Ion Tracks for Micro- and Nanofabrication

*From Single Channels to Superhydrophobic Surfaces*

REIMAR SPOHR
Dissertation presented at Uppsala University to be publicly examined in Polhemsalén, Ångström Laboratorium, Lägerhyddsvägen 1, Uppsala, Friday, January 29, 2010 at 10:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

A method is described for preset-count irradiations between 1 and 100 ions singling-out individual ions from an ion beam with more than a billion ions arriving per second. The ion tracks are etched in a conductometric system with real-time evaluation of the acquired data. The etch process can be interrupted when reaching a preset channel diameter. Cylindrical channels are obtained by adding surfactants to the etch solution forming a self-assembled barrier between etching medium and polymer. Asymmetric etching of single ion tracks leads to pH sensitive conical pores with diode-like properties. Using etched channels as template, homogeneous and multilayer magnetic single-wires are electrodeposited. The magnetoresistivity of the wires is studied. Single-track applications comprise critical apertures (cylindrical, conic, necked), asymmetric pores (pH sensitive, biospecific), Giant Magneto Resistance sensors, and spintronic devices.

On the basis of studies with individual ion tracks we tackled tilted multiporous systems such as ion beam lithography with a masked ion beam leading to micro-structures with inclined walls and anisotropic superhydrophobic ion track textures, analogous to biological shingle structures on butterfly wings. We demonstrated qualitatively, that the asymmetry of the texture translates into motion under ultrasonic agitation. This could lead to the development of rotary drives.

Keywords: Ion track, single ion, real time, phase detection, conductometric cell, conductometry, electro replication, microtechnology, nanotechnology, surfactant, self organization, GMR, magnetic, sensor technology, hydrophobic, tilted texture.

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ISSN 1651-6214
ISBN 978-91-554-7683-0
urn:nbn:se:uu:diva-111247 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-111247)
To my wife, Mechthild, and to our children, Heidrun, Guntram, Sigrid, and Thorben
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints were made with permission of the respective publishers.
Comments on my contributions

I confirm that reports (I) to (VI) cited above are based on apparatus and experiment conceived and significantly executed by me in collaboration with other persons. In reports (I), (II), (III), and (VII) I acted as principal experimentalist, data analyst, data interpreter and responding author and in reports (IV), (V), and (VI) as a tutor.

I. I conceived the irradiation, etching, and electro-replication system, performed major parts of the described experiments and writing. – The report reflects techniques developed in the frame of my professional work at GSI Darmstadt. It was stimulated by Flerov, Schmelzer, Armbruster, Klas Hjort, and Lars Westerberg.

II. I conceived the conductometric cell including electronics, electro-stopping, phase detection, and computer interface and performed major parts of the experiment, evaluation and writing. – The report on diode-like single-ion track membrane reflects the close relation between GSI and JINR Dubna (Russia), St. Petersburg, Gliwice (Poland), and London (GB). The work also profited from a long-lasting collaboration with JAERI, Takasaki (Japan) on gel-clad thermo-responsive channels. The breakthrough experiment is based on single-ion track etching, which I developed at GSI. It would not have been possible without input from Dubna and Berkeley.

III. I performed major part of described experiments and evaluation and writing. – The technique of surfactant assisted etching was inspired from Dubna, triggered by a visit of Leo Man from City University Hong Kong in Darmstadt, and performed in my home laboratory. The work profited strongly from interactions with Uppsala and Iasi University.

IV. The work on homogeneous (AMR) and multilayered (GMR) ferromagnetic nanowires reflects the output of a postdoctoral period of Takeshi Ohgai (Japan) under my supervision at GSI in the frame of a European Research Training Program. – The work combines single-ion etching developed at GSI with electrodeposition of magnetic multilayers developed at ILL Lausanne. Important stimuli came from Uppsala.

V. The work on current perpendicular to plane single-nanowire GMR sensor reflects the output of as postdoctoral period of Ionut Enculescu from Bucharest under my supervision at GSI in the frame of a European Research Training Program. Important stimuli came from Uppsala and Lausanne.

VI. Same as IV.

VII. I was responsible for the performed experiments and the major part of evaluation and the writing. The experiment was triggered from discussions with Lars Westerberg and profited strongly from facilities available at the Ångström and The Svedberg Laboratories of Uppsala University.
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1. Introduction

1.1. Discovery of ion tracks

One of the most fascinating developments associated with particle accelerators is the development of single-ion fabrication techniques. Using individual ions, structures can be fabricated down to the nanoscopic scale, which is the starting point for developing devices not possible using other techniques.

Etched ion tracks had already been seen on crystal faces during the late nineteenth century but were wrongly interpreted as crystal defects. [1] The discovery of nuclear decay\(^1\) and the development of the transmission electron microscope\(^2\) were necessary requirements for the discovery of etched ion tracks by D.A. Young in 1958, who interpreted them correctly as traces of disorder left behind by energetic ions [2]. Unlike the transient tracks of energetic particles in the cloud chamber (Wilson 1911, [3]) and in the bubble chamber (Glaser 1952, [4]), ion tracks can be stable over millions of years. An example of an ion track is illustrated in Fig 1, which shows the cross-section of a latent ion track caused by the passage of a \(^{129}\text{Xe}\) ion of 11.4 MeV/nucleon through a crystal of muscovite mica. [5]

![Cross-section of ion track in mica](image)

**Fig 1** *Cross-section of ion track in mica.*\(^3\) High resolution transmission electron micrograph. The elliptical zone is amorphous and has a diameter of about 6 nm. [6]

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1 Henri Becquerel, 1896; http://nobelprize.org/nobel_prizes/physics/laureates/1903/
2 Ernst Ruska and Max Knoll, 1931; http://nobelprize.org/nobel_prizes/physics/laureates/1986/
3 Johann Vetter, http://ion-tracks.de : Picture gallery : Track formation;
The diameter of latent ion tracks can be enlarged by selective etching, from their original size of few nanometers [7-8] to sizes up to several hundred micrometers. This chemical amplification opens-up a wide range of applications with variable shape and sizes ranging over orders of magnitude. Depending on the local concentration of the deposited energy and on the selectivity of the etch process, the result of ion track etching can range from a shallow depression to a deep hole with vertical walls. The smallest dimension that can be etched corresponds to the size of the activated zone, which has a diameter between 6 and 20 nm, depending on the ion species and the used recording material. The deposited effect depends on the atomic number of the used ion and varies over its path, as illustrated in Fig 2.

Fig 2 Variation of deposited energy as function of penetration depth\(^4\) [9-10]. Electronic stopping, \(S_e\), is responsible for the creation of columnar defects (latent ion tracks). Nuclear stopping, \(S_n\), is responsible for the creation of atomic defects at the very end of the latent ion track. The left regime corresponds to a straight ion path obtained by electronic stopping which is gradually decreasing the ion energy. The middle regime corresponds to a bumpy structure dominated by both, electronic, and nuclear stopping. The right regime corresponds to the preferential influence of nuclear stopping which is responsible for the creation of point defects.

\(^4\) Top of figure [9-10].
The track length corresponds to the distance over which sufficient energy is transferred to the solid to etch it selectively and can reach lengths up to about 1 mm [11-12]. However, until now, most experiments have been performed with track lengths between 1 and 100 μm.

The energy of a swift heavy ion is transferred to the solid via a secondary electron cascade spreading out radially from the ion path. In polymers, the electron cascade induces bond breaking and secondary chemical reactions, recorded as latent ion track with a diameter between 10 and 20 nm.

The application potential of ion track etching was recognized by Fleischner, Price and Walker in 1962 [13] and applied to biological filters [14].

Since then, ion track technology has been refined step by step. The first experiments with single ion tracks were performed by DeBlois and Bean [15] and by Possin [16]. On one hand, DeBlois and Bean refined the Coulter counter [17] down to the dimensions of a virus. On the other hand, Possin fabricated wires in mica with diameters down to 8 nm diameter for studying electron conduction in restricted geometry. Both groups selected single-track channels and wires from a number of mica membranes containing a small numbers of fission tracks.

A single contact technique was developed at EPFL, Lausanne, Switzerland [18] to contact exactly one wire from an ensemble of many wires growing at different speed. The technique uses a three-electrode system. Both sides of a multi-porous membrane are coated with a thin metal film. One metal film serves as cathode. The other metal film is located between the cathode and the anode and has an electrical potential floating between anode and cathode potential. As soon as the first wire contacts the floating-potential film, its potential drop is used to terminate the electro-deposition.

A new step of refinement is reached if the membrane contains exactly one ion track. For single-track fabrication, the penetration of the ion through the membrane must be detected to switch the ion beam off. [19] The detection of individual charged particles is possible by ionization chambers, by solid state detectors and by secondary electrons emitted from the entrance or exit of the irradiated solid. Single-ion detection opens the possibility to fabricate individual single-ion tracks on a routine basis which is a necessary requirement for systematic studies and practical applications.

The technique used perforated polymer film of 30 μm thickness for fabricating single-track membranes with 4 μm diameter measuring the deformability of red blood cells [20]. A later introduced technique used unperforated films on which the irradiated spots were marked by mechanical indentations [21-23].

Single-ion detection is a necessary requirement for a scanning ion microbeam [24] capable of fabricating arbitrary patterns with exactly one ion per pattern element. At present, the ion microbeam at GSI has reached an
1.2. Irradiating with heavy ions

Essential for the generation of ion tracks is a source of heavy ions of sufficiently high atomic number and energy. In principle, there exist four different ways to create artificial ion tracks in solids: Nuclear reactors, radioactive sources, ion accelerators and scanning ion microbeams (Fig 3).

Radioactive sources provide fission fragments with ranges up to several 10 μm. While α sources produce exactly one isotope (\(^4\)He) at well defined energy plus a recoil nucleus of small penetration depth, sources of heavy ions such as fission fragment sources have a broad energy and nuclear charge distribution. Low intensity alpha and fission sources are very convenient for generating ion-tracks in solids. They are interesting for low-dose irradiations
and further-development of ion track technology, such as testing of track-recording materials and refining etch recipes.

Reactors enable large-scale commercial applications such as the production of ion track filters with fluences up to $10^{10}$ fission-fragments per cm$^2$. The irradiations require access to a neutron outlet port of a reactor. They also require a converter foil that transforms the neutron flux from the reactor core into fission-fragments. For this purpose a $^{235}$U foil, inserted between the reactor and the track recorder, can be used. Nuclear reactors yield broad energy- and mass-distributions of fission-fragments. Due to their high intensity, beam collimation and large sample throughput is possible. The wide angular distribution of the created fission fragments is ideally suited for ion track filter production.

In contrast to radioactive sources, ion accelerators provide ion beams of well-defined nuclear charge and mass, energy, impact angle and angular spread. The can be rapidly switched-off after completion of the irradiation. The principle of a wide beam irradiation at a linear high frequency ion accelerator is illustrated in Fig 4 and the principle of a cyclotron in Fig 5.

![Fig 4](image) *Linear accelerator for wide beam irradiation of samples.* The ion beam can be either swept by a pair of deflector magnets corresponding to homogeneous field regions or defocused by one or several magnetic quadrupole lenses. For low fluence irradiations defocusing is preferred.

![Fig 5](image) *Principle of a cyclotron.* The ion beam is injected at point $A$, accelerated in the gap between two $D$-shaped electrodes to which a high frequency voltage is applied, bent by a homogeneous magnetic field and, after reaching the outer magnetic field boundary, ejected at point $B$. For non-relativistic ions, the frequency as well as the magnetic field can be kept constant.
The irradiation of a solid sample is characterized by the following projectile parameters (Table 1):

Table 1 *Typical irradiation parameters* for creating ion tracks in solids.

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>18 to 92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy [MeV/nucleon]</td>
<td>1 to 100</td>
</tr>
<tr>
<td>Impact angle [°]</td>
<td>0 to 90</td>
</tr>
<tr>
<td>Fluence [ions/cm²]</td>
<td>1 to 10¹²</td>
</tr>
</tbody>
</table>

1.3. Energy transfer to small volumes

The starting point of track formation is the transfer of energy from the projectile-ion to the target electrons and to the target nuclei in binary encounters, i.e. events involving only the projectile and one other particle at a time. This first step is understood much better than any of the successive steps involving many particles, in which the energy input of the projectile-ion is converted in a nonlinear way into a developable radiation effect, the latent track, and ultimately into the observed track. At low energies of the order of 0.1 MeV/u and less, the energy-transfer to atomic nuclei prevails (Nuclear stopping regime). At higher energies, above 0.1 MeV/u the energy-transfer to individual target electrons becomes important (Electronic stopping regime) and is responsible for the creation of ion tracks.

Two effects can be distinguished: (1) The collision between projectile and target nuclei prevailing at low energies, nuclear stopping, $S_n(E)$, and (2) the collision between projectile and target electrons, prevailing at high energies, electronic stopping, $S_e(E)$. Since nuclear stopping involves particles of similar mass, it induces an abrupt change of the projectile direction and energy. On the other hand, since electronic stopping involves a very heavy particle (the ion) interacting with a very light particle (a target electron) it corresponds to a gradual change of the projectile direction and energy and leads to a straight ion track.

Electronic stopping is responsible for the creation of columnar ion tracks. The energy-loss function $S(E)$ is split up into two terms, electronic ($e$) and the nuclear ($n$) stopping:

(Eq. 1) \[ S(E) = S_e(E) + S_n(E) \leftrightarrow \frac{dE}{dx} = \left( \frac{dE}{dx} \right)_e + \left( \frac{dE}{dx} \right)_n \]
While $S_e(E)$ corresponds to a quasi-continuous retardation of each projectile-ion, $S_n(E)$ reflects only the average retardation of many projectile-ions, since each individual scattering process corresponds to an abrupt change of the momentum and energy of the projectile. The concept of determining the energy loss function from binary encounters integrated over a finite target thickness is shown in Fig 6.

Fig 6  Concept of energy-loss calculation. (Left) Each impact parameter $p$ corresponds to a certain angular deflection $\phi$ of the projectile and thus to a certain energy-transfer $T$. By integrating over all accessible energy-transfers $T$ one obtains the average energy-loss $<T>$ of the projectile-ion per target particle. (Right) By multiplying the average energy-loss $<T>$ per target particle with the number $n=N.\Delta x$ of target particles present in a target of unit area and thickness $\Delta x$ one obtains the total energy-loss $\Delta E$ in the target. Dividing $\Delta E$ by $\Delta x$ yields the energy-loss function $(dE/dx) = N <T>$. This step is equivalent to projecting all cross-sections onto a plane.

If we know the transferred kinetic energy $T$ as function of the impact parameter $p$, we can determine the probability of this energy-transfer from the cross-section $2\pi p \, dp$:

(Eq. 2) \[ dT = T(p) \cdot 2\pi p \cdot dp \]

By integrating over all target particles contained within a thin target of thickness $\Delta x$ and unit surface area (Fig 6) we obtain the energy-loss of the projectile over the distance $\Delta x$. Electronic stopping concerns only the energy-transfer from a heavy projectile-ion to a much lighter target electron. The energy-loss is counted negative if the energy of the projectile is decreased.
where \( N_e = Z_2 \, N = Z_2 \, \rho / (A \, u) \) is the number of target electrons per unit volume, \( Z_2 \) its atomic number, \( N \) the number-density of the atoms of the target material, \( \rho \) the density of the target material, \( A \) the atomic mass number of the target material, and \( u \) the atomic mass unit. The upper integration limit \( p_{\text{max}} \) corresponds to a minimal quantum of energy that can be transferred to the target electron at a limiting impact parameter. Inserting as integrand \( dT = T(p) \cdot 2 \pi p \cdot dp \) from (Eq. 2) the main features of the electronic energy-loss function (stopping power) are obtained [35]

\[
(Eq. 4) \quad \left( \frac{dE}{dx} \right)_e = -N_e \cdot dx \int_0^{p_{\text{max}}} dT = -N_e \cdot dx \int_0^{p_{\text{max}}} T(p) \cdot 2 \pi p \cdot dp
\]

\[
(Eq. 5) \quad b = \frac{Z_{\text{eff}} \cdot e^2}{1 \cdot m_e v^2}, \quad Z_{\text{eff}} = Z \left( 1 - e^{-\frac{v}{v_0} Z^{-1/3}} \right)
\]

\( Z_{\text{eff}} \) is the effective charge of the projectile (which is partially ionized due to previous encounters with target electrons) and \( Z_2 \) is the nuclear charge of the target atom; \( v_0 = 2 \pi e^2 / h = 2.1847 \cdot 10^8 \) cm / s is the Bohr velocity. (Eq. 4) approximates experimental data for non-relativistic ion energies above the nuclear stopping regime. \( Z_{\text{eff}} \) is a function of the projectile velocity, and \( p_{\text{max}} \) corresponds roughly to the inverse of the average electron binding energy (ionization potential) of the target material.

In an ordered crystal, nuclear stopping leads to locally confined collision cascades consisting of disordered zones of small dimensions. Electronic stopping leads to a long-range disordered zone, the latent ion track (Fig 7). Ion tracks in crystals consist of a disordered track core with reduced density surrounded by a track halo with increased density.

As result of the primary ionization along the projectile-ion trajectory an ion cloud is formed. The corresponding electrons are emitted to large distances. In metals the ion cloud is neutralized immediately after the passage of the projectile ion. However, in insulators the return of the electrons to the ion cloud is inhibited due to electron traps. The ion cloud, containing a large amount of stored electrostatic energy expands explosively and becomes the driving force for an atomic collision-cascade.
1.4. Latent track – A quenched melt

As result of electronic and atomic collision-cascades close to the ion path, a rapidly quenched thermal spike is formed leaving behind a cloud of interstitial atoms and vacancies. At larger distances, the electronic collision-cascade leads to excited atoms and molecules prone to chemical reactions. Their local distribution can be obtained from computer simulations [37] and defines the starting condition for diffusion processes and long term secondary reactions. Ultimately, the atomic defects reorganize in the form of a track core, a chemically activated zone along the ion path of about 10 nm diameter. It involves the diffusion of many particles in a highly disturbed solid and

Fig 7  *Effect of nuclear and electronic stopping*. Top: schematic energy loss function \( S(E) \). Bottom left: defect cascade due to elastic scattering of nuclei. Bottom right: ion track due to inelastic energy transfer from the primary ion to target electrons. The track core corresponds to a Coulomb explosion of the target atoms caused by the passage of the primary ion [36].
can be described by semi-empirical models. The electronic defects may lead to chemically activated sites (radicals) up to distances of about 1 μm. While the energy transfer between the projectile ion and the target electrons and nuclei can be reduced to binary encounters, the resulting secondary cascade processes and chemical reactions become increasingly complex. Accordingly, three phases of ion track creation can be distinguished (Fig 8) corresponding to rapidly increasing time scale and complexity.

Fig 8  Three-phases of track creation: Left: Energy transfer to target electrons and nuclei occurring within a time scale between $10^{-17}$ and $10^{-12}$ s. Middle: Diffusion of electronic and atomic defects occurring within a time scale between $10^{-11}$ and one second. Right: Development phase. Track development requires times above one second.

The main goals of track formation theory are to understand the threshold of track formation, the magnitude and spatial distribution of the observed effect, and the saturation of the observed effect with increasing energy input.

In contrast to ordered crystals, polymers contain amorphous and crystalline zones (Fig 9 left). The passing ion breaks chemical bonds of the polymer chain (Fig 9 right). Close to the ion path, bond breaking prevails. Further away, released hydrogen atoms can induce cross linking of neighboring chains. The inner part is defined as track core. The outer part is defined as track halo. In comparison with the pristine material, the track core will etch at higher velocity while the track halo usually will etch at a lower velocity.

Fig 9  Creation of ion track in polymer: (Left) Polymers usually consist of disordered (top) and crystalline (bottom) zones. (Right) The ion track in a polymer consists of a core of reduced density containing broken polymer strands, surrounded by a track halo consisting of cross-linked polymer strands.
2. Fabrication of single channels and wires (Paper I)

2.1. Irradiating with a precise number of ions

The principle of an apparatus for the irradiation of polymer tape with a preset number of ions is illustrated in Fig 10.

A thin film window separates the accelerator vacuum from the tape irradiation system. After detecting a preset number of ions, the ion beam is switched-off by a beam shutter and the polymer foil is moved to a new position. To ensure that no further ion is hitting the target tape, the shutter has to be fast in comparison with the average time between ion counting events. A typical pulse height distribution of the detector is shown in Fig 11 and an overall view of the tape roller in Fig 12.

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**Fig 10** Principle of single-track irradiation apparatus used at the ion accelerators of GSI Darmstadt (Germany) and The Svedberg Laboratory of Uppsala University (Sweden).

**Fig 11** Pulse height distribution of single-track detector using $^{129}$Xe$^{27+}$ ions of 8.3 MeV/nucleon passing through a thin film window (consisting of 4 μm thick polyethylene terephthalate, PET) and a 30 μm thick PET tape tilted at 35° (total track length ca. 48 μm).
Fig 12  *System for piercing tapes with a preset number of ions*. Left: ion beam and diagnostic system for control of beam intensity and size. Right: tape roller detecting ions that penetrated the tape, marking the hit position by a needle indentation and shifting it to a new position.

As *ion detector* we use a PIN diode\(^7\) with an active area of about 4x4 mm\(^2\). In comparison to regular photo diodes, such infrared sensitive PIN diodes have a large depletion layer, nicely fitting to ion ranges between 20 and 30 \(\mu\)m or heavy ion specific energies between 2 and 3 MeV/nucleon. As long as the ion is completely stopped within the depletion layer, the resulting pulse height is proportional to its energy.

The tape roller is controlled using a LabVIEW\(^8\) based code. Its user interface permits to view the pulse shape of individual detector pulses (Fig 13).

If the ions have too high energy, they will penetrate through the depletion layer of the PIN diode. Consequently, the pulse height distribution becomes asymmetric. In this case the energy of the ions has to be reduced by inserting an energy-absorbing foil in front of the tape. It has to be sufficiently thick that the ions come to rest within the depletion depth. Once this is achieved, the pulse height distribution reflects a true picture of the ion energy distribution.

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\(^6\) Developed at GSI Darmstadt for use at The Svedberg Laboratory of Uppsala University, Sweden; http://rsp.eunitt.de/: Projects : Controlled Fabrication of Micro Channels : thumbnails


\(^8\) National Instruments http://www.ni.com
An overview of a pulse height recording of about 2400 single ion irradiations is shown in (Fig 14).

**Fig 14** Pulse height spectrum of single track irradiation system. Left: Each point corresponds to one single-ion irradiation. Right: Pulse height spectrum (log scale).

2.2. Controlled etching of single ion tracks

We use a conductometric cell (Fig 15) for ion track etching and replication. The current measurement is used to register the track break-through and follow the increasing track size until a preset value of the track diameter is reached. If calibrated by SEM observations, the etching can be interrupted at precisely the time required to obtain the preset etched channel diameter. The growth of ion track channels is controlled in real-time by electric current measurements. To minimize electrode polarization, a sinusoidal voltage of low amplitude is used. The phase shift between the applied voltage and the resulting current can be used to determine the capacitance and resistance of the system, consisting of the membrane which acts as a capacitance and the etched ion channel which acts as resistance. In this way, the membrane thickness as well as the channel diameter can be determined.
Fig 15  *Longitudinal section through conductometric cell*\(^9\) consisting of two cell halves between which the ion track membrane is inserted and compressed by a screw. Four filling/flushing tubes and two electrodes are shown. The cell is heated from the bottom and encased in an electrical shield. The whole assembly is enclosed by a thermal insulation (not shown).

### 2.1. Surfactant assisted etching of cylinders

Surfactants are elongated molecules with an asymmetry of the electric charge distribution along their axis. Usually one end of the molecule consists of a charged group and the other end of a neutral group. When immersed in water, the charged end attracts water dipoles, is hydrophilic, while the uncharged end is hydrophobic and is attracted by uncharged molecules, for example the surface of a polymer.

Surfactants are familiar etch additives in ion track technology since the very beginning. They are used to ensure a good contact between the etchant and the polymer during the initial stages of ion track etching, influence the etch properties, and are used to wet the finished products. Petzny and Quinn used surfactant molecules of well-defined length to reduce the etched track diameters in several steps, monolayer by monolayer [38].

When surfactants are applied during ion track etching, they associate their neutral end with the polymer and the charged end with the etchant. Since the

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surfactant occupies the surface, the surface will not be etched at the same speed as without the surfactant. As a general rule the addition of surfactants reduces the surface attack. However, the surface will still be etched at a reduced rate. This holds even during the first stages of track etching. The rate at which the etch medium penetrates into the ion track core is reduced. Break-through times are prolonged due to the reduced availability of etchant in the track core. The effect of the surfactant on the radial etch rate is shown in Fig 16.

![Surfactant assisted ion track etching](image)

**Fig 16**  *Surfactant assisted ion track etching.* Measurement of radial etch rate $V_r$ as a function of effective etch radius. Increasing the surfactant concentration decreases the surface attack.

The concept of surfactant assisted ion track etching is illustrated in Fig 17.

![Surfactant assisted ion track etching](image)

**Fig 17**  *Surfactant assisted ion track etching.* (From left to right) The penetration of the surfactant molecules into the etching zone is delayed by their size. Above a certain channel diameter they penetrate into the channel protecting the channel walls from further attack.

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10 Reprinted from NIM B, 265, n 1, Man, L.C.T; Apel, P.; Cheung, T.; Westerberg, L.; Yu, Peter K.N.; Zet, Cristian; Spohr, Reimar; Influence of a surfactant on single ion track etching. Preparing and manipulating individual cylindrical micro wires, p 621–625, Copyright 2007, with permission from Elsevier.

11 http://rsp.eunitt.de: Downloads : Ion track experiments for micro and nanofabrication
We have studied the effect of alkyldiphenyloxide disulfonate (Dowfax 2A1) on ion track etching in polycarbonate and demonstrated that it leads to nearly cylindrical tracks. [39]. Table 2 compares the conductometric diameter of track channels with the pore diameter determined after replication by SEM.

Table 2  *Comparing electro conduction with SEM observation.* Agreement of radii is better than 0.1 μm. [39]. Diameter ±0.1 μm. Length ± 3 μm.

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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calc.</td>
<td>SEM</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>9.8</td>
<td>5000</td>
<td>2.38</td>
<td>2.39</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>12.5</td>
<td>100</td>
<td>1.84</td>
<td>1.91</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>9.7</td>
<td>10</td>
<td>2.16</td>
<td>2.19</td>
</tr>
</tbody>
</table>

2.2. Electroreplication of nanochannels

For electro-replication, a transparent film of Au/Pd (thickness about 100 nm) is sputter-coated on one side of the membrane and its thickness increased by electrodeposition to a few micrometers to make it mechanically more stable. The membrane is inserted into a modified conductometric cell in which the right chamber is replaced by a block of copper serving as cathode. The left chamber is filled with an electrolyte containing the metal or semiconductor ions to be deposited. An example of an electroreplicated single-ion channel is shown in Fig 18. ¹²

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¹² Reprinted from NIM B, 265, n 1, Man, L.C.T; Apel, P.; Cheung, T.; Westerberg, L.; Yu, Peter K.N.; Zet, Cristian; Spohr, Reimar; Influence of a surfactant on single ion track etching. Preparing and manipulating individual cylindrical micro wires, p 621–625, Copyright 2007, with permission from Elsevier.
2.3. Data acquisition and display

The principle of the data acquisition system is shown in Fig 19. It consists of the computer, a data acquisition card containing one analog output and two analog input channels.

![Fig 19 Principle of data acquisition system.](image)

The computer controls the voltage which is applied to the conduction cell. The current output of the conduction cell is measured by a picoamperemeter. The voltage output of the picoamperemeter is digitized and read by the computer. The measurement is performed using a code based on the graphical programming language LabVIEW®.

As an example, the controlled etching of one single ion track is shown in Fig 20. From the real part of the current amplitude, essential ion track parameters can be determined. The average track etch rate can be determined from the break-through time. The etched track diameter corresponds to the conductivity. The bulk etch rate corresponds to the rate of conductivity change. The size of the track core and the size of the track halo can be determined from the rate at which the diameter changes.
Fig 20  *Etching of one single-ion track.*\(^\text{13}\) (a) Break-through followed by a quadratic increase of current with time. (b) Channel radius calculated from (a). (c) Radial etch rate calculated from (b). (d) Radial etch rate calculated from (b) and (c).\(^{[40]}\)

\(^{13}\) Reprinted from NIM B, 265, n 1, Leo C.T.; Apel, Pavel; Cheung, T.; Westerberg, Lars; Yu, Peter K.N.; Zet, Cristian; Spohr, Reimar; Influence of a surfactant on single ion track etching. Preparing and manipulating individual cylindrical micro wires, p 621–625, Copyright 2007, with permission from Elsevier.
3. Single-track applications (Paper II-VI)

3.1. Surface current in charged capillaries

The transport of ions in capillaries depends on the charge of the capillary wall. Neutral capillaries conduct ions of both polarities according to their specific mobility. The total current is proportional to the cross section of the capillary. This transport process is termed *volume conductivity*. However, if the capillary wall is electrically charged, a new conduction mechanism, *surface conductivity*, takes place. Charged groups, for example dangling carboxylic groups, can be formed on the etched channel wall by the etching process. They can dissociate into charged entities, according to

(Eq. 6) \[ R - COOH \rightarrow R - COO^- + H^+ , \]

whereby one entity, R-COO\(^-\), is firmly attached to the polymer wall and the other entity, H\(^+\), can dissociate from its counter-ion and diffuse or migrate under the influence of an applied electric field. While diffusing, it can be replaced by another positive ion, for example by Na\(^+\).

The influence of wall charges becomes important at low concentration of the electrolyte filling the channel and at small channel diameters. Negatively charged surfaces attract positive ions and repel negative ions. As a result a mobile counterion layer close to the surface is formed, compensating the surface charge. Within the counterion layer the ion concentration is locally increased, associated with an increased conductivity. The surface current depends on the charge density of the surface. With decreasing pore diameter, with decreasing concentration of the electrolyte filling the pore, and with increasing pH, the influence of surface conductivity becomes dominant. The corresponding processes are sketched in Fig 21, Fig 22, and Fig 23.

![Fig 21 Effect of pore size on surface conductivity of negatively charged track channels. With decreasing channel diameter the conducting surface layer consisting of counterions gradually fills out the whole volume of the channel. Correspondingly, surface conductivity becomes dominant at small channel diameters.](image-url)
Effect of $pH$ on conductivity of negatively charged track channels. [41-42] With increasing $pH$ the contribution of surface current increases. In the shown case, the counterions are firmly attached to the channel wall below $pH=3$ and fully dissociated above $pH=9$ where the surface current reaches an asymptotic value proportional to the charge density of the channel wall.

Fig 22  Effect of $pH$ on conductivity of negatively charged track channels. [41-42] With increasing $pH$ the contribution of surface current increases. In the shown case, the counterions are firmly attached to the channel wall below $pH=3$ and fully dissociated above $pH=9$ where the surface current reaches an asymptotic value proportional to the charge density of the channel wall.

Effect of concentration on conductivity of negatively charged track channels. [41-42] Upper curve (charged channel): With decreasing concentration, the current reaches an asymptotic value, reflecting the contribution of surface current. Lower curve (neutral channel): With decreasing concentration, the current decreases linearly, reflecting the dominance of volume conductivity.

Fig 23  Effect of concentration on conductivity of negatively charged track channels. [41-42] Upper curve (charged channel): With decreasing concentration, the current reaches an asymptotic value, reflecting the contribution of surface current. Lower curve (neutral channel): With decreasing concentration, the current decreases linearly, reflecting the dominance of volume conductivity.

3.2. Asymmetric pores as sensors

Ion track etching is governed by the selective removal of the latent ion track compared with the pristine material. Over short distances, the cone half-angle $\alpha$ depends on the track etch ratio, which is defined as the ratio of the track etch rate $v_t$ and the bulk etch rate $v_g$ according to
\[\alpha = \arcsin\left(\frac{v_g}{v_t}\right),\]

The cone half-angle \(\alpha\) can be increased either by increasing \(v_g\) or by decreasing \(v_t\). In polymers, \(v_g\) can be increased by adding organic solvents, e.g. methanol, the etching medium. On the other hand, the track etch rate \(v_t\) can be decreased by thermal annealing before etching is started. This, too, will increase the cone half angle \(\alpha\). Conical nanopores are obtained by etching a single ion track membrane from one side only and the asymmetry can be accentuated by retracting the etch-active OH\(^-\) ions from the etching tip [28].

One-sided ion track etching with an etching medium of low selectivity leads to conical pores. The selectivity of the etch medium will usually decrease with increasing temperature and increasing concentration of the etching medium. An example of a multi-porous membrane with conical pores is shown in Fig 24.\(^{14}\)

Conical pores provide the possibility of current rectification [28]. The effect depends on the pH of the used electrolyte. This opens the way to pH-sensing asymmetric pores and membranes. Furthermore, pH-sensitivity can be transformed into bio-specific sensitivity by coupling a proton-producing enzyme to the pore wall, whereby the enzyme senses the presence of its substrate.

An example would be glucose-oxidase attached to the pore wall. In a medium containing glucose, the glucose-oxidase would locally decrease the pH and change the current through the pore.

In contrast to a semiconducting diode, the current above a certain threshold increases roughly linear with voltage. In other words, switching corresponds roughly to two different effective channel diameters before and after switching (Fig 25).

\(^{14}\) [http://ion-tracks.de: Picture gallery: Track etching](http://ion-tracks.de)
3.3. Magnetic layers – Entry to spintronics

Electro-deposition is a common technique for selective deposition of metals according to their electro-negativity. A mixed electrolyte containing copper as well as cobalt ions deposits pure copper at low and an alloy of copper and cobalt at high deposition voltage. If the electrolyte contains a large fraction of cobalt, the resulting alloy contains a large fraction of the latter metal and is magnetic. Neighboring magnetic layers can have parallel or anti-parallel magnetic orientation. The orientation and electric resistance of the multilayer wire depends on the applied external magnetic field. The magnetic orientation of thin layers can be flipped by spin-polarized electrons from the neighborhood. This opens a door to spin-dependent devices [43-45].

The electrical resistance of ferromagnetic materials depends on the magnetic orientation of the material. The magnetic orientation can be influenced by external magnetic fields. The phenomenon called \textit{magnetoresistance} corresponds to the resistance change of an electric conductor when subject to an external magnetic field. In general, the conductivity increases with increasing order. Homogeneous magnetic materials such as iron, cobalt, and nickel show a resistance, which depends on the direction of the external magnetic field with respect to the direction of the electric current. This effect is called \textit{Anisotropic Magneto Resistance} (AMR). The effect is of the order of few percent.

Much larger magnetoresistivity can be obtained for layered magnetic materials. They consist of interlaced layers of magnetic and non-magnetic materials sufficiently separated from each other to weaken the coupling between neighboring magnetic layers to such a degree that an external magnetic field is able to influence the long-range magnetic order of the material.

Usually neighboring magnetic layers prefer an antiparallel orientation at zero magnetic field strength, $B=0$. The likelihood to orient randomly in-
creases with the nonmagnetic spacer thickness. The instability of this situation can be used to create so-called Giant Magneto-Resistance (GMR). [46-48] If such a multilayer – or superlattice – structure is subject to an external magnetic field parallel with the plane of the magnetic layer, its magnetic orientation will strongly be influenced by external magnetic fields. Accordingly, the electric resistance will depend on the external magnetic field. In contrast to AMR, which is only few percent, GMR can reach several ten percent.

The regular setup of GMR sensors is based on the planar geometry of thin magnetic films separated by a nonmagnetic spacer. The electric current is in the same plane as the thin films. However, few years after the discovery of the GMR effect, a different, quasi-one-dimensional geometry was introduced, where the electric current is perpendicular to the thin magnetic films [49]. It was studied in multilayered nanowires formed by electrodeposition into nanopores using a polymer membrane as template. Electrodeposition is performed in a mixed electrolyte consisting of a nonmagnetic as well as of a magnetic material, and the composition of the nanowires is modulated over distances of about 10 nm by varying the electrodeposition potential. Initially the multiporous membranes were filled with Cu/Co multilayers [49]. However, it became soon evident that single channel filling offers the advantage of higher resistance in a conveniently accessible resistance range [50].

We used single ion channels [32], [51-52] for the fabrication and study of GMR sensors, as well as the single contact technique [18] to contact exactly one wire from an ensemble of many wires growing at different speed [30-31], [33].

The single contact technique [18] stands logically between the single-track techniques described previously and the multi-track techniques described in the following chapters.
4. Introduction to multi-track applications  
(Paper VII)

4.1. Random textures with controlled porosity

Irradiations with wide ion beams lead to randomly distributed tracks, arriving at different times and locations, similar to raindrops. Every ion impinging on the surface leads to a latent ion track, which can be etched to a conical shape or to a cylinder, depending on the selectivity of the etching medium. Due to the overlapping of neighboring tracks in random track distributions, the resulting texture shows local fluctuations but for sufficiently large samples, precisely predictable global properties result. The most important global property is the effective porosity of the resulting texture. It can be determined from a simulation in which circular disks are punched-out at random from a surface of unit size. The resulting perforated surface has an effective porosity $P_{\text{eff}}$ [53] given by

\begin{equation}
P_{\text{eff}} = 1 - e^{-P},
\end{equation}

where the effective porosity, $P_{\text{eff}}$, is defined as the fraction of planar surface, removed by track etching. The nominal porosity, $P$, is defined by the equation $P = F \cdot A$, where the fluence $F$ is the number of impinging ions per cm$^2$ and $A = \pi r^2 / \sin(\alpha)$ is the area of the track cross section. The area $A$ depends on the track radius $r$ and the inclination angle $\alpha$. The track radius increases linearly in time according to $r = v_b \cdot t$, where $v_b$ is the bulk etch rate.

The wetted area fraction $f$ corresponds to the area of the flat tops and decays exponentially with the nominal porosity $P$:

\begin{equation}
f = e^{-P}.
\end{equation}

The fluence $F$ required for achieving a given fraction $f$ of wetted area at an etched radius $r$ is:

\begin{equation}
F = \frac{P}{A} = -\frac{\ln(f)}{\pi \cdot r^2}.
\end{equation}

This equation can be used to determine the requested ion fluence when aiming at a texture with prescribed size scale given by $r$. 

35
4.2. Simulation of 3D random texture

For demonstrating the formation of a texture consisting of flat tops surrounded by steep valleys, a computer simulation was performed assuming vertical irradiation. Etched tracks were randomly distributed and represented by white circular disks on a dark background. In this way, a 2D random distribution of circular etched tracks was simulated. Translating darkness to height using the program ImageJ [71] yields a 3D image closely resembling the experimental texture for vertically incident ions (Fig 26).

![3D simulation of ion track texture assuming an incidence angle $\alpha = 90^\circ$. The porosity increases from top left to bottom right: $P = 0.11, 1.4, 2.3, 3.4$ corresponding to $P_{\text{eff}} = 0.10, 0.75, 0.90, 0.97$. With increasing porosity the area of the flat tops decreases.](image-url)
4.3. Ion beam lithography

Microtechnology is based on lithographic techniques using visible light, ultraviolet radiation, electrons and low energy ions. In connection with masks, swift heavy ions can be applied as a deep cutting tool with the possibility to cut materials at an angle different from 90°. The possibility of cutting at an angle is a unique property of ion track technology. Due to the high energy density deposited in ion tracks, even radiation resistant materials such as quartz can be cut. This, too, is a unique feature of ion track technology. A necessary condition for this oblique cutting ion lithography is to reach sufficient effective porosity \( P_{\text{eff}} \approx 1 \) to remove most of the material. An example is shown in Fig 27.

![Ion lithogram of quartz crystal](image)

Fig 27  Ion lithogram of quartz crystal irradiated at 90° with \(^{129}\text{Xe}\) of 11.4 MeV/nucleon at a fluence of 2.6x10\(^9\) ions per cm\(^2\). [54]

The depth definition of ion lithography is influenced by range straggling and by the effective porosity \( P_{\text{eff}} \). For heavy ions in targets of low atomic number (such as polymers) range straggling is of the order of a few percent. A simulation of the effective porosity \( P_{\text{eff}} \) as function of depth is shown in Fig 28. Three stages can be discerned. The originally flat surface (a) is textured during etching (b) until the tracks are completely etched and the overlapping spherical sections yield increasingly smooth final surfaces (c). [34]
Ion lithography offers a new way to impose a tilted etch anisotropy on amorphous as well as on single crystalline materials, as is demonstrated for single crystalline quartz, chosen due to its significance in microsystem technology. In this way, the technique enables to fabricate inclined structures [54] (Fig 29).

![Fig 28 Depth definition in ion lithography assuming an ion fluence $F = 10^6$ cm$^{-2}$, a bulk etch rate $v_b$ of 1 μm/min, a track etch rate $v_t$ of 5 μm/min, and an ion range of 50 μm.]

![Fig 29 Tilted ion lithogram of quartz crystal irradiated at 45° with $^{129}$Xe of 11.4 MeV/nucleon at a fluence of 2.6x10$^9$ ions per cm$^2$. [54]]
5. Tilted Superhydrophobic Texture (Paper VII)

5.1. Lotus effect stimulates innovation

Biomimetic materials are a source of inspiration resulting in new technology [55-57]. One example is the lotus effect [58], associated with the water repellent “self cleaning” property of a lotus leaf. Water drops roll easily over lotus leaves and, while rolling, collect and remove smaller particles. As a result, lotus leaves emerge astonishingly clean even from muddy water. A detailed analysis reveals that the surface of the leaf consists of microscopic hills covered with nanoparticles of water repellent wax crystals (Fig 30).

![Fig 30 SEM of lotus leaf with regular pattern of microhills (left) covered with water-repellent nanowhiskers (right).](image)

The lotus effect is based on the reduction of contact area between water and solid by a water repellent microstructure. In the superhydrophobic state, water drops are supported by the protruding tips of the microstructure. The lotus effect induced new industrial products such as paints, impregnations of textiles, and water repellent windshields [59]. It stimulated a wealth of new research systematized on the basis of the equations of Young [60], Wenzel [61], and Cassie and Baxter [62] and the theoretical treatment of the phenomenon is still in discussion [63]. For quantitative prediction of contact angles a thermodynamic treatment has been proposed, taking into account the kinetics of dewetting [64]. For describing superhydrophobicity the term roughness was introduced. Roughness is the ratio of the actual surface area over the apparent area of the substrate. Roughness is always larger than 1. Cassie and Baxter introduced the term wetted area fraction $f$, with $0 < f < 1$. It is applicable to the superhydrophobic state in which only the protruding
tips are in contact with water. There are a number of studies based on the concept of wetted area fraction $f$ using regular patterns. [59], [65-66].

Recently random patterns of etched ion tracks were rendered superhydrophobic. [67-68]. The patterns consisted of vertical ion track textures at a fluence of $5 \times 10^9$ with aspect ratios between 0.5 and about 15. The surfaces were rendered superhydrophobic by grafted perfluoroctyltrichlorosilane, CF$_3$(CF$_2$)$_7$SiCl$_3$.

In contrast to these previous studies [67-68] using 100 times higher fluence and vertical ion incidence, we used inclined ion track textures at a fluence of $5 \times 10^7$ cm$^{-2}$. Instead of the term fractal dimension we introduce the term wetted area fraction $f$, defined in ion track technology as the flat area remaining on top after track etching, and its complement, the term effective porosity, $P_{\text{eff}} = 1 - f$, with $0 < P_{\text{eff}} < 1$, corresponding to the fraction of the originally flat surface which has been removed by track etching. Inclined textures lead to anisotropic surface properties. This possibility has been studied on biological samples [69] but not yet been applied to super hydrophobic surfaces. Such an oblique texture can translate vibration into motion.

5.2. Contact angle expected from theory

The equation of Young [60] is derived assuming that under equilibrium conditions the horizontal forces per unit length of the contact line are balanced (Fig 31), (Eq. 11):

$$F_{sl} + F_{i} \cdot \cos \theta = F_{s}.$$  

Fig 31  Force equilibrium at contact line of water drop on hydrophobic surface. According to Young [60], the horizontal forces per unit length of the contact line (small circle) are balanced under equilibrium conditions.

Multiplying by unit length yields the equilibrium of surface energies:

(Eq. 12) \hspace{10pt} \gamma_{sl} + \gamma_{i} \cdot \cos \theta = \gamma_{s} \hspace{10pt} \text{or} \hspace{10pt} \gamma_{i} \cdot \cos \theta = \frac{\gamma_{s} - \gamma_{sl}}{\gamma_{i}}.$$

(Eq. 13)
Starting from here, Cassie-Baxter [62] derived the following equation, assuming for superhydrophobic surfaces a reduction of the solid-liquid surface by a factor \( f \):

\[
\cos \theta_{CB} = f (1 + \cos \theta_Y) - 1.
\]

(Eq. 14) 

The contact angle expected from the Cassie-Baxter equation (Eq. 14) contains the constant \( \cos \theta_Y \) of Young’s law (Eq. 13) from which it is derived. Inserting our experimental advancing contact angle \( \theta_a \) for a flat surface, \( \theta_a = 97^\circ \), it is possible to plot the expected contact angle, \( \theta_{CB} \), as function of the effective porosity, \( P_{\text{eff}} \) (Fig 32). The expected contact angle has a vertical tangent at \( P_{\text{eff}} = 1 \). Since the pin density approaches zero for \( P_{\text{eff}} \to 1 \), one cannot expect the Cassie-Baxter model to work in the vicinity of \( P_{\text{eff}} = 1 \).

![Fig 32](image)

**Fig 32 Expected contact angle from Cassie-Baxter equation (Eq. 14) assuming that the punching-out of a certain surface area is responsible for a proportional reduction of surface energy. At \( P_{\text{eff}} = 0 \) the curve has been fitted to the experimentally determined contact angle for a flat surface, \( \theta_Y = 97^\circ \).**

5.3. Preparing samples with deep crevices

We use the optically transparent recording side of normal CD and DVD disks as ion track sensitive polymer. They consist of polycarbonate [70], which, due to its good optical properties (corresponding to high homogeneity down to the molecular scale), is ideally suited as an ion track sensitive material. We therefore suggest using CDs and DVDs a standard material for future ion track studies. This material could become a convenient alternative to CR39 (allyl diglycol carbonate), a fully cross-linked polymer widely used for eyewear and lenses.

The samples were irradiated with \( 5 \times 10^7 \) Br\(^{7+} \) ions per cm\(^2 \) at the Tandem Accelerator of the Ångström Laboratory at Uppsala University. The irradiated samples were etched in 5 M aqueous NaOH solution using traces of 0.1% of the surfactant alkylidiphenyloxide disulfonate (Dowfax 2A1). [39]

The etch time was varied in steps between 0 and 60 min. After etching, the material was flushed with distilled water and cleaned in an ultrasonic bath.
The samples were left to dry in a horizontal position after removing excess water from the surface with cleanroom tissue. The surface morphology was observed in a high resolution SEM at the Micro Structure Laboratory MSL (Ångström Laboratory, Uppsala University) (Fig 33, Fig 34). These samples were irradiated at The Svedberg Laboratory or Uppsala University with $(1.2\pm0.4)\cdot10^7 \cdot 10^7 \cdot 129 \cdot Xe^{27+}$ ions/cm$^2$ of 8.3 MeV/nucleon at an angle of 45°.

The textured samples were plasma treated in an inductively coupled plasma reactor (ICP PlasmaTherm SLR 1401) at the MSL (Micro Structure Laboratory, Ångström Laboratory, Uppsala University). Process parameters were: 10 mbar of $C_4F_8$ gas, 500 W power, 5 min processing time. In the plasma, the $C_4F_8$ (octafluorocyclobutane) molecules disintegrate into four fragments of $CF_2$. These radicals diffuse to the surface of the textured material where they bind chemically. A PTFE-like film of molecular thickness is formed making the sample water repellent.

Fig 33  *Tilted ion track texture* with inclination angle $\alpha = 45^0$ and effective porosity $P_{eff} \approx 0.7$. At this porosity a distribution of irregularly shaped flat tops becomes prevalent. In the superhydrophobic state, the flat tops are responsible for carrying the water drops.

Fig 34  *Tilted ion track texture* with inclination angle $\alpha = 45^0$ and effective porosity $P_{eff} > 0.95$. The distance between the flat tops has considerably increased.
5.4. Characterizing top plane flatness

The flatness of the samples after 10 min etching was characterized by AFM profilometry (AU04 PSIA XE150, http://parkafm.com/) along the horizontal lines of Fig 35. Sample flatness is better than 5 nm in the planar top area of the sample. When scanning over the sharp edges of the etched track holes, the measured profile is distorted due to the finite tip radius and aspect ratio. Depending on the scan direction the AFM tip shows an overshoot when leaving the etched pore. The entry of the AFM tip provides a correct signal of the edge. The measured profiles of the etched pores reflect the tip profile and not the profile of the etched pores which are about 180 times deeper.

Fig 35  *Atomic Force Micrograph* (AFM) of sample 2 in Table 2. Sample area 10 x 10 μm. Profile scans were taken along the black horizontal lines (Fig 36).

Fig 36  *AFM profilometry* along the two horizontal lines of Fig 35. (Top): The flat area has a roughness smaller than 5 nm. (Bottom): The etched pore profile reflects the AFM tip profile and shows an overshoot.
5.5. Contact angle measurements

*Used methods*

**Sessile drop method:** The drops were inflated until they reached approximately spherical shape with a diameter of 2.0 to 2.3 mm. After completing growth, they were observed, still in the advancing phase. Right and left advancing contact angles were averaged for about 10 different drops and the results plotted in Fig 39.

**Pulled drop method:** Drops of 1.1 - 1.5 mm diameter were extruded from a syringe of 0.4 mm diameter and pulled over the surface with the syringe. The movement was performed in stroke direction and against stroke direction (defined in Fig 42). For both directions, both, the advancing and the receding contact angle were measured.

![Figure 37: Geometry of contact angle measurement.](image)

**Fig 37** *Geometry of contact angle measurement.* For contact angles $\theta \rightarrow 180^\circ$ the observation angle $\beta \rightarrow 0$. Correspondingly the observation error increases with a vertical tangent at $\theta \rightarrow 180^\circ$ (Fig 40, Fig 41).

To determine the contact angle of water, we used a setup illustrated in Fig 37 and deposited water drops from a capillary of 0.40 mm diameter onto the textured surface. For determining the contact angles we used the program ImageJ [71] with the plug-in DropSnake [72] (Fig 38 right).

![Figure 38: Contact angle measurement.](image)

**Fig 38** *Contact angle measurement.* Left: large drop on superhydrophobic surface. Right: Determination of contact angle using program DropSnake [72].
The contact angle of 12 samples with identical fluence of $5 \cdot 10^7$ ions per cm$^2$ but different porosities (obtained by different etch times) was determined with sessile expanding drops and plotted in Fig 39.

**Fig 39**  *Advancing contact angle, measured by sessile drop method*, as a function of effective porosity $P_{\text{eff}}$. The surface becomes superhydrophobic at $P_{\text{eff}} \approx 0.7$.

**Measurement error**

The observation of contact angles becomes increasingly difficult when the contact angle approaches $180^\circ$. For small drops this means that it becomes impossible to see the contact line if the observation angle is close to zero. For a drop of 1 mm diameter, a misplacement of the reference baseline by 40 μm induces a shift of the contact angle by $17^\circ$ (Fig 40, Fig 41).

**Fig 40**  *Influence of reference baseline shift on contact angle*. For spherical drops, a shift of the reference baseline by $x$ reduces the contact angle $\theta$ by $\delta = \arccos(1-x/r)$. 


5.6. Directed transport by tilted textures

Our experiment shows four different angles, depending on the stroke direction and on the movement direction of the contact line away from or toward the drop (advancing or receding) (Fig 43). Since $\alpha < \beta$ the retaining force $F_\alpha > F_\beta$. Similarly, since $\gamma < \delta$ the retaining force $F_\gamma > F_\delta$. One can therefore expect that drop movement with the stroke direction is easier than against the stroke direction. Correspondingly the “self cleaning” property should be enhanced in stroke direction, similar to scales on a human hair (Fig 44), which provide it with a “self cleaning” property.

Fig 41 Influence of shift of reference baseline on contact angle. For a spherical drop of $r = 0.5$ mm diameter, a misplacement $x$ of the reference baseline by 40 $\mu$m reduces the contact angle from $180^\circ$ to $163^\circ$.

Fig 42 Definition of stroke direction of tilted ion track texture

Fig 43 Drop motion on tilted texture. Our experiment shows a significant difference of the contact angle with and against the stroke direction. We found $\alpha < \beta < \gamma < \delta$, indicating retaining forces $F_\alpha > F_\beta > F_\gamma > F_\delta$. Top: Water drop moving left, i.e. in stroke direction. Bottom: Water drop moving right, i.e. against stroke direction.
5.7. Mimicking nature – Our approach

Due to the high energy density, deposited in the core of an ion track, already one single ion track can be developed – in contrast to so-called “disperse” radiations, such as photons or electrons, where only the combination of many particles renders a material developable. Due to the high linearity of the ion track it prescribes a preferential direction or anisotropy in the irradiated solid. This feature can be used to generate tilted structures.

Human hair has a scale structure pointing from root to tip. Accordingly it has a “self cleaning” surface which moves dust preferentially away from the body. The fur of mules does neither get dirty nor wet. Mimicking this feature can be interesting for technological applications.

When setting a water drop on the tilted obstacle of Fig 45, the angle $\alpha$ on the steep side is larger than the angle $\beta$ on the flat side of the obstacle. Accordingly the curvature and thus the surface energy of the respective surface elements will be larger on the left side than on the right side. Under static conditions, the forces $F_1$ and $F_2$ will cancel each other. However, if the drop is moved, the asymmetry of the curvature is translated into an asymmetry of forces (Fig 45). The steep side will experience a stronger force than the shallow side. At the same time, the shallow side will be wetted easier than the steep side. A receding contact line will thus encounter a stronger force when moving from left to right than in the opposite direction.

![Fig 44 Scale structure of human hair](image)

Fig 44 Scale structure of human hair (63µm diam.). The stroke direction of hair scales points away from the body. The combined action of neighboring hair strands leads to a preferential transport of particles away from the body.

![Fig 45 Translating stroke into force asymmetry](image)

Fig 45 Translating stroke into force asymmetry. Grainy gray: water. Dark gray: hydrophobic pin. The asymmetry of the angles leads to an asymmetry of the forces which can be ordered according to $\alpha > \beta \rightarrow F_1 > F_2$.
The legs of a water strider (Fig 46)\textsuperscript{15} are covered with a super hydrophobic structure of feathered, water repellent hairs (setae). When pushing itself forward, asymmetric dimples are formed in the water surface, similar to Fig 45 but upside-down. To support this analogy, we performed a qualitative experiment translating fluid vibration into motion. A super hydrophobic disk was floated with its superhydrophobic side pointing downward to the water surface of an ultrasonic bath causing it to rotate.\textsuperscript{16} The demonstration is based on an irradiation with $(1.2 \pm 0.4) \cdot 10^7 \ ^{129}\text{Xe}^{27+}$ ions/cm$^2$ of 8.3 MeV/nucleon at an angle of 45°. The disk was etched in 5 M NaOH at 66º C for 300 min and coated with a water repellent layer of CF$_2$ radicals. The rotation stopped after few minutes due to wetting of the structure.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{water_strider.png}
\caption{Photo of water strider\textsuperscript{14} using for its propulsion the dynamic asymmetry of the dimples formed at the tip of its legs. [55].}
\end{figure}

For demonstrating that our structure is comparable to a biogenic structure, we have placed water drops of similar size on top of a lotus leaf and on top of a super hydrophobic ion track texture and viewed them with a CCD microscope [73] (Fig 47) and with a stereomicroscope (Fig 48).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{water_drops.png}
\caption{Top view of water drops on lotus leaf (left) and on tilted super hydrophobic ion track texture (right).}
\end{figure}

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\textsuperscript{16} http://movie1a.eunitt.de (PC) or http://movie1b.eunitt.de (Mac).
Fig 48  *Side-view of water drops* on lotus leaf (left) and on artificial ion track texture (right).
6. Conclusions and Outlook

Heavy ion accelerators paved the way to a widespread use of ion tracks as a precision tool. By now, the technique is capable to generate individual micro- and nanochannels with an unprecedented aspect ratio up to $10^4$ and arbitrary tilt angle.

The high local concentration of energy deposited by swift heavy ions in solids opens a new route to nanotechnology. [34] In contrast to other techniques, each ion “carries along its own mask”. In other words, it induces a structure without any further requirement, such as a mask. Using individual ions, structures down to the nanoscopic scale can be fabricated. Since their aspect ratio can be very high, they may act as quasi one-dimensional objects as soon as the wavelength of an interacting particle, such as a photon, electron or phonon, becomes comparable to their diameter.

Etched ion track channels can be shaped into conical pores with asymmetric current-voltage characteristic, similar to electrical diodes. [28] The electrical resistance can tell about the pH of the electrolyte filling the pores. Enzymes can be attached to the pore wall for translating the concentration of a specific substrate molecule into an electrical signal. The pores can be rendered biospecific by attaching proteins and DNA. [74]

On the basis of single-track studies it became possible to control the diameter of etched channels with high precision. We have shown here, that the techniques developed to control single-track etching and replication can be transferred to random multi-track systems entering a new era of mask-less patterning of biomimetic materials and textures. The techniques can also be applied to scanned single-ion microbeams [75-76] enabling regular pattern of individual ion tracks.

We have documented a new approach for the creation of cylindrical channels using self-assembling surfactant monolayers for protection of exposed surfaces with exception of the actively etching track tip, which, due to its small size, is inaccessible for the surfactant molecules. [39] This concept can lead to unexpected new shapes in the future.

Using single ion channels we were able to fabricate magnetic multilayers with stable electrical contacts [32], [51-52], which is very important for the development of durable devices. This technique can be applied to spin-valve structures.

Until now, new studies, using etched tracks as templates, focused mainly on nanowires. However, since the conductance of channels increases as the square of their diameter, using wide cylindrical channels can be advantageous. Using wide channels may increase our chances to create high quality superlattices consisting of well-defined monolayers in etched track channels.
Such superlattices in large cylindrical geometries could be grown – and eroded – at will in “slow motion” under full electrical control. In this way the gap between electrodeposition and epitaxial deposition could be decreased.

Biological evolution depends on the breaking of symmetries for realizing new functions. Ion track etching offers a new way to break symmetry by inclined textures with morphologies similar to scales, feathers, or fur. In the future it may be possible to induce a directed transport of small particles on tilted textures by vibration. We have fabricated a tilted texture, based on ion tracks, rendered it superhydrophobic and demonstrated the possibility of active transport. In the future an “inverted” technique based on replication (Fig 49)\(^{17}\) can be even better because it may enable mass production.

As a first step toward replication we suggest to increase the cone angle of the etched tracks. This can be done by decreasing the deposited energy density of the ions used for irradiation. Furthermore, it will be advantageous to coat the surface of the template with an anti-sticking agent, to release the mold more easily.

Once this technique is established, one could, for example, mimic the setae of geckos, microscopic fine hair attaching to objects via Van der Waals forces, and explore the sticking coefficient of the resulting hairy structures on flat surfaces.

Finally, we found that CDs and DVDs, now quasi household items, are ideally suited for fabricating surface textures based on etched ion tracks. CDs and DVDs are made of polycarbonate [70], which, due to its high homogeneity down to the molecular scale, is ideally suited as an ion track sensitive material. We therefore suggest using CDs and DVDs as easily accessible material for future ion track studies. This material could become a convenient alternative to the widely used CR39 (allyl diglycol carbonate, a fully cross-linked polymer used for eyewear and lenses).

\(^{17}\) Johann Vetter (GSI), http://ion-tracks.de : Picture gallery : Track replicas

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7. Svensk sammanfattning


Avhandlingen handlar om konsten att framställa enstaka jonspår och användningen av enstaka såväl som ett stort antal jonspår i ett material. 


Om man nu vill använda jonspårstekniken som verktyg i mikro- och nanoteknologi, måste man kunna behärska framställning av nästan identiska cylindriska nanokanaler. Här hjälper ett litet trick också. Såpbubblor består av självorganiserade monolager av tensidmolekyler som bygger en stabil vägg som förhindrar diffusion mellan båda sidor av väggen. Tensider är långa molekyler med en vattenälskande (hydrofil) och en vattenavstötande (hydrofob) ände. De är mycket större än joner av etsmedlet (Na⁺ och OH⁻). I etsbadet formerar sig ett spärrande mellanlager av tensidmolekyler mellan

Modern mikroteknologi beror på strålningskänslig film som man strukturerar med hjälp av ljus, ultraviolett strålning, elektroner, eller röntgenstrålning. Som strukturgivande elementet används en mask. Jonspårstekniken kan användas som djupskärande metod för mikromekaniska system. För det behöver man till exempel hundratusen jonspår per kvadratmillimeter, vilket man vid jonspårserjämsenhet kan nå inom bräkviden av en sekund. Förde-


8. Acknowledgements

Special thanks to my supervisor Lars Westerberg, who generated and catalyzed many of the ideas presented here and who has been my close partner and tutor throughout this work.

I would like to thank my assistant supervisor Björgvin Hjörvarsson for providing the platform for this work in the environment of a cooperative group. He and his group have contributed in many subtle ways to my well-being. Thanks to all members of this group.

I keep in my memory late Christoph Schmelzer who has set me literally on the track.

Thanks to Hans Siegbahn who supported this continuation to a doctoral degree after I obtained a filosofie licentiat degree under the supervision of late Kai Siegbahn.

This interdisciplinary work would not have been possible without the input from many people working in different fields. I am particularly grateful for discussions, valuable hints, new insights, and support from the following persons:

Adrian Rennie (Uppsala), Andrea Taroni (Uppsala), Bernd Eberhard Fischer (GSI), Can Quan (Beijing), Christina Trautmann (GSI), Cristian Zet (Iasi), Dobri Dobrev (Sofia), Filip Heijkenskjöld (Uppsala), Gunjana Sharma (Uppsala), Günther A. Wagner (Heidelberg), Göran Rämme (Uppsala), Helge Kiesewetter (GSI), Igor Gunko (Darmstadt), Ionut Enculescu (Bucharest), Johann Vetter (GSI), Kai Kolari (Helsinki), Karl-Ontjes Groeneveld (Frankfurt), Norbert Angert (GSI), P. Buford Price (Berkeley), Pavel Apel (Dubna), Peter Armbruster (GSI), Philipp Blaszczyk (Darmstadt), Reinhard Neumann (GSI), Roland Pettersson (Uppsala), William Thielicke (Hamburg), Volker Ziemann (Uppsala), Yuri Korchev (London), and Zuzanna Siwy (Irvine).

Special thanks to the accelerator teams at The Svedberg Laboratory (Uppsala), at the Tandem Accelerator (Uppsala), and at GSI (Darmstadt) for all support during the setup and irradiations.

I would like to thank the crew at the Micro Structure Laboratory (Uppsala) for their support when working with advanced equipment.

Thanks to Mats Block (Botanical Garden, Uppsala University) who has provided us with a lotus leaf.

Elisabeth and Sone Kjellström (Uppsala) have provided me with the opportunity of many stimulating interdisciplinary encounters at their house.

Klas Hjort (Materials Science, Ångström Laboratory of Uppsala University) has given the incentive to build a tape roller at GSI Darmstadt in the
framework of the European Research Training Network No HPRN-CT-2000-00047.

I would like to thank the engineers at GSI Darmstadt for their support during construction, building and test of the tape roller as well as the conductometric cell.

This work was supported by a guest professorship grant from the Wenner Gren Foundation (Sweden) and by Ångpanneföreningens forskningsstiftelse, Grant Nr. 08-197 (Sweden).
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Acta Universitatis Upsaliensis

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