

Scientific Report

***”Nanowires: Bridging the Gap between
Materials Science and Biology”***

ESF PESC Exploratory Workshop (EW04-102)

**Convened by:
Kornelius Nielsch and Oliver Hayden**

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1. Executive Summary

Low-dimensional materials have found widespread attention as novel building blocks for numerous applications in biotechnology and medicine. Recently, a hype appeared to the rational synthesis of semiconducting, metallic and polymeric nanowires. The biggest problem so far is the “potential barrier” between the inorganic science and their biological counterpart. The Exploratory Workshop of the European Science Foundation (ESF) tried to unite scientists working with diverse materials and techniques for the goal of forming a European discussion platform for the sake of nanobiotechnology with nanowires (www.nanowire.at).

Despite the marvellous scenery of the Austrian Alps at Bad Hofgastein, the thirty workshop members enjoyed a tight program of physics, chemistry and biology with and around nanowires for three days (May 26th-28th). Amongst the participants, Prof. Evgeny Givargizov from the Russian Academy of Sciences, a true pioneer in the field of semiconducting nanowires, presented novel nanowire probes for biological force microscopy.

To ensure intense and sometimes controversial discussions different inorganic topics (e.g. synthesis) were carefully combined with biologically-relevant subjects (e.g. toxicology). In addition, speakers were invited, who referred the basics of relevant technologies for biological nanowire applications, such as manipulation (microfluidics and optical tweezers), low-level measurements, magnetics, photonics and plasmonics. Although, the combination of biology and nanowires is still in its infancy, a number of participants presented exciting new applications, such as for biosensors, electrochemistry, cell manipulation or hierarchical self-assembly.

A direct result of the exploratory workshop was the start of a project to test the diverse nanowire and nanotube materials for their toxicological relevance. Due to the enormous number of people interested in this workshop the organization of a European conference will be planned, which will cover the emerging field of nanowires and their biological applications.



Workshop participants during a walk in the Austrian Alps. Picture courtesy of Dr. Mato Knez.

1.1. Committee

The scientific committee was formed by Kornelius Nielsch and Oliver Hayden.

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1.2. Workshop participants

The workshop was attended by 30 scientists from academia and industry. The majority of the participants were young researcher from 14 European countries as well as participants from Russia and Israel. Female scientists were well represented.

1.3. Technical program

The highly interdisciplinary program consisted of 27 talks (4 keynote lectures) and 2 demonstrations. The talks were well prepared and presented for an audience with diverse scientific background (medicine, biology, chemistry, physics).

The keynote lectures with biologically and material science related topics initiated the sessions. Every talk was followed by a brief discussion. Additional breaks during the sessions allowed additional discussion and exchange of ideas in smaller groups in a relaxed atmosphere. Demonstrations with electronic and optical equipment were performed for a better understanding of nanowire/nanotube manipulation and electronic measurement techniques. This allowed the participants to get in contact with different experimental techniques and limitations for future nanowire/nanotube research.

1.4. Social program

Breaks for a hiking trip or get-together gave the participants the opportunity the chance to get to know each other or to plan already their first collaboration.

2. Scientific Content of the Workshop

Nanowires and non-carbon based nanotubes are novel building blocks in the toolbox of nanotechnology, which can be used as unique inter-connectors between the nano- and macroscale world. The diameter of these low dimensional materials spans the range from truly atomic or molecular one-dimensional systems to hundreds of nanometers with a length scale up to macroscopic sizes. The materials used for nanowires cover diverse materials, such as polymeric, superconducting, semiconducting, thermoelectric as well as magnetic materials. In addition, the controlled formation of radial and axial heterostructures as well as the combination with biological systems by using wet chemistry results in a versatile platform technology.

Potential applications for nanowire and nanotubes are ranging from novel types of microelectronics in three dimensions toward gene delivery and cancer diagnostic in medicine and biotechnology. Due to the high surface area nanowires are very suitable ultra-sensitive sensors with the dimensions in the sub-50 nm range. Multi-component nanotubes can exhibit multifunctional properties, for example optical and magnetic properties, and a high affinity to certain biomaterials. In contrast to spherical nanoparticles, which have been extensively explored from the early 90s up to now, nanowires and nanotubes are more appropriate for electrically-driven devices.

Nanowires can be rationally synthesized in both gaseous and liquid phase using either catalysts or templates. Each synthesis approach has its advantages concerning the material properties and disadvantages for certain applications. In Europe, research in the field of nanowires has mainly been focused on the material properties of nanowires rather than on their applications. In general, the research progress made in this novel field (e.g. semi-conducting nanowires) compared to the United States has been fairly slow. The interest of industrial research in nanowires often differs and a number of companies are already trying to develop their own research in this field. The workshop will offer the opportunity to discuss both point of views, needs and expectations of nanowires and their applications between participants of industry and academia.

Major application fields were discussed including the interest in nanowires by the semiconductor industry, electrical and optical biosensing, as well as nanowire and nanotubes as novel tools for medical and molecular biological applications. A final goal of this workshop is the discussion between participants from industry and academia about the development of applicable hierarchical nanosystems.

3. Assessment and Outcome of the Workshop

The main topic of this workshop was to bridge the gap between the material science and the biology using nanowire building blocks. Since this field is a rather novel topic in Europe basic topics, such as synthesis, manipulation, characterization and device fabrication, have been discussed. Around half of the participants have not yet experimentally worked with this type of material but with e.g. nanoparticles for biological applications. The workshop was therefore strongly influenced by the expertise of the participants with nanoparticles. The discussions were frequently controversial, which allowed every participant to evaluate the unique advantages and limitations with nanowires. This environment was therefore extremely fruitful concerning the work of this emerging community. In the course of the talks the following major outcomes for the immediate future in this field emerged:

- Access for the participants to different nanowire materials (semiconducting, polymeric, metallic, etc.) for biological applications and characterization (optical and electrical)
- Health risk evaluation (a collaboration between a number of participants started right at the workshop to test the cancerogenicity of nanowires)
- The organization of an additional European conference around this topic due to the enormous interest from numerous applicants for this workshop, who could not participate.
- “Nanoparticle” groups starting to work with nanowires as well as physical groups exploring nanowire applications from e.g. biosensors.

The organizers are therefore convinced that the workshop achieved its goal as an “exploratory workshop” to establish a discussion platform and to initiate novel

research in the proposed direction. For the near future the following outcome of this workshop is envisioned:

- Organisation of a succeeding workshop or conference on the applications of inorganic and organic nanowires and nanotubes in biotechnology in Fall 2006 or Spring 2007. This workshop or conference should be opened for the whole European scientific community.
- Application for an European Research and Training Network (RTN) on the synthesis and bio-related applications of nanowires. This potential network should especially stimulate the activities on nanowires in Eastern Europe.
- Several participants are currently organising bi-national collaboration between participants of this workshop on certain aspect, e.g. on the nanowire synthesis or toxicity.
- Stimulation for new funding programs in this field by national funding agencies.

4. Workshop Participants

The list of participants is provided below.

- Dr. Jörg Ackermann
Faculté des Sciences de Luminy, Marseille, France
- Dr. Erik Bakkers
Philips Research Laboratories, The Netherlands
- Dr. Alberto Bianco
Institut de Biologie Moléculaire et Cellulaire, CNRS, France
- Prof. Werner Blau
Trinity College, University of Dublin, Ireland
- Dr. Bruno Chaudret
Laboratoire de Chimie de Coordination, CNRS, France
- Colin Freeland
Elliot Scientific Ltd.
- Prof. Evgeny Givargizov
Shubnikov Institute of Crystallography, Russian Academy of Sciences, Russia
- Prof. Godnic-Cvar
Department of Occupational Medicine, Medical University of Vienna, Austria
- Dr. Oliver Hayden
Institute of Analytical Chemistry, University of Vienna, Austria
- Iddo Heller
Kavli Institute of NanoScience, Delft University of Technology, The Netherlands
- Dr. Rainer Hillenbrand
Max-Planck-Institute of Biochemistry, Germany
- Dr. David Juncker
Micro and Nanosystems Group, ETH Zürich, Switzerland
- PD Dr. Anton Köck
ARC Seibersdorf Research GmbH
- Dr. Nina Kovtyukhova
Department of Chemistry, Pennsylvania State University, USA

- Dr. Katerina Luterova
Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic
- Prof. Stephen Mann FRS
School of Chemistry, University of Bristol, Great Britain
- Dr. Kornelius Nielsch
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- Prof. Günter Reiss
Department of Physics, University of Bielefeld, Germany
- Prof. Lars Samuelson
Division of Solid State Physics, Lund University
Nanometer Structure Consortium at Lund University, Sweden
- Prof. Thomas Schalkhammer
Attphotronics Biosciences, Austria
- Ing. Wolfgang Setzer
Setzer Messtechnik, Keithley
- Dr. Robert Stark
BMBF Nanotechnology Research Group
Ludwig-Maximilians-University Munich, Germany
- Dr. Marc Tornow
Walter Schottky Institute, Germany
- Prof. Manuel Vázquez
Materials Science Institute Madrid, Spain
- Richard White
University of Cambridge, Great Britain
- Prof. Itamar Willner
Institute of Chemistry, The Hebrew University of Jerusalem, Israel
- Dr. Margit Zacharias
Max-Planck-Institute of Microstructure Physics, Germany

5. Scientific Program and Abstracts

Time	Thursday, May 26th	Friday, May 27th	Saturday, May 28th
0800-0830	Registration		
0830-0900	ESF	Vasquez	Hillenbrand
0900-0930	Givargizov	Reiss	Elliot Scientific/Freeland
0930-1000		Coffee	Break
1000-1030	Coffee	Mann	Funding
1030-1100	Samuelson/Martensson		Concluding remarks
1100-1130		Willner	
1130-1200	Zacharias		
1200-1230			
1230-1300	Lunch	Lunch	
1300-1330			
1330-1400	Welland	Kovtyukhova	
1400-1430	Niinistro	Ackermann	
1430-1500	Bakkers	Juncker	
1500-1530	Blau	Coffee	
1530-1600	Coffee	Hayden	
1600-1630	Chaudret	Schalkhammer	
1630-1700	Nielsch	Luterova	
1700-1730	Heller	Break	
1730-1800	Köck	Tornow	
1830-1900	Break	Stark	
1900-1930	Bianco	Break	
1930-2000	Godnic-Cvar	Keithley/Setzer	
2000-2030	Break		
2030-2100			
2130-2200	Dinner	Dinner	
2200-2230			



European Science Foundation Exploratory Workshop

Nanowires: Bridging the Gap between Materials Science and Biology

The exploratory workshop will enlighten the applications and limitations of nanowires from the perspective of leading experts. Researchers from academia and industry are invited "to bridge the gap" from materials science to biotechnology and medicine.

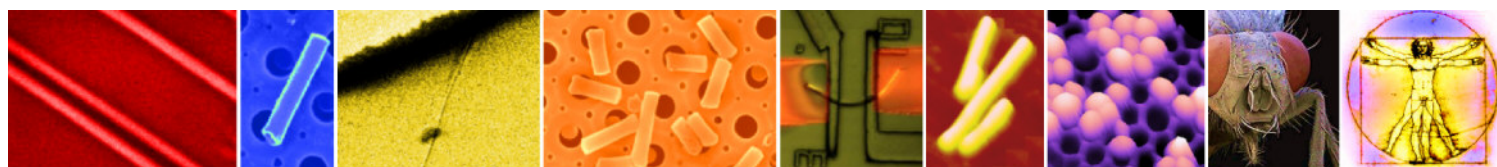
**Bad Hofgastein
Salzburg, Austria
May 26th-28th
2005**

Hotel Moser
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Programm

Thursday, May 26th 2005

08:00 – 08:30 Registration and Welcome

08:30 – 09:00 ESF

09:00 – 10:00 Whisker Nanoprobes for Biological Force Microscopy*
E.I.Givargizov

10:00 – 10:30 Coffee Break

10:30 – 11:30 Nanowires for nanoscale devices and interfacing to the bioworld*
Thomas Mårtensson and Lars Samuelson

11:30 – 12:00 ZnO Nanowires and Nanowire Arrays: Ways for a controlled synthesis
Margit Zacharias

12:00 – 13:30 Lunch

13:30 – 14:00 Growth and Characterisation of SiC and ZnO nanowire structures and devices
M.E. Welland

14:00 – 14:30 NANOSTRUCTURES BY ATOMIC LAYER DEPOSITION: CONTROLLING AND COMBINING MATERIALS AT ATOMIC AND MOLECULAR LEVEL
Lauri Niinistö

14:30 – 15:00 Charge-sensitive photoluminescence from nanowires
Erik P.A.M. Bakkers

15:00 – 15:30 Nanowire Systems for Opto- and Nano-Electronic Applications
W. J. Blau

15:30 – 16:00 Coffee Break

16:00 – 16:30 Organometallic Approach to Nanorods and Nanowires
Bruno Chaudret

16:30 – 17:00 FROM SELF-ORDERING TOWARDS IMPRINT LITHOGRAPHY: LARGE-SCALE SYNTHESIS OF MONODISPERSE NANORODS
Kornelius Nielsch

17:00 – 17:30 Individual Single-Walled Carbon Nanotubes as Nanoelectrodes for Electrochemistry
I. HELLER

17:30 – 18:00 Integrated Electrical and Optical Nanosensors
Anton Köck

18:00 – 18:30 Break

18:30 – 19:00 Functionalised carbon nanotubes for drug delivery: cellular penetration and toxicity effects
Alberto Bianco

19:00 – 19:30 What do we know about biological effects of natural and man-made fibres?
Jasminka Godnic-Cvar

19:30 – 20:00 Break

20:00 – 22:30 Dinner

Friday, May 27th 2005

08:30 – 09:00 Composite magnetic nanostructures prepared by anodization & electrodeposition: Highly ordered arrays of nanowires in membranes
M. Vázquez

09:00 – 09:30 Magnetic Nanoparticles as Markers for magnetoresistive Biosensors
G. Reiss

09:30 – 10:00 Coffee Break

10:00 – 11:00 Bio-related Routes to Nanowire Synthesis and Self-assembly*
Stephen Mann

11:10 – 12:00 Biocatalytic and Bio-Templated Synthesis of Nanowires*
Itamar Willner

12:00 – 13:30 Lunch

13:30 – 14:00 Layer-by-layer Assembly approach to templated synthesis of Segmented and Tube-Encapsulated Metal Nanowire Devices
Nina I. Kovtyukhova

14:00 – 14:30 Gel-layer-assisted, directional electropolymerization: versatile method for high resolution patterning of membrane templates with polymer nanowires and Molecular gels: guide for supramolecular assembly of nanowires?
Jörg Ackermann

14:30 – 15:00 Microfluidic Capillary Systems: An Effective Liquid Transport System For Miniaturized Bioassays
David Juncker

15:00 – 15:30 Coffee Break

15:30 – 16:00 Semiconducting nanowires for optical and electrical detection of biological species
Oliver Hayden

16:00 – 16:30 OPTICAL NANOCLUSTER-DEVICES
T. Schalkhammer

16:30 – 17:00 Laser with silicon nanocrystals – dream or near future?
Kateřina Luterová

17:00 – 17:30 Break

17:30 – 18:00 Orientation Switching of Functional DNA Monolayers
Marc Tornow

**18:00 – 18:30 Nanomanipulation and nanolithography by atomic force microscopy:
towards nanorobots**
Robert W. Stark

18:30 – 19:00 Break

19:00 – 20:00 Keithley/Setzer**

20:00 – 22:30 Dinner

Saturday, May 28th 2005

**08:30 – 09:00 Nanoscale resolved optical microscopy
and infrared spectroscopy by light scattering from a tip**
Rainer Hillenbrand

09:00 – 09:30 Elliot Scientific/Freeland

09:30 – 10:00 Break

10:00 – 10:30 Funding***

10:30 – 11:00 Concluding remarks***

*** Plenary talks**

**** Talk with electronic measurement experiments**

***** Funding and concluding remarks will be discussed during a hiking trip
(weather dependent)**

**Abstracts
of
Lectures**
(in chronological order)

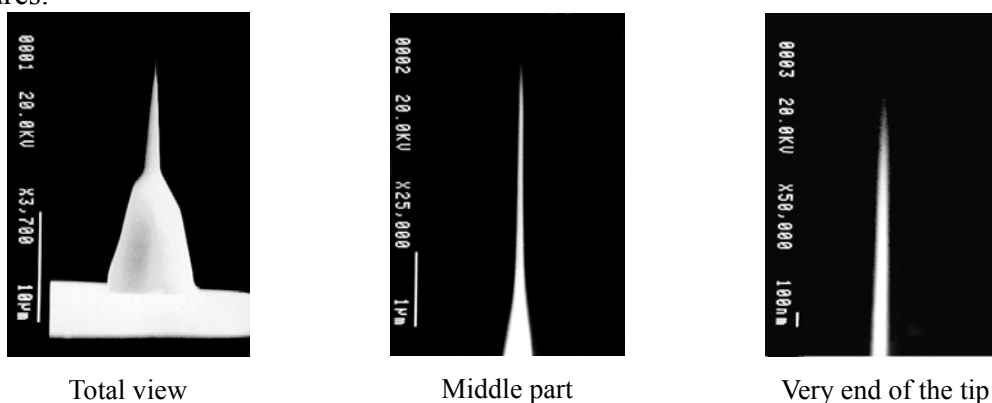
Whisker Nanoprobes for Biological Force Microscopy

E.I. Givargizov

Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia

Biological force microscopy (BFM) as a version of the atomic force microscopy (AFM) has become a rapidly developing interdisciplinary field of research in recent years. It is based on using tip probe and is critically dependent on the geometry of the tip. Commonly, the probe is monolithically formed on the end of a special console, or cantilever. The demands to the tip are contradictory. The resolving power of the probe devices is determined by the radius of curvature of the very end of the tip: the smaller the radius the better is the resolving power. From this point of view, the radius must be done as small as possible. However, thinning of the tip involves mechanical vibrations that decrease the resolving power. This contradiction can be solved provided the tip has a massive basis (at least several micrometers in diameter) and a short small-curvature-radius upper part. Another parameter important for study of highly developed surfaces/objects such as biological macromolecules is a cone angle of the upper part.

Such a spectrum of parameters is difficult to ensure by a standard technology that is currently used for production of the tip probes. The technology consists in chemical or/and electrochemical etching of single-crystalline silicon wafers. The tip probe with the optimal combination of parameters, namely 2-5 nanometer curvature radius, and with the cone angle 2-3 degrees can be prepared by a controlled crystalline whisker growing from vapor phase according to the vapor-liquid-solid (VLS) mechanism described in [1,2]. The whisker probe, single-crystalline in its nature, is shown in the figures.



The uniqueness of BFM is the possibility to study biological objects in their native conditions. There are 2 versions in BFM:

- (1) studies of morphological structure (topography) of the biological objects adsorbed on surfaces, our whisker probes allowing the study of nuclear nanopores (=“negative nanowires”) in proteins, of individual macromolecules, etc;
- (2) compositional identification of some molecules. For the latter studies, the probe should be modified (“functionalized”) by coating with specific molecules/molecular groups. This allows, e.g., to study forces between complementary strands of DNA,

interactions between antibodies and antigens, ligands and acceptors, to map a distribution of various molecules on substrates, to realize single molecule spectroscopy of biomolecules, etc.

- [1] *R.S.Wagner and W.C.Ellis, Appl. Phys. Lett. 4 (1964) 89.*
[2] *E.I.Givargizov, J. Vac. Sci. Technol. B11 (1993) 449.*



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Nanowires for nanoscale devices and interfacing to the bioworld

Thomas Mårtensson and Lars Samuelson

Solid State Physics / The Nanometer Consortium, Lund University, Sweden

Nanowire (NW) technology has come to offer a versatile toolbox for a variety of fields such as electronics, photonics and biology. With the technology becoming more mature, focus will shift more and more from NWs themselves to what they can do for us in terms of improved and new applications. In this talk we will give an overview of our NW research and discuss how NWs may be used in the next generation of life science research.

In our approach NWs are grown on crystalline substrates (III-Vs or Si) from well-defined seed particles. The crystal orientation of the starting wafer determines the NW growth direction. This provides for exact control of direction, diameter and length. Metal-organic vapor phase epitaxy (MOVPE) and chemical beam epitaxy (CBE) are used which allows fast switching of precursor material to create accurately controlled radial (core-shell) and axial heterostructures for band gap engineering.^{1,2}

The NW morphology alone makes them highly interesting objects for many applications. Besides control of diameter, length and directions we have worked on lithographic control of the seed particles³ and controlled branching of NW structures.⁴ For lithographic control we used electron beam lithography or nanoimprint lithography doing individual definition of the seed particles to form accurate arrays of vertical NWs. Such site controlled arrays could function e.g. as filters for nanofluidics. Controlled branching of NWs to create “nanotrees” was achieved by a second deposition of seed particles on the first generations of NWs, thus “branches” on the “trunk” were formed.

A key issue is also interfacing NW technology with existing technologies.

Using heterostructures and band gap engineering a set of interesting devices such as single-electron transistors (SETs),⁵ resonant tunneling diodes (RTDs)⁶ and single electron memory devices were realized. Controlled growth of III-V NWs on Si will allow for these advanced III-V heterostructure devices to be integrated directly onto mainstream Si technology. We have previously demonstrated epitaxial growth of III-V NWs on Si from Au aerosol particles⁷ and continue work in this direction doing III-V NWs on Si with lithographic control and III-V NWs on micro-engineered Si structures such as e.g. cantilevers.

Also taking into account the many results from other groups there is no doubt that NW technology is indeed a powerful toolbox ready for applications in biology and

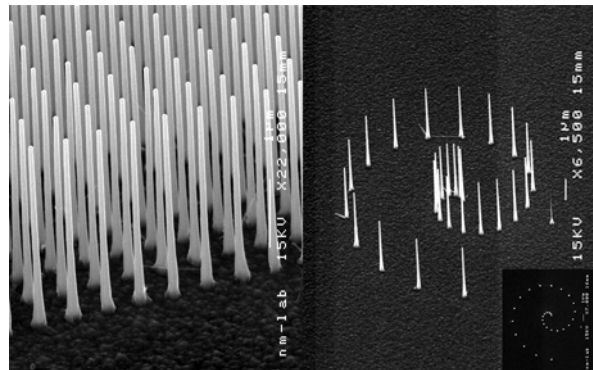


Figure 1 Nanowire arrays defined by EBL

life science. As a demonstration we will discuss some initial results on how NWs and nanowire arrays can be used in interacting with live tissue in guiding growing axons and in probing cells.

- [1] *Samuelson, L. Self-forming nanoscale devices. Materials Today* **6**, 22 (2003)
- [2] *Björk, M. T., et al. One-dimensional steeplechase for electrons realized. Nano Letters* **2**, 87 (2002)
- [3] *Mårtensson, T., et al. Nanowire arrays defined by nanoimprint lithography. Nano Letters* **4**, 699 (2004)
- [4] *Dick, K. A., et al. Synthesis of branched 'nanotrees' by controlled... Nature Materials* **3**, 380 (2004)
- [5] *Thelander, C., et al. SETs in heterostructure nanowires. Appl. Phys. Lett.* **83**, 2052 (2003)
- [6] *Björk, M. T., et al. Nanowire resonant tunneling diodes. Appl. Phys. Lett.* **81**, 4458 (2002)
- [7] *Mårtensson, T., et al. Epitaxial III-V nanowires on silicon. Nano Letters* **4**, 1987 (2004)



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ZnO Nanowires and Nanowire Arrays: Ways for a controlled synthesis

Margit Zacharias

Max Planck Institute of Microstructure Physics, Halle, Germany

During the last years, semiconductor nanowires have received increasing attention as potential building blocks for nanoscale electronic and optical devices. A variety of methods has been employed for the manufacturing of nanowires. These methods include chemical vapor deposition, pulsed laser deposition, chemical beam epitaxy, metalorganic vapor phase epitaxy, and thermal evaporation methods. Frequently, the preparation requires complicated experimental setups or do not permit the desired degree of growth control with respect to position and size of the wires. The grown nanowires were often curved and tangled together, without any control over positions, size (etc.).

For vapor-liquid-solid growth the deposition of metal dots at specific positions can establish selective starting points for the growth. In the talk the growth of ZnO nanowires will be discussed. The successful fabrication of periodically arranged single-crystalline ZnO nanowire and nanopillar arrays are demonstrated by combining substrate patterning and the catalyst-directed epitaxial growth. The pillars show strong excitonic emissions up to room temperature. The growth process and the detailed investigation will be reported.





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Growth and Characterisation of SiC and ZnO nanowire structures and devices

M.E. Welland

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The recent interest in nanostructured materials is based on the exploitation of the interdependency between physical properties, shape and size at nanometre lengthscales. The additional fact that the surface area increases with the reciprocal of size means that surface properties also become critical in nanostructured materials. Examples of both 'bulk' and surface properties of nanostructures are described below. Several techniques have already been developed for synthesising silicon carbide (SiC) material in the form of nanospheres and nanowires/rods. Here, we report the synthesis of a distinctly different kind of SiC nanostructure in the form of three-dimensional crystalline nanowire based flower-like structures and arrays of coaxial rods. Interest in such structures centres around the combination of a simple growth process based on SiC nanowire formation, with a resultant complex structure having potentially complex mechanical and optical properties; the latter a consequence of the wide band gap of bulk SiC. The synthesis of these SiC nanostructures is via a vapour-liquid-solid (VLS) process, on which a detailed study of both the chemical and structural composition has been carried out. In addition, we demonstrate the unique physical properties of the films through a photoluminescent study of the optical properties and a dynamic wetting study of the surface chemical/mechanical properties. In respect of ZnO we have developed a growth protocol that allows for the fabrication of hierarchical structures that, for example, combine 1D ZnO nanowires with 3D crystals. We are able to incorporate such structures on an individual basis into field effect transistor devices where it is possible to determine the field dependent transport properties of the material and the surface electronic properties.



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NANOSTRUCTURES BY ATOMIC LAYER DEPOSITION: CONTROLLING AND COMBINING MATERIALS AT ATOMIC AND MOLECULAR LEVEL

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Atomic Layer Deposition (ALD) is an advanced method for growing thin films and thin film structures in a surface-controlled way [1]. It is based on alternating chemisorption of the precursors, followed by surface reaction and desorption of the gaseous side-products. One ALD cycle produces a monolayer or a distinct fraction thereof and by repeating the cycle films of desired thickness (from a few nanometers upwards) can be homogeneously grown on large-area flat or porous substrates. Furthermore, the layers can be doped by ALD and, when needed, interfaces and surfaces modified in a controlled way. ALD is especially well-suited for the deposition of binary films from inorganic or organometallic precursors [2], but organic and bio-organic molecules can be used as well. Amino-functionalized overlayers on silica can be prepared by sequential ALD-reactions from aminosilanes and water and the resulting materials offer a wide range of applications in biochemistry and catalyst technology, for instance [3].

There are several recent examples in the literature where metal oxide layers with thicknesses of a few nanometers have been successfully grown by ALD and the ultrathin films and nanolaminates characterized by HRTEM and other means [4,5].

Nanostructures can be grown by ALD, but this field is still largely unexploited. A recent example will be presented to illustrate the potential which ALD has in nanostructure engineering for applications in biotechnology [6].

- [1] *L. Niinistö et al., Phys. Stat. Solidi a 201 (2004) 1443-1452.*
- [2] *M. Putkonen, L. Niinistö, Topics in Organometallic Chemistry, in press.*
- [3] *S. Ek, E.I. Iiskola, L. Niinistö, Langmuir 19 (2003) 3461-3471*
- [4] *J. Niinistö et al., J. Appl. Phys. 95 (2004) 84-91.*
- [5] *B. S. Lim et al., Appl. Phys. Lett. 84 (2004) 3957-3959.*
- [6] *M. Knez et al. MRS Spring Meeting, Symposium M, San Fransisco 2005.*



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Charge-sensitive photoluminescence from nanowires

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Our main goal is the integration of III-V semiconductors on silicon. That would enable the integration of the opto-electronic properties of the III-V materials with mature silicon technology. However, issues such as lattice and thermal expansion mismatch have prevented the monolithic integration of III-V materials with silicon. Recently, the principle of epitaxial growth of III-V nanowires on group IV substrates has been demonstrated.^{1,2} For instance, the optically active materials GaAs and InP have been grown directly on Si(111). To characterize the nanowires optically, microphotoluminescence has been used. In this paper I will discuss three subjects: luminescence of doped nanowires, surface passivation to increase the luminescence efficiency, and the possibility to use the nanowires as a charge sensor.

To be able to fabricate (opto-)electrical devices, we should have quantitative control of electrical doping in the nanowires. We have used low-temperature microphotoluminescence to study the effect of incorporating electrical dopants into InP nanowires. Besides conduction-valence band electron-hole recombination, we have also observed impurity-induced transitions.

These nanowires have a high ratio of surface to bulk atoms, which might lead to non-radiative decay. In order to increase the emission intensity of InP nanowires we have passivated the surface of individual wires *in situ*. We show that the luminescence efficiency of InP nanowires can be improved by orders of magnitude by a photo-assisted wet chemical etching in a butanol solution containing HF and the indium-coordinating ligand tri-octyl-phosphineoxide (TOPO).³

Both the emission intensity and the wavelength of a nanowire are sensitive for its environment. We will show the effect of an electric field on the luminescence and how that might be used to detect small numbers of biomolecules.

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Nanowire Systems for Opto- and Nano-Electronic Applications

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This talk will present a summary of the research in the area of templated and self-assembling nanowires in my group. The work focuses on three distinct materials systems:

- Nanoporous Alumina Membranes as templates for metallic, semiconducting and polymer nanowires.
- Nanowires based on hexa-*peri*-hexabenzocoronene assembled by Molecular Self-Assembly.
- Carbon Nanotubes and their Assemblies with Biomolecules

Application demonstrations in electrically conducting composites, electrical nano-interconnects and in polymer optoelectronic devices are reviewed.

Self-ordered porous alumina membranes (PAM) are very suitable templates for the fabrication of nanowire and nanomagnet arrays. With high aspect ratio (>10) magnetic wires, such arrays exhibit a so-called 2D polycrystalline arrangement of the pores and have a pore diameter distribution of about 8%. Filled PAM can also be used as a nano-structured array electrode in an organic sandwich type device. With optimisation the structure we have demonstrated may be useful for producing arrays of nano-sized light sources and may improve the understanding of current density limitations in arrays of nano-sized organic devices. As patterning and interconnect technologies advance it may eventually be possible to address individual nanowires in filled PAMs and consequently individual nano-dot devices too.

On a molecular scale, the accurate and controlled application of intermolecular forces can lead to new, previously unachievable, nanostructures. This is why Molecular Self-Assembly (MSA) is a highly topical and promising field of research. MSA encompasses all structures formed by molecules selectively binding to a molecular site without external influence. With many complex examples all around us in nature (us included), MSA is a widely observed phenomenon that has yet to be fully understood. Our ultimate goal is to understand how to form ordered functionality-tailored nanostructures via self-assembly in solution. At present, the physics of a single molecule and its bulk molecular crystal is much better understood compared to the intermediate size range of small molecular assemblies. Therefore, research has focused on ordered assemblies of *identical* molecules that self-assemble in solution. The strategy is to use conventional investigation techniques to determine the physical structure, electronic properties and other interesting physical phenomena of simple MSAs, which will then pave the way for an understanding of more complex MSAs. In this respect, hexa-*peri*-hexabenzocoronene (HBC) derivative molecules offer a good molecular template from which to advance to complex MSAs. HBCs are beautiful examples of molecular plate like structures. Symmetrically substituted HBC-C_{8,2} molecules self-assemble in solution into nanowires of several hundred nanometres

length and 3 nm diameter. At high concentrations, these molecular nanowires assemble further into entropically favourable nanowire bundles of several tens of micrometers length and typically tens of nanometres diameter. The ordered alignment of the molecules in the assembly ensures a homogeneous electronic coupling along the length of the nanowire. This in turn leads to the extended delocalisation of the exciton eigenstates, which is confirmed by sharp peaks in their optical spectra.

Over the past decade one-dimensional nanotubes such as carbon nanotubes (CNT) have generated much interest due to their exceptional electronic and mechanical properties. For example, multiwall carbon nanotubes (MWNTs) have been grown by catalytic chemical vapour deposition using iron catalyst particles drop cast onto etched silicon wafers. For trench widths below 0.5 μm the number of “interconnecting” tubes growing from one side of the trench to the other increases sharply. A significant proportion of these “interconnects” are found to be Y-junction and multiple junction MWNTs. A systematic study of the effects of each of the growth conditions (temperature, run time, gas flow, catalyst concentration and trench width) versus interconnect yield was carried out. Densities of ~ 1.6 interconnects per micron of trench are obtained, with junction structures accounting for 38% of these interconnects. Densities can be controlled through modification of chemical vapour deposition conditions.

Perhaps the most serious practical problem with application of CNTs relates to the fact that they are insoluble in all known solvents. This severely limits our ability to carry out solution based processing or characterization. While nanotubes can be rendered soluble by covalent functionalization, this process strongly modifies their physical and chemical characteristics. The only way to disperse untreated nanotubes in the liquid phase is to add a stabilizer such as a surfactant or a polymer and to form composite dispersions. However, this can limit the possibilities for intrinsic characterisation of the nanotubes themselves. In addition, single walled nanotubes (SWNTs) are produced with a range of electronic structures, which depend on their roll-up vector. While this initially seemed like a huge advantage, separating metallic from semi-conducting SWNTs is currently proving problematic. A number of solution based techniques have been published to date, but none have demonstrated complete separation and all have been on a relatively small scale.

Interest in studying the biological application of solid-state devices based on nanomaterials has increased significantly over the years. The potential use of CNTs in biorelated areas has prompted many researchers to investigate the functionalisation of CNTs with biological macromolecules such as proteins and oligosaccharides. Combining the unique electronic properties of carbon nanotubes with remarkable biomolecular recognition capabilities could lead to miniaturised biological electronics and optical devices including sensors. We have shown that MWNTs can be selectively dispersed from MWNT soot using biomolecules, provided the molecular weight of the biomolecule is sufficient to induce MWNT wrapping. This phenomenon has led to the development of a water based room temperature procedure to purify MWNT soot. Of the biomolecules used Chitosan showed the best selectivity by retaining up to 60% MWNTs and 3.4% GPs in solution. TGA showed that it is

possible to remove the bound biomolecules from the MWNTs by heating the MWNT-biomolecule solution to between 600°C and 675°C to produce pure MWNTs.



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Organometallic Approach to Nanorods and Nanowires

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The use of organometallic precursors allows the synthesis in mild conditions of metal nanoparticles displaying a controlled size and surface environment. We have evidenced recently the ability of these particles to change their size or shape according to the properties of the surface ligands present. In this respect nanorods of controlled aspect ratio and nanowires can be easily produced. We have also studied the coordination of various classes of ligands on the properties (both physical and chemical) of the particles. The synthesis has been extended to oxides such as ZnO for which it is also possible to control the size, monodispersity and the shape of the particles. Nanorods of various aspect ratio and nanowires were produced in this way. The lecture will focus on the synthesis of nanoparticles of anisotropic shape and describe the role of coordination chemistry to orientate the growth of the particles, to control their monodispersity and shape (spheres, rods, cubes, wires). A special point will be devoted to the organization of the particles in 2D or 3D super-lattices of nanoparticles. Finally, we will report recent results concerning the functionalization of the particles and their relevance to biology.

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FROM SELF-ORDERING TOWARDS IMPRINT LITHOGRAPHY: LARGE-SCALE SYNTHESIS OF MONODISPERSE NANORODS

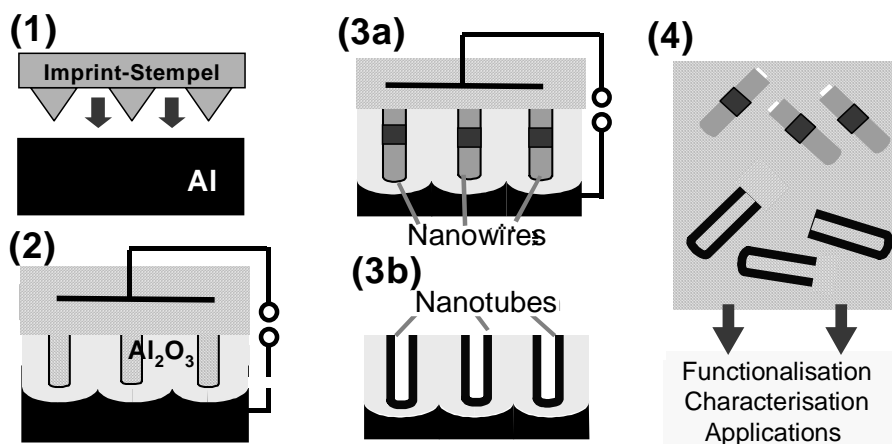
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Monodisperse nanorods are highly desirable for many applications in magnetic storage, sensing, nanoelectronics and for biomedical applications ranging from diagnostics of cancer cells to drug delivery. In the recent year, self-ordered alumina pore channel arrays, based on an approach of Masuda et al. [Science 1995, 268, 1466], have attracted a lot of interest as a template material for the synthesis of nanowires and nanotubes with a defined diameter ($\sim 10\%$). In analogy to polycrystallites, the pore channels are hexagonally self-arranged in domains. When we introduce imprint lithography in the fabrication process of our templates, a monocrystalline arrangement of pore channels on a cm^2 -scale is obtained and the deviation of the pore diameter is reduced to less than 2%. In the first part of this presentation an overview about the recent developments of porous alumina as a template system will be given.



Subsequently, we will show several examples on the synthesis of nanowire and nanotubes based on polymers, noble metals, ferromagnetic and thermoelectric materials. The nanowires and nanotubes are produced by using a pulsed electrodeposition process with conducting materials in perfectly ordered alumina pores channel arrays or by multilayer coating of the oxide pore walls with polymers, oxides and metals. After the growth process the nanowires and nanotubes can be transferred into solutions or integrated in microelectronic devices by a selective chemical etch of the aluminum oxide matrix.



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Individual Single-Walled Carbon Nanotubes as Nanoelectrodes for Electrochemistry

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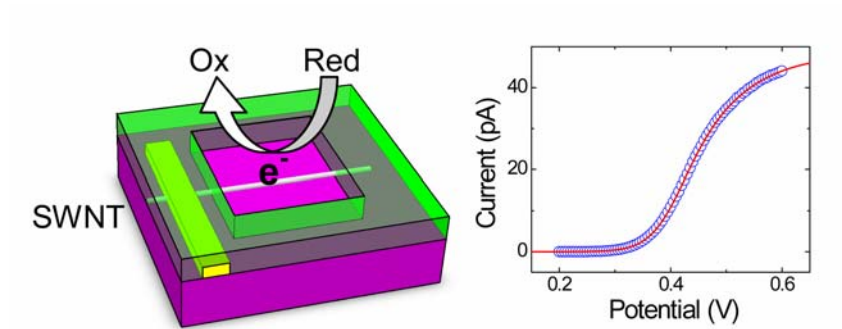
We study the potential of single-walled carbon nanotubes (SWNT) as nanoelectrodes for electrochemistry. It has previously been demonstrated that the conductance of SWNTs can be tuned in a field-effect-transistor configuration via an electrochemical potential applied to the electrolyte. In these approaches, the coupling between the device and the electrolyte is solely electrostatic, and no charge is transferred across the liquid-SWNT interface. Here we demonstrate that individual SWNTs can also be used as electrodes for electron transfer reactions, that is, electrochemical reactions in which electrons are exchanged between a SWNT and redox-active molecules in solution. Due to its unique and well-defined geometry with a critical dimension in terms of a nanometer radius, the SWNT allows for very high steady-state current densities at the electrode surface, making it well suited for probing the electrode kinetics of fast electron transfer reactions. Electrochemical experiments on individual SWNTs have been lacking thus far.

SWNTs are grown on an insulating substrate by chemical vapour deposition, and contacted with metal electrodes constructed through nanolithography. The metal electrodes are insulated from solution by a layer of resist. We perform cyclic voltammetry in a low-current measurement setup with ferrocene-derivatives in aqueous solutions, using the SWNT as a working electrode. A steady state electrochemical current that corresponds to the oxidation of ferrocene at the SWNT sidewall is observed. The electrochemical current is proportional to the exposed length of SWNT. The rate of electron transfer to SWNTs is observed to be very fast. Nonetheless the observed current-voltage characteristics are non-Nernstian, and a kinetic limitation on the electrochemical current can be resolved in dc transport measurements due to the high diffusive flux of redox molecules resulting from the nanometer diameter of SWNTs. Butler-Volmer kinetics can be used to describe the kinetic limitation for the oxidation of ferrocenes, yielding an electron transfer rate of $k_0 = 4 \pm 2$ cm/s. The fabrication of devices has proven to be non-trivial due to a suppression of the electrochemical current on some batches of samples, which is possibly related to contamination.

Interestingly, metallic and semiconducting SWNTs yield similar current-voltage characteristics. We show that this behaviour is consistent with a theory of electron transfer in which the electronic structure of the SWNTs is explicitly taken into account. The low SWNT quantum capacitance leads to an interesting interplay of effective electrochemical gating and electrochemical charge transfer.

In pursuing the goal of wiring a single redox enzyme to a SWNT to directly measure the catalytic activity through electrochemical charge transfer, we have immobilized redox proteins on SWNT-felt electrodes and measured the direct electrochemistry.

Current efforts include the immobilization of enzymes on individual SWNT devices with the aim of detecting the electrocatalytic current generated by a single enzyme molecule.



Further information: I. Heller et al, Nano Letters **2005**,1,137

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Integrated Electrical and Optical Nanosensors

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Sensors for chemical and biochemical substances with nanowires as the sensing probe are a very attractive application area. Nanowire sensors are smaller, more sensitive, demand less power, and react faster than their macroscopic counterparts. Arrays of nanowire sensors could provide real-time information regarding the concentration of a specific analyte as well as its spatial distribution. The integration of nanosensors with microelectronics for integrated sensing and signal processing is of high interest for many applications. One of the biggest challenges for integrating microelectronics and biotechnology is the need to develop interfaces that are compatible with microelectronics fabrication processing methods and that provide the required selectivity and stability when exposed to biological environment. Problems related with the integration of nanosensor elements, microelectronic circuitry and optoelectronics will be discussed. New approaches for electrical and optical nanosensors will be presented. The combination of micro- and nanoelectronics and biosystems can provide the fabrication of novel single nanodevices with top-to-bottom functional design.



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Functionalised carbon nanotubes for drug delivery: cellular penetration and toxicity effects

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Carbon nanotubes (CNT) are attracting the attention of several scientists, due to their unique structural, mechanical, electronic and biological properties [1, 2]. These nanoobjects hold a lot of promises for biomedical applications for different reasons: water solubility induction, high stability of the dispersion, lack of intrinsic immunogenicity and efficient payload capacity [3, 4]. Their organic functionalisation has allowed not only an improvement of their solubility [5], but it has also opened the way to more interesting potential uses, such as novel vectors for cell internalisation of therapeutic molecules [6-10].

In this Communication, we will present an efficient strategy for the functionalisation of carbon nanotubes (Figure) and some examples of their potential biological applications in the field of drug delivery. In particular, we will describe the capacity of CNT to cross the cell membranes and to distribute into the cell compartments, and we will address the critical toxicity issue.

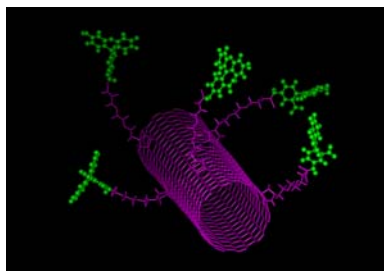


Figure. Molecular model of CNT functionalised with a fluorescent probe.

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What do we know about biological effects of natural and man-made fibres?

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Man-made vitreous fibres (MMVF) and nanowires are newly designed fibres that become increasingly important in new technologies. The unique physical and chemical characteristics of the nanosized materials are so revolutionary and broadly applicable, that they managed to bring about the industrial revolution of the 21st century. But, our knowledge on their behaviour in the human body and environment is still scarce.

The man-made vitreous fibres and nanotubes resemble in their appearance asbestos fibres. All these materials can release airborne respirable fibres during their production, transportation, application and displacement. The major concern is thus, whether man-made fibres can (due to the features they share with asbestos fibres) after being inhaled, induce inflammation, lung injury, lung carcinoma and eventually mesothelioma like asbestos fibres. Therefore, man-made (vitreous) fibres have been thoroughly evaluated for their hazardous effects in humans. Although the respirable particles released from man-made vitreous fibres have some physical properties (same aerodynamic properties) similar to asbestos, at present, no disease in humans has resulted from exposure to vitreous fibres. The clue is - their much lower biopersistence in the lungs (enhanced clearance due to transversally cleavage)! Thus, man-made vitreous fibres compared to amphibole asbestos - are harmless.

Little is known about the adverse effects of carbon nanomaterials (SWNTs, MWNT, and C60) in the human body and in the environment. A couple of studies investigated the adverse effects of nanotubes in vitro and in animal models (one even an environmental animal model study). Unfortunately, the early few reported data are equivocal. They range from harmless to carcinogenic. Thus, if nanotubes are biopersistent in the lungs (concerning transversally cleavage or breaking, and digesting in acidic environments), deducing from the pathophysiology of asbestos and MMVF, - the adverse effects of nanofibres (nanotubes) will resemble the harmful effects of asbestos fibres. At present we lack not only measurements of occupational exposures, we lack well controlled animal studies with realistic exposures to different kinds of nanofibres. On top of it, the exaggerating effect of other confounders (e.g. cigarette smoke, which increases the risk of mesothelioma due to asbestos fibres 10 times) has to be thoroughly studied. A great deal of investigation is needed to unveil the potential biological hazards of nanofibres in the human world – to be able to prevent environmental and occupational disasters, and in addition, to communicate the outcome truthfully to the public.



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Composite magnetic nanostructures prepared by anodization & electrodeposition: Highly ordered arrays of nanowires in membranes

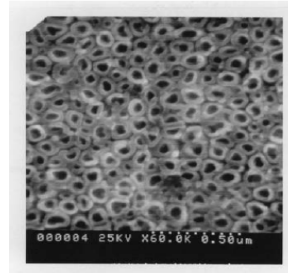
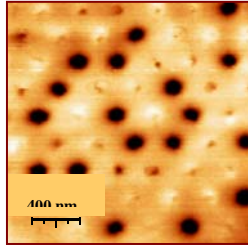
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Nanoporous membranes are produced by the two-anodization process by which nanopores self-assemble with long range ordering of hexagonal symmetry. Geometrical characteristics of nanopores in i.e., alumina membranes, are controlled by production parameters: i) Lattice parameter of hexagonal symmetry and nanopores diameter are determined by selected anodization bath (sulfuric, oxalic, and phosphoric acids determine 65, 105 and 500 nm lattice parameter, and 35, 65 and 180 nm nanopore diameter, respectively). Control of continuous increasing in diameter is further achieved by subsequent treatment in sulfuric acid, ii) Length of nanopores is tailored by the time of second anodization, from hundreds to thousands μm , iii) Size of crystalline pores domains, up to few μm^2 , is controlled by time of first anodization. Alternatively, crystalline single-domain ordering is achievable by nanoimprinting. Nanopores are subsequently filled by electrodeposition with metallic, particularly magnetic, elements as Ni, NiFe alloys or Co. Optimization of the array and membrane characteristics is finally done i.e., polishing of both surfaces, or fixing onto suitable substrates.

Geometrical, structure and filling degree of arrays and membranes are characterized by: X-ray diffraction, Scanning Electron Microscopy, Atomic Force Microscopy, Rutherford Back Scattering [1], or Synchrotron radiation, while magnetic properties can be determined by VSM and SQUID magnetometers and Ferromagnetic Resonance, FMR, for the arrays as a whole, and by Magnetic Force Microscopy, MFM, to determine the magnetic state of individual nanowires. Our group has been particularly interested in the magnetic behavior of these nanostructures [2] i.e., magnetostatic interactions as determined by compared analysis of VSM hysteresis loops [3], angular dependence of FMR response [4], MFM images (left figure) of individual nanowires, and modelling [5] of multipolar magnetic interactions. Interest is extended to alternatives as self-aligned titania nanotubes arrays [6] (right figure), which can be subsequently filled with different materials, or arrays of multilayer, i.e., Co-Cu, nanowires with tailored individual lengths.

Present interest is broadening involving double-template replication technique to obtain also metallic membranes, i.e., nanoporous Ni membrane, or nanoporous polymeric membranes where biological units can be fixed for particular sensing devices, or alternatively allowing us to produce composite nanostructures consisting of arrays of nanowires embedded in membranes with multifunctional possibilities: metallic (non-magnetic)/metallic (magnetic) for optomagnetic sensing [7], ferromagnetic/antiferromagnetic for magnetic storage media, magnetic/polymeric media for magnetic polymers, doped semiconductor/semiconductor for luminiscence sensing, mixed oxides/oxides for magnetoresistive complex structures, etc...



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Magnetic Nanoparticles as Markers for magnetoresistive Biosensors

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The detection as well as the manipulation of single molecules on a common technological platform is of great interest for both basic research on biological or chemical systems as well as for applications in, e.g., antibody detection. A promising approach is the detection of small magnetic carriers with the newly developed magnetoresistive sensors which would be capable of creating a completely electronic measurement system. Moreover, this system would be additionally compatible with a main stream development in microelectronics, namely the so called MRAM.

Both the principles of the measurement technique as well as new developments in the preparation of magnetic carriers are demonstrated. It is shown that paramagnetic beads can be detected by new magnetoresistive sensors yielding a purely electronic signal. The results for Giant Magnetoresistance sensors are compared to an analysis of the same biological systems marked with fluorescence dyes. This shows, that down to a concentration of about 10 pg/ μ l of, e.g., DNA molecules, the magnetoresistive technique is competitive to nowadays standard analysis methods. The capability of the Tunneling Magnetoresistance sensors to detect even single markers is additionally demonstrated by a model experiment using the tip of a magnetic force microscope to mimic the presence of a magnetic particle on top of the sensor surface.

The magnetic carriers detected by the sensors consist nowadays mostly of nanoscale paramagnetic magnetite particles embedded in a polymer matrix with total sizes from some μ m down to about 100nm. They are linked to, e.g., DNA or proteins (often by a avidin-biotin bond) and thereby enable highly specific detection of complementary molecules. These magnetic particles suffer from their broad size distribution and the relatively small magnetic moment. With the new synthesis of superparamagnetic or ferromagnetic nanocrystals of mainly 3-d materials like Co or Fe, magnetic markers with superior magnetic moments, smaller size and size distribution and even adjustable shape can be produced. Here, the question about their potential to replace magnetite is addressed. Starting from a magnetic analysis of the corresponding magnetophoretic mobility of Co and FeCo based alloys their synthesis and resulting microstructural and magnetic properties as function of the underlying particle size distribution and the stability of the oleic acid ligand are discussed. Moreover, the magnetic particles offer an additional feature: They can be manipulated on chip via currents running through specially designed line patterns. We show that this manipulation can be performed in a precise and reproducible manner, enabling locally enhanced concentration or even the measurement of binding forces with very low loading rates.



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Bio-related Routes to Nanowire Synthesis and Self-assembly

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The formation of high aspect ratio structures such as nanowires and nanofilaments represents a major synthetic challenge that often requires high temperature and the use of catalysts. In contrast, biological systems produce highly elongated soft materials under ambient conditions by uniaxial self-assembly based on collective weak interactions that exhibit a strong directional bias. In some cases, for example the assembly of virus coat protein subunits around a single RNA macromolecule, this process involves the use of templates; alternatively, high aspect ratio structures such as collagen fibres can be assembled by a series of hierarchical interactions involving oriented self-aggregation.

In this talk, we explore the potential of using bio-related routes to nanowire synthesis and self-assembly at room temperature and pressure. This principle will be illustrated using several examples of our most recent work involving; (a) use of bio-nanostructures such as tobacco mosaic virus particles as templates for the synthesis of metallic nanowires [1], (b) formation of silica nanofilaments by co-assembly with anionic porphyrins [2] or chiral lipids [3], (c) spontaneous linear assembly of Au nanoparticle chains by coupled self-aggregation (unpublished work), and (d) generation of complex structures based on nanofilament synthesis and directed aggregation in confined reaction media such as water-in-oil microemulsions [4-6].

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Biocatalytic and Bio-Templated Synthesis of Nanowires

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Biomolecules act as templates or as effective catalysts for the generation of metallic or semiconductor nanowires.¹ DNA was used as a template for the construction of metallic nanowires. The easy synthesis of numerous DNA shapes and ordered base sequences, the availability to manipulate DNA by enzymes, the targeted association of metal-ions or intercalators to DNA, and the specific binding of proteins to defined based sequences, provide very useful means to apply DNA as templates for the synthesis of nanowires. We have used a Au nanoparticle (NP)/intercalator (doxorubicin) conjugate as a functional unit to generate Au-nanoparticle wires by their intercalation into double-stranded DNA, followed by photochemical crosslinking.² A different method has involved the use of cancer cells, and specifically telomerase extracted from cancer cells, to synthesize nucleic acid templates (telomers) consisting of constant repeat units. The association of Au nanoparticles through Au-NP/complementary nucleic acids, followed by the catalytic enlargement of the NPs led to the formation of metallic nanowires.³

A different approach to generate metallic nanowires has involved the use of actin filaments⁴ as templates. Monomers of G-actin functionalized with Au-NPs (1.2 nm) were polymerized and subjected to catalytic enlargement of the Au-NPs. Au wires of 1 μm to 2 μm length and 80 nm – 120 nm width and height were generated. The Au nanowires exhibited conductivity of bulk gold. The polymerization of G-actin monomers onto the \pm ends of the Au-NP-functionalized actin filaments yielded patterned nanowires. The catalytic enlargement of the Au-NPs generated Au-nanowires tethered at their ends to actin motor proteins. The resulting composite structures acted as nano-transporters upon immobilization on a myosin interface. The addition of ATP led to the motility of the nanowires at a speed of 25 nm \cdot s⁻¹. The perspective of the nanostructures to assemble nanocircuitry and to act as transporter units will be discussed.

Enzymes allow the biocatalytic growth of metallic, semiconductor, and insulating nanowires. Au-NP-functionalized oxidases (e.g., glucose oxidase, galactose oxidase) were deposited on Si supports by dip-pen-lithography. The biocatalytic generation of H₂O₂ in the presence of glucose or galactose, respectively, enabled the H₂O₂ mediated enlargement of the Au NP, to yield continuous, orthogonally-deposited, gold wires (10 μm – 20 μm long and ca. 150 nm wide).⁵ Using other enzymes conductive polymer and semiconductor nanowires were grown. The potential applications of these “biocatalytic inks” in the fabrication of nano-devices will be discussed.

A further perspective of nanowires includes the synthesis of composite polymer nano-rods for bioelectrocatalytic applications. Polyaniline/Au NPs⁶ or polyaniline/carbon nanotube⁷ rods were prepared on electrode supports by electrodeposition in alumina membranes associated with electrodes, followed by the dissolution of the membrane

template. The composite rods reveal improved charge transport properties as compared to non-modified polyaniline rods. The functionalized polyaniline rods were coupled to the effective electrochemical activation of the biocatalytic oxidation of glucose in the presence of glucose oxidase.

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Layer-by-layer Assembly approach to templated synthesis of Segmented and Tube-Encapsulated Metal Nanowire Devices

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In the past few years there has been a dramatic increase in research activity on high aspect ratio inorganic nanoparticles, which has been stimulated by the availability of new techniques for making nanotubes, wires, scrolls, and ribbons from various materials, and by interest in the new physical properties of these unique forms of matter. Research in this field is also driven by the real practical potential of using nanowires and nanotubes as components of electronic circuits, magnetic media, sensors, resonators, solar cells, and bioseparations and drug delivery. Functionalized metal nanowires have been extensively studied by us and other groups for a number of these applications. Metal nanowires provide reliable control over physical dimensions, surface chemistry and transport properties, and can be easily prepared and functionalized by low-temperature techniques.

Our approach to electronically functional metal nanowires combines template electrochemical synthesis with established wet chemical methods for making thin-film devices. We have recently demonstrated the applicability of two layer-by-layer assembly techniques to template membranes with cylindrical pores [1-4]. A variety of building blocks, such as semiconductor particles, short individual single-walled carbon nanotubes (SWNT), polymers, and molecular precursors, can be alternately adsorbed one-layer-at-a-time inside or around metal wires as segments or shells. We have also prepared free-standing semiconductor/polymer and silicon oxide nanotubes. Important advantages of this strategy are (i) precise control over tube wall thickness, which is easy achievable by washing between adsorption steps in order to remove weakly bound particles or molecules, and (ii) the possibility of organizing chemically and geometrically different blocks within a single nanostructure. For example, a gold nanowire coated with 12-nm-thick multilayer $\text{TiO}_2/\text{W}_{12}\text{O}_{41}$ /Polyaniline/SWNT tube-shell with a built-in p-n heterojunction is shown in Figure.

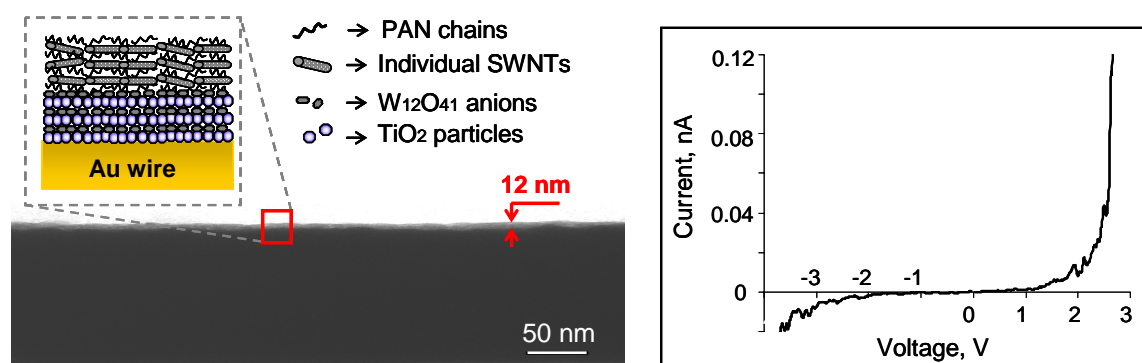


Figure. *Left:* TEM image of a $\text{Au}@\text{(TiO}_2/\text{W}_{12}\text{O}_{41})_3\text{(PAN/SWNT)}_3\text{PAN}$ nanowire and a schematic diagram of the multilayer shell structure; *Right:* I-V characteristic of a $\text{Au}@\text{(TiO}_2/\text{W}_{12}\text{O}_{41})_3\text{(PAN/SWNT)}_3\text{PAN//Au}$ nanowire device.

This presentation summarizes our progress in the synthesis and characterization of the composite wire@tube nanostructures, and considers perspectives of their application as nanoelectronic devices and sensors.

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Gel-layer-assisted, directional electropolymerization: versatile method for high resolution patterning of membrane templates with polymer nanowires
and
Molecular gels: guide for supramolecular assembly of nanowires?

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Research into 3D nanocomputing structures is important for the development of the next generation of computers. The main task in constructing a 3D chip stack is to vertically connect existing 2D chips. Hence we have focused on the fabrication of highly conducting polymer micro/nano-wires embedded in polycarbonate membranes which allow high density interconnections in 3D stack.^[1] In order to control the polymer deposition in the membrane locally, a novel gel-layer assisted, directional electrochemical process has been developed that leads to high resolution micro-patterning of polycarbonate membrane substrate with nanowires bundles (figure 1).^[2]

AND

The supramolecular self-assembly of well-designed molecular systems offers one versatile routes toward functional nanostructures and nanomaterials. For example, organo- and hydrogelators are an emerging class of small molecules that self-assemble into long fibers at low concentration (figure 2). The self-recognition and self-assembly processes responsible for gelation provide a means to control the spatial arrangement of individual molecular components within fibrillar aggregates.^[3-5] The use of such organizational factors and so molecular driving forces for the hierarchical self-assembly of inorganic nanoparticles such as nanowires will be discussed.

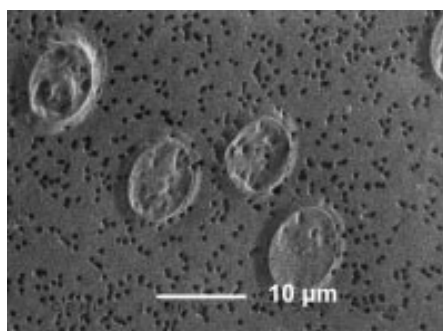


figure 1

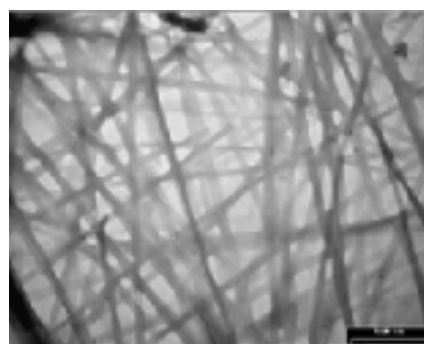


figure 2

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Microfluidic Capillary Systems: An Effective Liquid Transport System For Miniaturized Bioassays

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The analysis of a sample for the presence of a biological analyte requires three fundamental building blocks: A liquid transport system for loading and flushing the sample, a biochemical ligand that is specific for the analyte, and a sensing unit – *e.g.* a nanowire – that produces a measurable signal upon binding of the analyte and the ligand. The use of a nanowire as sensing unit will allow further miniaturizing the analysis system provided that the transport of minute amounts of sample in and out of a detection chamber can be solved in an effective manner too. Here we present microfluidic capillary systems that use programmed capillary effects for controlling the transport of liquids in and out of miniaturized sensing chambers[1,2]. The flow of liquids is self-powered and self-regulated by coding capillary forces into the structures and by using evaporation to flush large volumes, akin to a tree that can pump nutrients from the soil up to the canopy and regulate the uptake. This approach offers an intuitive macro to micro interface that avoids fluidic and electrical interconnections, complex peripherals, and dead-volumes while affording the use of conventional micropipettes for loading the reagents into the microfluidic system. Further, the use of soft lithography for making capillary systems in elastomeric materials lets one envision a simple integration with a nanowire-sensor. Moreover, such capillary systems are amenable for the oriented immobilization of the nanowires on a substrate, for the subsequent chemical processing of individual nanowires, and for the selective functionalization of nanowires with biomolecules.

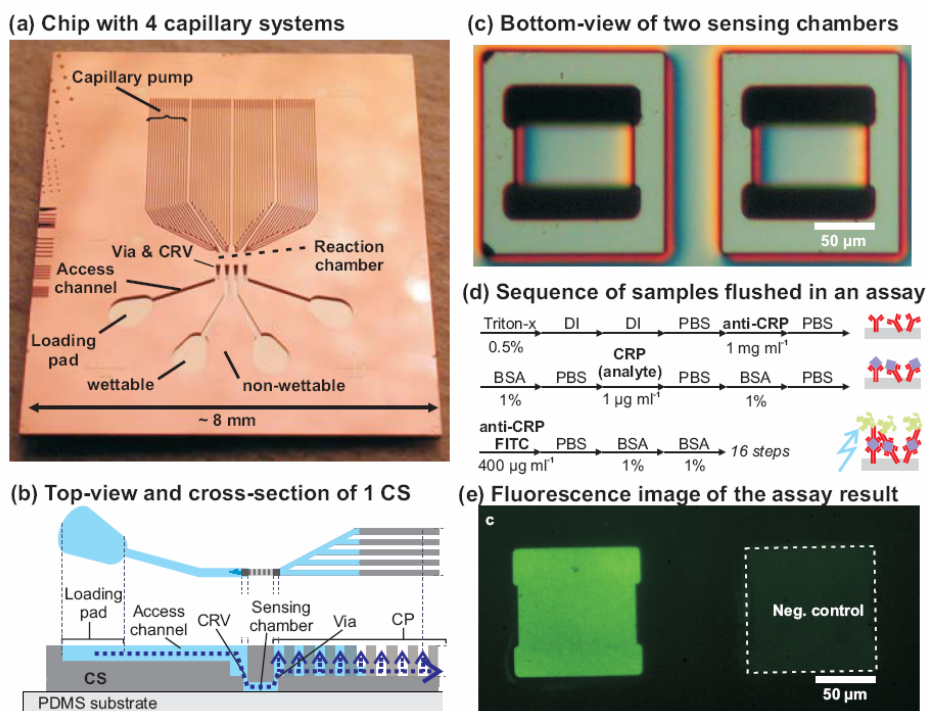


Fig 1. Capillary systems and their application to miniaturized fluorescent immunoassays. (a) Micrograph of a chip with 4 capillary systems showing their loading pads and capillary pumps. Liquids that are delivered into the loading pad flow through the reaction chamber (bottom side, not visible) into the capillary pump. The surface chemistry and geometry control the flow that automatically starts on loading the pad, and stops when the pad is empty while always keeping the sensing chamber filled. (b) Schematic of a CS with the basic functional units, including the capillary retention valve (CRV). (c) Bottom view through a transparent substrate of 100- μ m-wide reaction chambers. (d) Sequence of solutions flushed through the reactions chamber with volumes ranging between 300 – 600 nl only in each step, which includes the functionalization of the substrate surface with antibodies in step 5. Using evaporation, the flow of the analyte, step 9, can be adjusted for long flushing times and maximal sensitivity. The use of nanowires could help reduce the number of pipetting steps required. (e) Fluorescence image showing the result for this assay with a negative control on the right.

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Semiconducting nanowires for optical and electrical detection of biological species

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Semiconducting nanowires are one of the most promising low dimensional materials for “bottom-up” fabrication of nanodevices. The synthesis and fabrication of nanoscale photonic and electrical devices from silicon and cadmium sulphide nanowires is presented. The nanowires are grown by CVD and pulsed laser deposition using the vapor-liquid-solid growth mechanism.

Arrays of silicon nanowire FET devices are fabricated with standard optical lithography. These ion-sensitive nanowire FETs (nanoISFETs) were integrated in microfluidic channels and used for electrical biosensing. The functionalization of the nanowire surfaces as well as the binding event of single viruses was observed in-situ with fluorescence microscopy (**Fig. 1a** and **1b**). Photonic sensing applications are demonstrated with integrated nanoLEDs of crossed n-CdS and p-Si nanowires to perform nanoscale fluorescence spectroscopy and cellular imaging of quantum dot labelled fibroblasts (**Fig. 1c** and **1d**). Applications of these nanoscale light sources for near-field applications will be discussed.

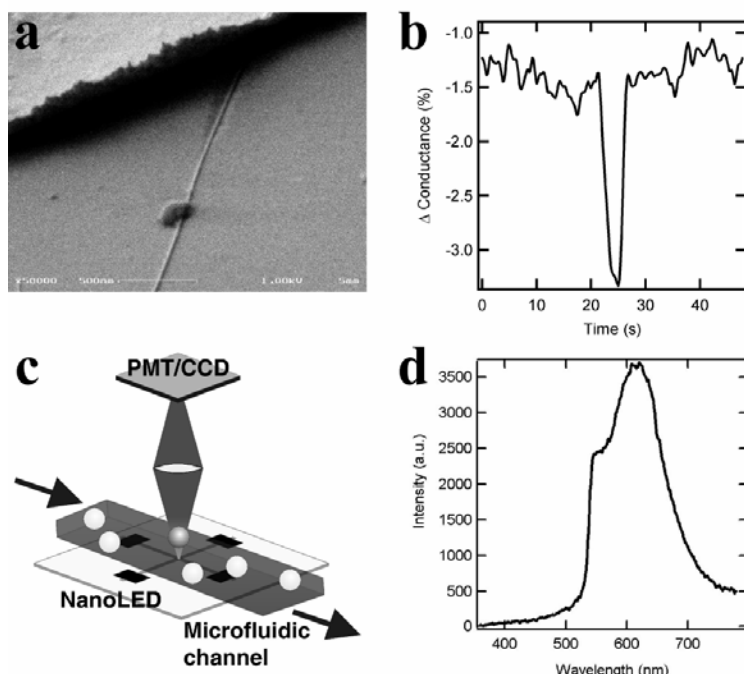


Fig. 1. **Single analyte detection with nanowire devices.** a) SEM micrograph of an influenza virus adhered on a 20 nm silicon nanowire b) Conductance changes of a 20 nm p-Si nanowire functionalized with influenza antibodies due to a reversible single virus binding. c) Integrated nanoLEDs as nanoscale light source for fluorescence spectroscopy in micro-fluidics. d) Quantum dot emission

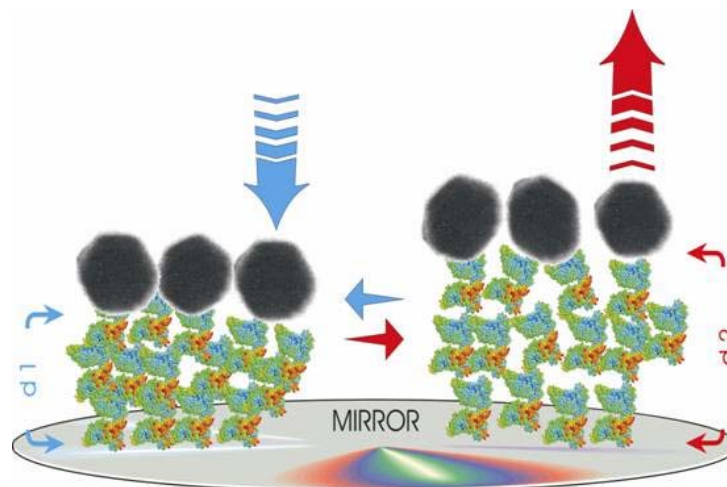


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OPTICAL NANOCUSTER-DEVICES

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Resonance enhanced absorption is observed if a light-absorbing cluster or cluster layer is positioned in nano-distance to a reflective mirror and illuminated from the particle side with light. At a certain wavelength the electromagnetic wave reflected from the mirror has the same phase as the incident wave at the position of the absorbing nano-cluster particle. This assembly is a nano-interference system; its feedback mechanism intensifies the absorption of light at a well defined wavelength, resulting in "anomalous absorption". At a specified mirror cluster distance and a well-defined angle of light reflection (and observation) only a sub-set of waves, in a narrow range of wavelengths, is in phase. The almost complete absorption of those light waves and the high reflectivity at any other wavelength results in a visible color response.

The REA set-up in combination with a biological recognition system such as DNA-DNA or protein-protein allows to generate an optical signal by:

- 1 Inducing distance changes of the cluster - mirror distance via (bio)molecular interactions
- 2 Inducing changes in the packing density or spatial arrangement of the cluster layer (e.g. via enzymes)
- 3 Changing the number of clusters (via capture (bio)assays)

Such changes modify the color due to a spectral shift of the absorption maximum or the color intensity due to a strong change in light absorption (at a defined wavelength, often in the visible or IR-spectrum).

Based on the REA-phenomenon (developed and optimized by Attophotonics Biosciences GmbH, Austria, Vienna and NovemberAG, Germany Erlangen) a number of commercial products had been constructed. *Brandsealing^R* uses the patented REA cluster technology to produce optical codings. Cluster REA thin film systems show a characteristic color-flip effect and are extremely mechanically and thermally robust. This is the basis for its application as an unique security feature. The specific spectroscopic properties as e.g. narrow band multi-resonance of the cluster layers allow the authentication of the optical code which can be easily achieved with a mobile hand-held reader developed with Siemens AG, Germany. Thus, these features are machine-readable which makes them superior to comparable technologies.



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Laser with silicon nanocrystals – dream or near future?

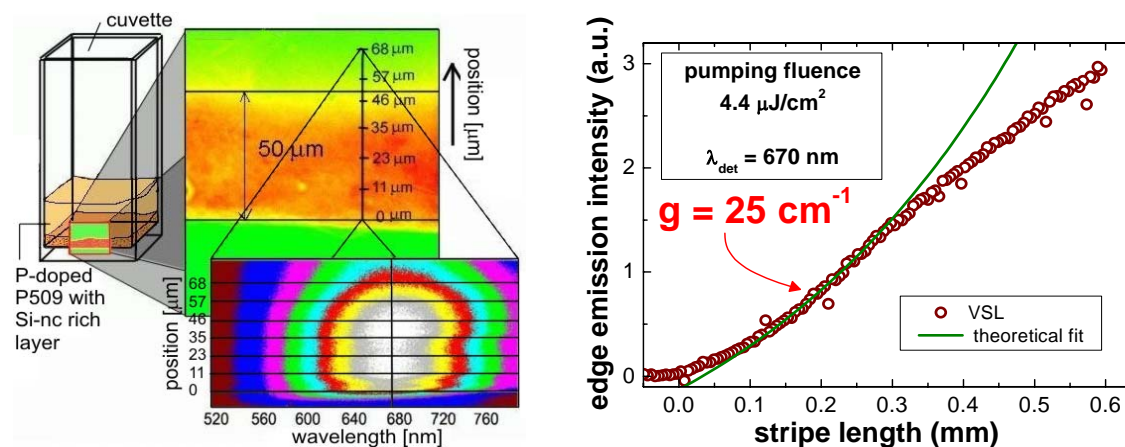
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Stimulated emission from *nanocrystalline silicon* in the visible has become a hot topic during past years because a positive optical gain due to stimulated emission is a necessary condition to build a *silicon laser*. In 2000, L. Pavesi et al. from the University of Trento announced observation of *optical gain* in an ensemble of silicon nanocrystals. A fundamental qualitative step in the field has been accomplished quite recently, when successful performance of Raman laser in *bulk* silicon has been announced, although immediate applicability of this type of laser seems to be doubtful. However, it appears that not all samples containing silicon nanocrystals exhibit optical gain and the requirements for the sample preparation and structure have not been fully clarified so far. To contribute to the solution of these problems, we search for the optical gain in two types of materials containing silicon nanocrystals: Porous silicon embedded in pulverized form into a sol-gel derived SiO₂ matrix (see figure).

This material enables to reach *higher concentration* of Si nanocrystals in the SiO₂ matrix than standard technologies. Si-ion implanted silica glasses with waveguiding properties.

This technology produce an efficient active *planar waveguide* formed by a layer of Si nanocrystals. The waveguiding could improve the conditions for occurrence of optical gain as it prevents the spontaneous emission from escaping without being amplified. We observed small optical gain in both types of materials, however, under different pumping conditions.



Left: Microphotograph (top) of porous silicon grains embedded in the SiO₂ matrix luminescing orange under UV excitation. Bottom image shows a crosssection of photoluminescence spectra through the sample.

Right: Exponential increase of luminescence measured from the sample edge (VSL) as a function of the length of the excited region indicates the presence of the stimulated emission (optical gain). Theoretical fit (full line) reveals positive optical gain coefficient of 25 cm⁻¹. Deviation of the VSL data from the theoretical curve for long stripe lengths is due to gain saturation.

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Orientation Switching of Functional DNA Monolayers

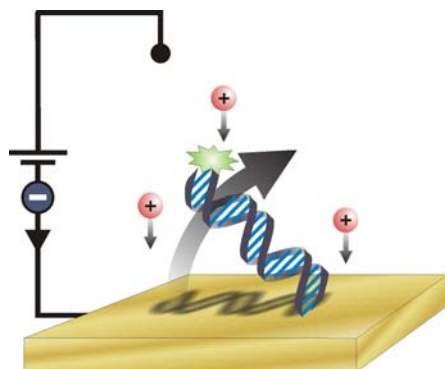
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Monolayers of DNA immobilized on solid substrates are of increasing importance for applications such as DNA-based sensors and microarrays. An active manipulation of the molecule probe layer on the surface can significantly enhance its functionality in sensing devices, or even lead to completely new schemes of detection.

I will report on our recent work on the electrical manipulation of short oligonucleotide strands which are end-tethered to gold surfaces in electrolyte solution, being monitored in a contactless mode by fluorescence techniques. By applying alternating electrical bias potentials to the supporting Au-electrodes we are able to induce a switching of the DNA layer conformation between a 'lying' and a 'standing' state. I will demonstrate how such switchable bio-molecule layers open new prospects in label-free bio-sensing, such as for the detection of DNA hybridization. In general, this scheme can be extended to any specific binding reaction of target molecules to the probe strands, based on the change of certain molecular properties after binding (e.g., size, charge, mechanical stiffness).

Recently, we have been studying the DNA dynamics by using time resolved measurement techniques. I will briefly discuss the observed distinct differences in the kinetics of single and double stranded DNA, and compare our results to hydrodynamic simulations.



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Nanomanipulation and nanolithography by atomic force microscopy: towards nanorobots

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Technologies that allow one to control and manipulate nanoscale objects are thought to be key technologies for the upcoming decades or even century. The problems we are currently confronted with were already foreseen by Richard Feynman in 1959. Nearly fifty years later, there are two fundamental questions that are not yet fully answered: “How do we write small?” and

“How do we manipulate and control things on a small scale?”. Science and technology have made tremendous progress in providing us with various methods to write on a small scale. Manipulating and controlling things on the nanometer scale, however, turned out to be far more difficult. Handling nanoscale objects includes finding these objects, tracking and moving them. Technologies are sought after that allow one to pick and place or cut and fuse in a completely alien environment. Thus, there are two important lines of investigation towards nanoscale manipulation: nanopatterning, where strategies are developed that allow us to generate arbitrary nanostructures (cf. Figure 1), and nanotelerobotics, where the nanoworld is translated into a virtual reality that allows us to interact with smallest objects.

Current research towards nanopatterning includes nanostructured surface functionalization and directed self-assembly of nanoscale objects. Surface properties such as wettability, adhesion, friction and specific chemical interaction can be controlled with nanometer resolution. Controlled positioning of particles, clusters or single molecules allows for the investigation of new chemical processes, predefined molecule interaction and the direct assembly of new chemical compounds.

Although various nanomanipulation methods have been developed, systems based on scanning probe microscopes offer the most versatile approach. Among the other instruments of the scanning probe microscope family the AFM has the widest range of application, both for imaging and for nanomanipulation. However, standard AFM systems are restricted to small working areas and operating speed efficiency is quite limited. To enhance and expand the capabilities of the AFM for manipulation we have developed a combined system. In this system, we conjoin an AFM for high resolution imaging and manipulation with video microscopy and non-contact ablation by a

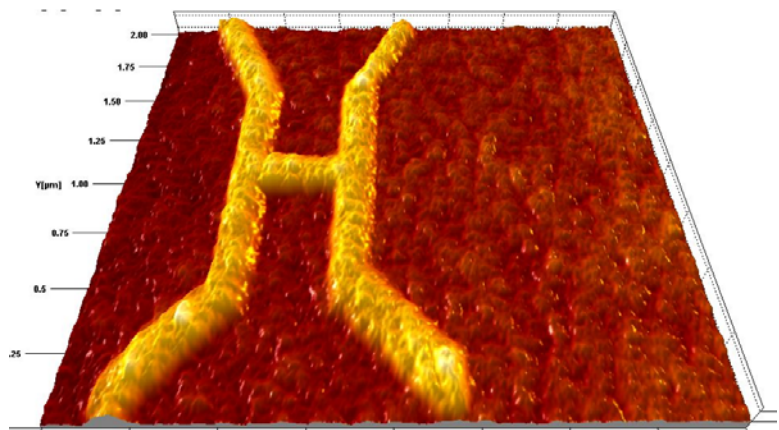


Figure 2: SiO₂ Structure generated by local anodic oxidation.

ultraviolet (UV) microbeam laser for large scale manipulation of biological specimen [1-3].

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Nanoscale resolved optical microscopy and infrared spectroscopy by light scattering from a tip

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We demonstrate that (apertureless) scattering-type scanning near-field optical microscopy (s-SNOM) allows optical imaging at 10 nm spatial resolution [1]. In our s-SNOM the tip apex of an atomic force microscope (AFM) is illuminated either by a HeNe laser at 633 nm or a CO₂ laser at about 10 μ m wavelength. The light scattered from the tip in near-field interaction with the sample surface is detected interferometrically and allows material-specific imaging at a spatial resolution independent of the wavelength or to visualize the optical eigenfield patterns of plasmon-resonant nanoparticles [2].

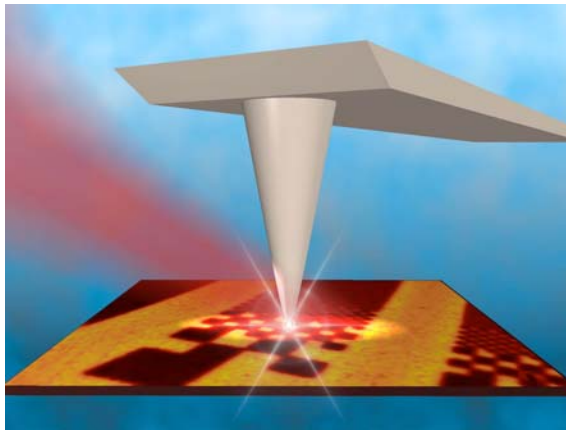


Figure:

Illustration of s-SNOM imaging. A sharp tip illuminated by focused laser light scans a sample surface and simultaneously acts as mechanical and optical probe.

Probing a SiC sample with our s-SNOM at mid-infrared wavelengths we observe that the optical near-field interaction between tip and a flat surface can be strongly enhanced due to near-field excitation of lattice vibrations, more precisely by phonon polaritons. Near-field spectroscopy in the range 9.2 - 11.2 μ m yields a resonant light-matter near-field interaction of unprecedented dynamic range and spectral sharpness [3]. This phonon-enhanced near-field interaction is not only sensitive to the local chemical composition but also to the local structural properties of a sample. Besides chemical microscopy it thus allows to map crystal quality [4], lattice defects, polytypism or crystal orientation at nanoscale resolution. Altogether we envisage applications in optical nanospectroscopy and imaging of physical, chemical and biological nanocomposites, nanoparticles or nanowires.

A more general view of surface phonon polaritons in nanostructures - particularly nanowires made of polar materials (e.g. SiC) - suggests phonon photonics [5], an infrared nanotechnology for manipulating, guiding and controlling infrared light in nanoscale devices.

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