the selective receptor for the selective detection of SO_2, a Pt (II) complex ($PtI(4\text{-}COONC_4O_2H_2\text{-}2,6\text{-}\{CH_2N(CH_3)_2\}2\text{-}C_6H_2)$, above the polymer (PEI) adsorbed above the CNTs. The NAS blocking molecule reacts with the remaining free amino groups of PEI (Figure 4b) and prevents interference caused by potential acid-base reactions of the amino groups with an interferent gas (e.g. acidic gases such as CO_2). The device was exposed to increasing concentrations of SO_2 in the gas chamber (Figure 5). The response and stabilization times were about ten and three minutes, respectively. The sensitivity was estimated to be –0.0279 μA/(% v/v).

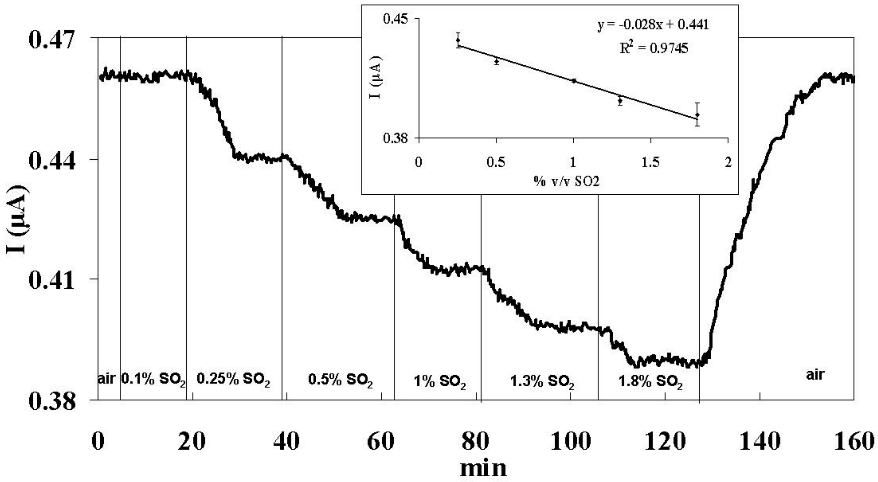


Figure 12. Time dependence of the source-drain current (I), at Vg = +5V and Vsd = 0.25 V as concentrations of SO_2 increase. The inset plots the source-drain current over the SO_2 concentration. The error bars were obtained from two independent tests using the same device.

The minimum SO_2 concentration detectable with the CNTFET device so far has been 0.05%. The response and stabilization times were about ten and three minutes, respectively. The sensor can be effectively regenerated by exposing it to the air atmosphere at room temperature for twenty minutes, thus returning to the initial baseline.