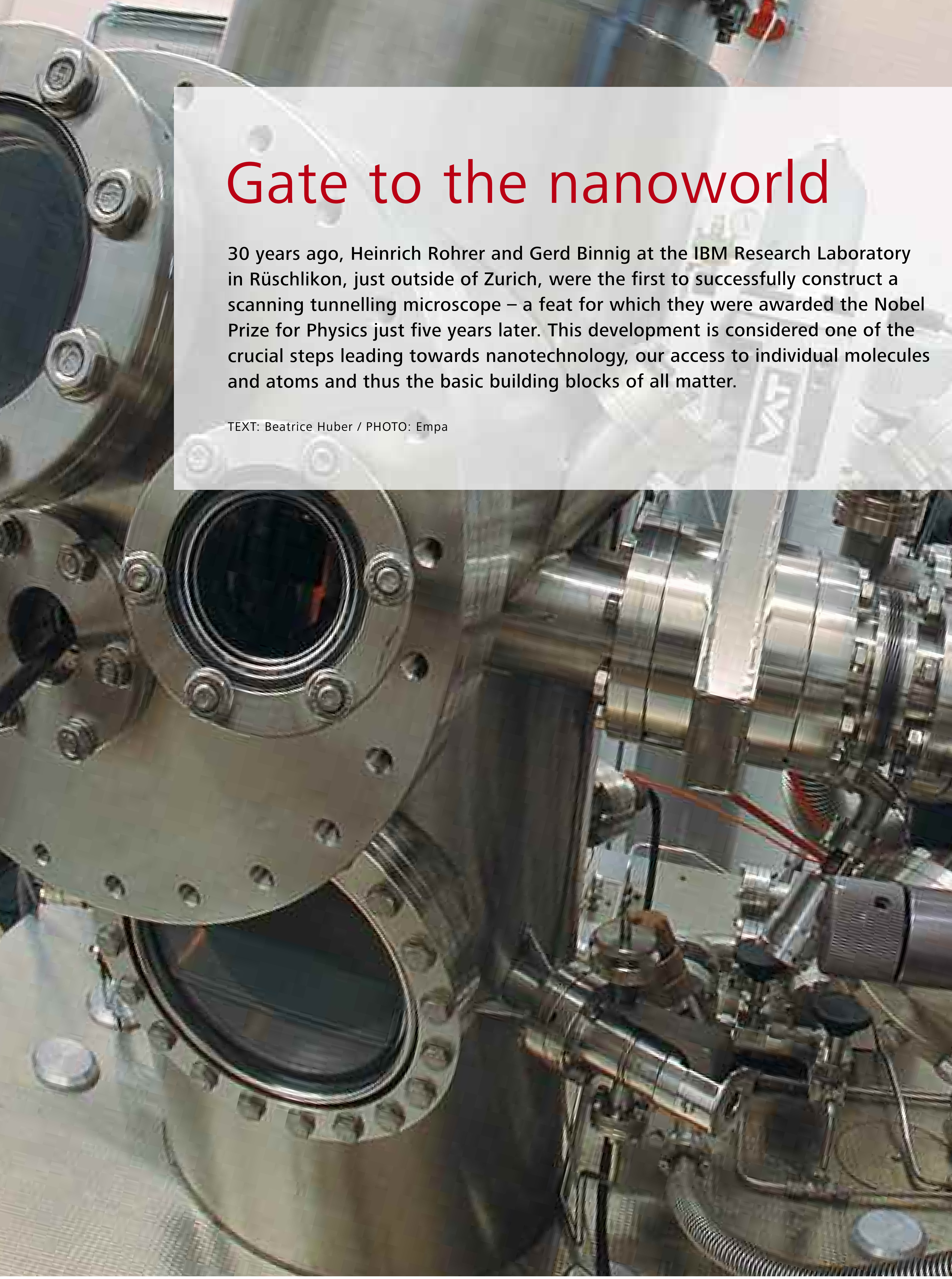
Gate to the nanoworld

30 years ago, Heinrich Rohrer and Gerd Binnig at the IBM Research Laboratory in Rüschlikon, just outside of Zurich, were the first to successfully construct a scanning tunnelling microscope – a feat for which they were awarded the Nobel Prize for Physics just five years later. This development is considered one of the crucial steps leading towards nanotechnology, our access to individual molecules and atoms and thus the basic building blocks of all matter.

TEXT: Beatrice Huber / PHOTO: Empa



This year, the scanning tunnelling microscope – the photo shows one set up at the Empa site in Thun – is celebrating its 30th birthday.

Nanotechnology as we know it today would not even exist without the instruments that allow us to peer into the world of the infinitesimal so we can analyse and manipulate it. Scientists at Empa use equipment such as electron microscopes, scanning tunnelling microscopes and atomic force microscopes for their research, and are also expanding the areas in which these tools can be used, as the articles on the following pages illustrate. This year, the scanning tunnelling microscope is celebrating its 30th birthday. In 1981, Heinrich Rohrer and Gerd Binnig at the IBM Research Laboratory in Rüschlikon developed the first instrument of this type which had the necessary precision and stability. Just a few years later in 1986, their work was honoured with the Nobel Prize in Physics.

A microscope which scans the surface

The scanning tunnelling microscope isn't a "real" microscope because it doesn't generate a direct optical image of the object being examined. Instead, the instrument examines the profile of a surface with a scanning tip whereby there's always a tiny distance between the tip and the surface. This prevents anything from being damaged during the scanning process. For its measurements, the microscope uses what is known as the quantum tunnelling effect. This quantum-mechanical effect, which gives the microscope its name, allows an electron (or some other particle) to drill a tunnel through a potential barrier which, according to classical physics, would be impenetrable. This movement of electrons creates a measurable current despite the fact that the scanning tip and the surface don't make contact. Flash memories, such as the chips in USB sticks, are also based on the tunnelling effect.

In 1986, Rohrer and Binnig shared the Nobel Prize in Physics with the German electrical engineer Ernst Ruska, who had already developed the electron microscope in the 1930s. Instead of normal light, that instrument uses an electron beam and with it achieves considerably higher resolution. Traditional optical microscopes have a resolution of approximately 200 nanometres, whereas these days electron microscopes have increased this to approximately 0.1 nanometre. Just like scanning tunnelling microscopes, electron microscopes have also long since become indispensable tools in nanotechnology. //

Research Programme set into motion

What opportunities do nanomaterials offer, and which risks do they entail? The National Research Programme NRP 64 intends to fill in existing gaps in knowledge and in this way contribute to the long-term success of nanomaterials. Empa is participating in four of the 17 sponsored projects.

TEXT: Beatrice Huber

Information technology, electronics, construction materials, environmental technology, energy technology, household appliances, textiles, cosmetics, foodstuffs, medicine – there's practically no limit to where nanomaterials can be put to use. Around the world there are already more than a thousand products on the market which contain nanomaterials. In the area of nanosciences, Swiss research institutes, including Empa, are among the world leaders. Nanomaterials offer enormous opportunities for Switzerland as a location for research and industrial applications. Their economic success, however, can only be long-term if possible risks can also be evaluated in a reliable manner.

Exploring opportunities and risks

The projects which are part of the recently initiated National Research Programme "Opportunities and Risks of Nanomaterials" (NRP 64) should therefore not only explore the opportunities which nanomaterials offer towards improving our health, environment and use of natural resources but also possible risks. Within an NRP, researchers from various disciplines collaborate on projects which are intended to contribute to the solutions of key present-day problems. The Swiss Federal Council sets the focus; the NRPs are carried out by the Swiss National Science Foundation (SNSF).

NRP 64 places its focus on synthetically manufactured nanomaterials. A "nanomaterial" is considered one which has structural components with at least one dimension of less than 100 nanometres. In this programme, especially those materials will be examined where there is a high probability of human or environmental exposure. One of the goals of NRP 64 is also to create the basis for developing tools to monitor and evaluate the effects of nanomaterials on people and the environment.

At the end of November 2010, the SNSF approved 17 project proposals from the 44 which were submitted, and is financing them for the first three years with CHF 6.3 million. Empa researchers are heading up three of these projects and are participating in yet another. //

Is nano sustainable in the long run?

In order to master challenges such as climate change or shortages of natural resources, we need long-term solutions. Nanotechnologies and nanomaterials can provide new approaches. The Swiss Academy of Engineering Sciences (SATW), along with leading Swiss nano experts such as Pierangelo Gröning, a member of Empa's Board of Directors, has published a brochure addressing long-term sustainability and nanotechnology. It also calls for a public discussion about the associated opportunities and risks. That's because nanotechnologies will enjoy success over the long term and make a contribution to sustainable development only if they do not entail any major risks. This brochure (in German) can be downloaded in PDF format at *www.satw.ch/nano*.

Empa as junior partner at the new IBM nanocentre

In May 2011, the new Centre for Nanotechnology will be opened on the grounds of the IBM Research Laboratory in Rüschlikon, in other words in the very location where the scanning tunnelling microscope was developed 30 years ago. The centre, which cost roughly CHF 90 million and will be operated jointly by IBM and ETH Zurich, is a further milestone for Switzerland as a key location for nanotechnology. Empa will also conduct research there as a junior partner.

Overall, it provides a 1000 square metre cleanroom along with six "noise-free" laboratories. These were constructed eight metres below ground level on a massive foundation and are completely shielded from external influences. This is necessary because work at the nanometre scale must be done very precisely, and even the smallest fluctuations in temperature as well as any noise, vibrations or electronic fields can be disruptive.

How nanotechnologies will impact our future

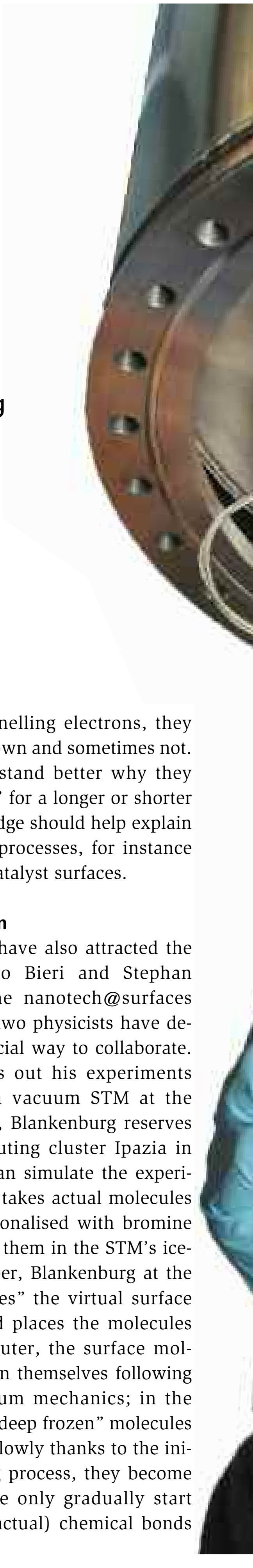
In order to develop innovative technologies efficiently, as well as to finance and regulate them, sound decisions must be taken which are based on the latest knowledge and findings. This is also the case with nanotechnology. The Swiss NanoConvention 2011 supports decision-makers in this role. It offers a platform where leaders from research and industry, key figures in innovation and technology, entrepreneurs, investors as well as administrators and politicians can gather to discuss ideas and exchange viewpoints – or even develop new ones. The participants will receive in-depth information about one of the most important emerging technologies of the 21st century and its potential for innovative approaches, products and services. In parallel to the Swiss NanoConvention, the NanoPubli event is inviting the general public to become informed about the world of the extremely small, first-hand at an exhibition and during lectures.

The central topics of the event are the major challenges of our time such as securing a sustainable energy supply and a clean environment along with the future of medicine with nano-therapeutics and diagnostics plus the development of innovative functional materials and their numerous industrial applications. Another focus will be the potential risks associated with free nanoparticles along with how society sees and addresses these issues.

swiss
nano
convention

In short, the Swiss NanoConvention is the showplace for nanotechnology in Switzerland. Because it is being organised jointly by the "who's who" of the Swiss nano community, it's the ideal place to get to know the leading minds and foremost proponents of nanotechnology.

Further information, including the programme and registration, is available at *www.swissnanoconvention.ch*



Happy Birthday!

Thirty years after the first successful experiments, it's hard to imagine industry and research without the scanning tunnelling microscope (STM). This and its further development, the atomic force microscope (AFM), not only display individual atoms but can also manipulate them. And if that's not enough, by combining these with other measurement methods, we'll soon be able to draw three-dimensional "chemical maps" which show how materials are built up, nanometre by nanometre.

TEXT: Martina Peter / PHOTOS: Empa

When it comes to small dimensions, we're "blind" – the resolution of the human eye is only 0.2 millimetre. In other words, people can only distinguish between two points if they're separated by a distance of at least 0.2 millimetre. For anything smaller we need visual aids – magnifying glasses and microscopes.

Optical microscopes can see approximately 1000 times "better" than the human eye and thus have a resolution of roughly 0.2 micrometre. But because the diameter of an individual atom is approximately 0.2 nanometre, that's not sufficient. What are the options when we can no longer see anything and orientation becomes difficult? Quite simply, touching and feeling the surrounding environment. It's exactly this principle which makes the scanning tunnelling microscope and atomic force microscope useful for creating images with resolutions at the atomic level.

"Magnifying glass" for the nanoworld

In STM, an extremely small electrically conductive needle, whose tip consists of a single atom, is brought close to the sample to be examined (which also must be electrically conductive). If the distance is only a few atomic diameters and if voltage is then applied, an electric current (the tunnelling current) starts flowing without the need for the needle and sample to touch each other. At a constant tunnelling current, a high-precision mechanism pushes the tip over the sample's surface thousands of times so it scans line by line. In this way, the tip "feels" the sample's electron density, which normally correlates with the position of the atoms. The up and down movement which is carried out in order to keep the tunnelling current constant is recorded by a computer and converted into a three-dimensional image of the surface.

In the last 30 years, STM and further developments of it have become a dominant fixture in research institutes around the world. Today's equipment, however, delivers far more than fascinating images of surfaces; it can manipulate atoms and molecules, such as pushing them around, arranging them in patterns and even more.

The scanning tunnelling microscope as a tool

At Empa, for instance, the chemist Karl-Heinz Ernst uses an STM to set molecules in motion. He heads up the Molecular Surface Science group and specialises in phenomena such as molecular self-assembly and crystallisation. For this, he uses an ultra-high vacuum unit which works at temperatures near four Kelvin, in other words, near absolute zero. "I'm interested in how molecules jump around when you tickle them," jokes Ernst, who is also a professor at the University of Zurich. "If we start molecules vibrating with tunnelling electrons, they sometimes break down and sometimes not. We want to understand better why they sometimes 'survive' for a longer or shorter time." This knowledge should help explain complex chemical processes, for instance what happens on catalyst surfaces.

Research in tandem

Surface molecules have also attracted the attention of Marco Bieri and Stephan Blankenburg of the nanotech@surfaces Laboratory. These two physicists have developed a very special way to collaborate. While Bieri carries out his experiments with an ultra-high vacuum STM at the Empa site in Thun, Blankenburg reserves time on the computing cluster Ipazia in Dübendorf so he can simulate the experiments. When Bieri takes actual molecules – monomers functionalised with bromine atoms – and places them in the STM's ice-cold sample chamber, Blankenburg at the same time "prepares" the virtual surface on a computer and places the molecules on it. In the computer, the surface molecules begin to align themselves following the laws of quantum mechanics; in the STM in Thun, the "deep frozen" molecules begin to warm up slowly thanks to the initiation of a heating process, they become active and likewise only gradually start forming the first (actual) chemical bonds with each other.

Thanks to extensive know-how and much experience, Empa is in a position to develop new equipment and measurement techniques which push the state-of-the-art.

These chemical reactions are extremely difficult to observe with the STM because they occur almost instantaneously. It takes a great deal of experience and patience to get oriented on the surface and recognise how the patterns and supramolecular systems build up. Because the tip of the STM isn't constantly optimally sharp and sometimes unintentionally "picks up" molecules from the surface, the images don't always correspond to the actual conditions on the sample. One of Bieri's main tasks is to identify STM images with excessively monotonous symmetries without irregularities as spurious results, known to the researchers as artefacts.

Using a Skype video conference, Bieri receives support from his colleague at the high-performance computer. Blankenburg informs him what he should be observing according to the simulation. In return, Bieri reports about unexpected phenomena which Blankenburg then inputs into his computer model – for example, the highly original way in nature how a molecule twists around on itself during polymerisation.

Both scientists agree that by working together they are able to much more quickly interpret experimental data, and in the process generate new knowledge such as about the reaction mechanisms of complex chemical processes. For roughly a year, the team has been using this tandem method, the combination of experiments and computing

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power. And they have done so with great success. Among other things, a much cited article describing graphene nanoribbons, published this past summer in the renowned scientific magazine Nature, is based on this new method (see EmpaNews 31).

Twenty-five years of atomic force microscopy

A tip with a diameter of only a few nanometres also plays the key role in one of the most important further developments of the STM, the atomic force microscope. While the STM measures the tunnelling current, the AFM records the forces which arise when a tip placed on a cantilever is slid over the "mountains and valleys" of the sample surface. Depending on the shape of the tip and its condition, it becomes possible to investigate a variety of physical properties on the sample. Hans Josef Hug, head of the Nanoscale Materials Science Laboratory and professor of physics at the University of Basel, lists a whole "zoo" of forces which can be detected with the AFM: from electrostatic and magnetic forces, through van der Waals and Casimir forces, to those created by covalent and ionic bonds. "The principle of the AFM brings us much further along in many areas: frictional forces give us insight into tribology; magnetic forces help us optimise the storage of electronic data; while information about local hardness or local adhesion provide us with important findings concerning the micromechanical properties of materials," explains Hug. "At Empa there's hardly a single force which we can't record," he adds, with a wink.

Empa's User Lab

Numerous AFM and STM experts are at work all across Empa, and they make their knowledge available to many others besides their own in-house colleagues. The doors to the Swiss Scanning Microscopy User Lab (SUL) are also open to external clients and partners. With an array of AFMs, they can investigate topologies and measure local friction, as well as do in-depth studies of the contact potential and local mechanical properties of their materials. Whether on their own or with assistance, for each there's a tailor-made solution.

"This technical knowledge is nurtured by our research," emphasises Hug. Empa is in an ideal position to develop new equipment and measurement techniques which push the state-of-the-art. He is convinced that "only in this way can we stay at the leading edge, fulfil users' future requirements and be able to provide competent answers to their questions."

Developing new instruments

To do so, some boundaries must be transcended. "AFM and STM aren't really instruments for chemical analysis," notes Hug. "If we deposit unknown atoms or molecules on a well-defined surface, AFM and STM by themselves won't tell us exactly what they 'see' there." In the NanoXAS project, Empa researchers working together with colleagues from the Paul Scherrer Institute thus want to overcome this deficiency. For this, they are combining two measurement techniques: X-ray absorption analysis shows which chemical elements are present in the region under investigation, while AFM determines the sample's topography and other local properties. The result is a nearly nanometre-exact "chemical map" of the material. With it, the researchers hope to be able to selectively improve materials for future applications, such as developing more powerful digital cameras with a significantly increased amount of memory than is commonplace today.

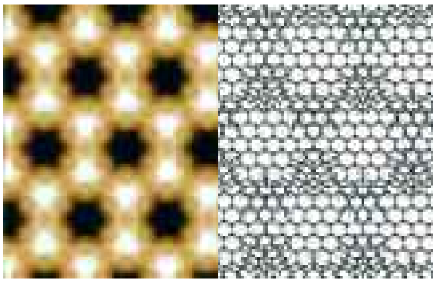
Hug has numerous other ideas in mind, and when he starts talking about them, his pioneering spirit takes flight. "We've learned how to do imaging with STM and AFM and to perform manipulations at the atomic level. However, with this capability we should also advance into areas where until now we've not been able to conduct investigations," he speculates. "In the nanoworld, for example, we 'touch' things without sensing how strongly we are handling them with our 'nanohands'." That's a hurdle we must overcome."

Thus, his next project within the EU Seventh Framework Programme, which goes by the name MDSPM (Multidimensional Scanning Probe Microscopy), has the goal of developing an AFM which can measure forces simultaneously vertically (perpendicular) and laterally (from side to side) with almost unbelievable precision. It recognises differences in the region of a millionth of a nano-Newton. Hug surmises that our understanding of how chemical reactions take place or how energy is lost through friction could possibly change radically. //

1
Bromine-containing polymer on a silver surface, as revealed by experiments using a scanning tunnelling microscope and computer simulations.

2
The image shows the inner workings of an atomic force microscope; a cantilever (see photo) scans the surface.

1



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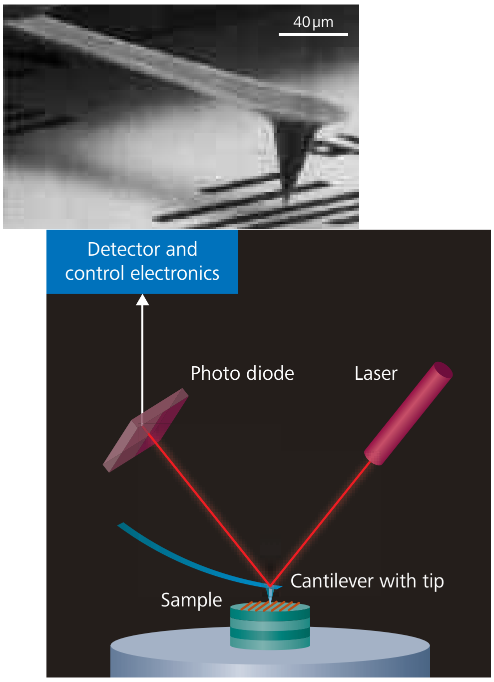

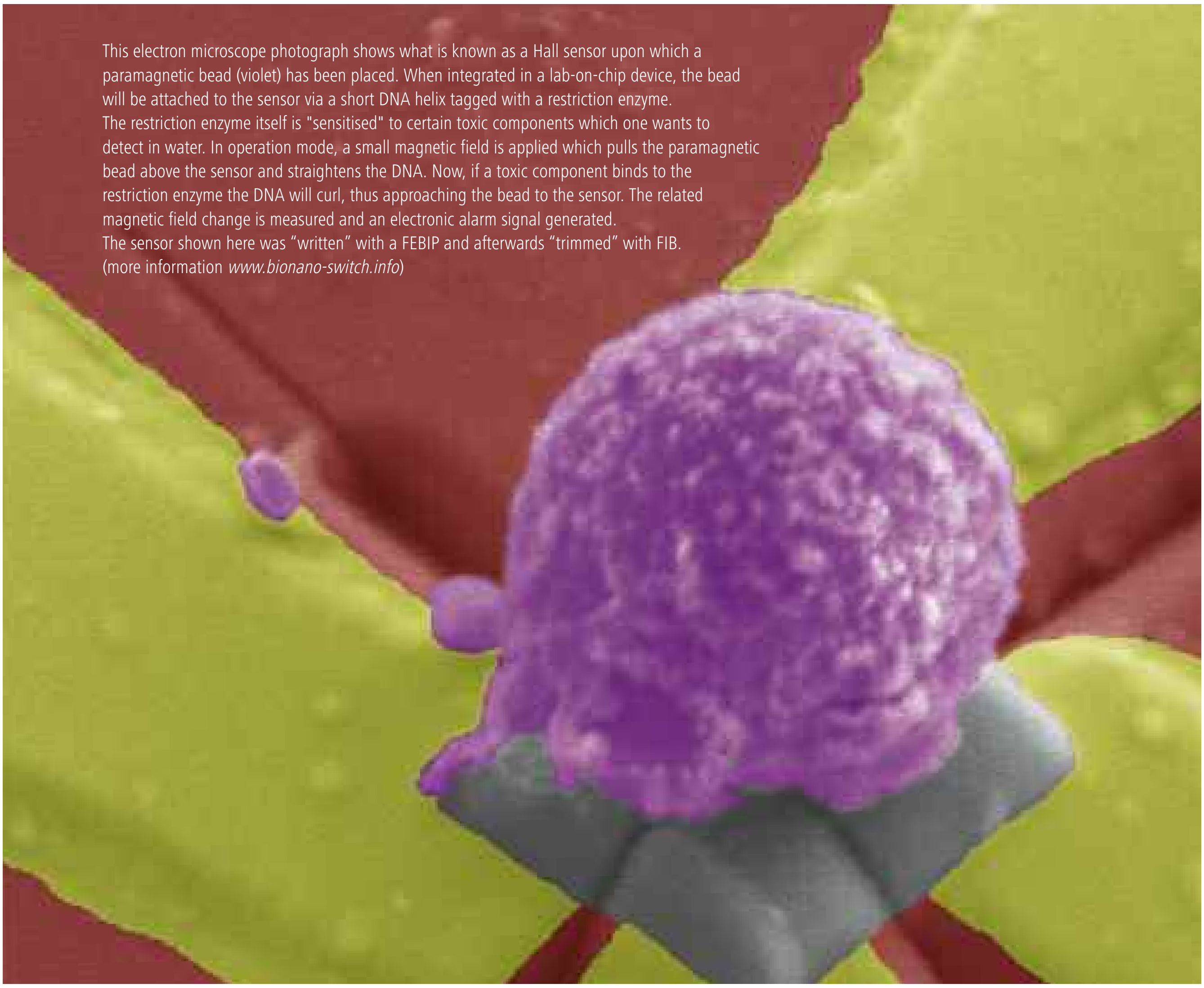

This electron microscope photograph shows what is known as a Hall sensor upon which a paramagnetic bead (violet) has been placed. When integrated in a lab-on-chip device, the bead will be attached to the sensor via a short DNA helix tagged with a restriction enzyme.
The restriction enzyme itself is "sensitised" to certain toxic components which one wants to detect in water. In operation mode, a small magnetic field is applied which pulls the paramagnetic bead above the sensor and straightens the DNA. Now, if a toxic component binds to the restriction enzyme the DNA will curl, thus approaching the bead to the sensor. The related magnetic field change is measured and an electronic alarm signal generated.
The sensor shown here was “written” with a FEBIP and afterwards “trimmed” with FIB.
(more information *www.bionano-switch.info*)

Chemistry with electron beams

Focussed electron beams are used in electron microscopes to allow us to see extremely small objects, and today such investigations have become routine. More recently, however, electron beams are being used for chemical reactions. For example, surface structures measuring only nanometres across can be “written”. Empa researchers are perfecting this technology and are searching for completely new application areas.

TEXT: Beatrice Huber / PHOTOS: Empa

Instruments such as electron microscopes, scanning tunnelling microscopes and atomic force microscopes have opened our eyes to the world of the infinitesimally small. They have for the first time made it possible for those working in research and industry to fabricate targeted structures with nanometre feature sizes. However, these instruments can do much more. For instance, the electron microscope can also be used for chemistry. In this case, suitable gas molecules are injected close to a sample which is already in the microscope’s vacuum chamber. These adsorb on the

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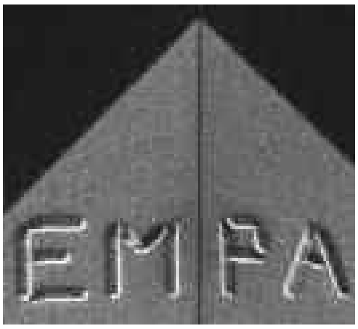
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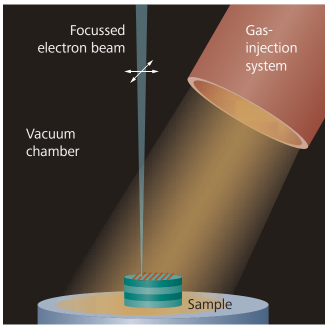
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sample in a reversible manner. The focussed electron beam, which normally serves to make objects visible, now instead induces chemical reactions of the adsorbed gas molecules, but only at the spot where the beam strikes the surface. The resulting non-volatile molecular fragments then remain permanently on the sample while the volatile fragments are removed by the vacuum system. By moving and holding in a programmed pattern, the electron beam can “write” a three-dimensional nanostructure.

Small, minimally invasive, direct

In technical jargon, this process is called FEBIP: focussed electron beam induced processing. A team led by Empa researcher Ivo Utke specialises in FEBIP, and uses it as an extremely flexible fabrication method for prototyping nanocomponents, in order to solve specific questions and problems in applied nanoelectronics, nanophotonics and nanobiology. The group is continually working to refine FEBIP and to open up new application areas. “With the help of a precisely positioned electron beam, it’s possible to remove or apply surface structures with nanometre precision and in virtually any desired three-dimensional shapes,” explains Utke. “FEBIP is especially attractive because it is minimally invasive.”

FEBIP exhibits other decisive advantages. With it, structures can be placed, shaped and manufactured all in a single maskless step. That’s not the case with other processes, which often need at least three steps. First a “mask” is fabricated on the probe, and then the material for the structure is deposited. Then, finally, the mask must be removed.

Nanostructures stabilise lasers

The vertical cavity surface emitting laser (VCSEL) is a semiconductor laser which is often used in data transmission for short-distance links like Gigabit Ethernet. These lasers are very popular in telecommunications because they consume little energy and can be simply fabricated in volumes of many tens of thousands on a single wafer.

However, long-wavelength VCSELs, those which work in the wavelength region above 1300 nanometres, can exhibit one weakness. Because of the cylindrical structure in which the lasers are built up on the wafer, the polarisation of the emitted light can sometimes change during operation. Polarisation is a property of certain waves, such as light waves, and it describes the direction of oscillation. A stable polarisation is necessary in order to reduce transmission errors and to use VCSELs in future silicon photonics. But thanks to FEBIP, Empa researchers, together with scientists from the Laboratory of Physics of Nanostructures at EPFL and its spin-off BeamExpress, can provide assistance. “We’ve written flat grating structures on the VCSELs with an electron beam,” says Utke in describing their solution, “and the gratings were effective in stabilising the polarisation.”

The search for the perfect composition

The scientists of Utke’s team believe that beyond specific applications, it’s just as important to refine and further develop FEBIP. Here a central aspect is to understand the physical-chemical processes in the vacuum chamber and with this to be able to exactly control the synthesis of material.

This was successful, for instance, in the case of a Hall sensor smaller than a micrometre in size. Hall sensors, named after the US physicist Edwin Hall, are used primarily to measure magnetic fields. In this particular application, the tiny sensor was used to measure the field produced by small (para)magnetic beads. These beads are functionalised, for example, with suitable biological substances so that they can react with other biological molecules such as antibodies. At the moment, this concept is being researched around the world, especially for diagnosing illnesses. Here the goal is to integrate a complete medical laboratory onto a chip the size of a finger, creating what is known as a Lab-on-Chip device. The research team, which also involves members of Empa’s Electron Microscopy Centre, is examining how the performance of a Hall sensor changes if the applied surface structures are made up of cobalt and carbon in various combinations. To do this, they use a gas-injection system in the vacuum chamber to supply two gases, one for cobalt and one for carbon. Of course, the goal was to find the optimal ratio. This turned out to be a cobalt proportion of approximately 65 per cent. Almost as important, however, was the knowledge acquired about how this ratio could be controlled: by using a pulsed electron beam. Control was thus achieved with a simple physical parameter, specifically, time.

Different processes skilfully combined

The Empa researchers also tried to combine different methods in a single vacuum chamber. This has the advantage that the samples must not be reintroduced into or taken out of the vacuum chamber multiple times – both of these are time-intensive procedures.

Nanowires made of semiconductor materials such as silicon are intended for use in nanoelectronics – a further miniaturisation of microelectronics – in order to provide the interconnections between extremely tiny electronic components. However, it’s not trivial to fabricate individual nanowires at predefined locations on structured substrates. Until now, bunches of nanowires without a preferred orientation frequently appeared from which individual wires then had to be selected. The Empa team, together with researchers from Germany’s Max Planck Institute of Microstructure Physics, the Institute for Photonic Technologies and the Max Planck Institute for the Science of Light, have combined three methods: focussed ion beam (FIB), focussed electron beam induced processing (FEBIP) and the vapour-liquid-solid (VLS) method.

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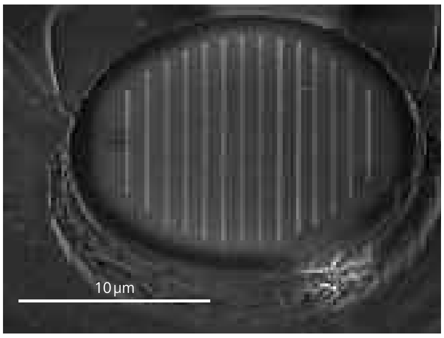
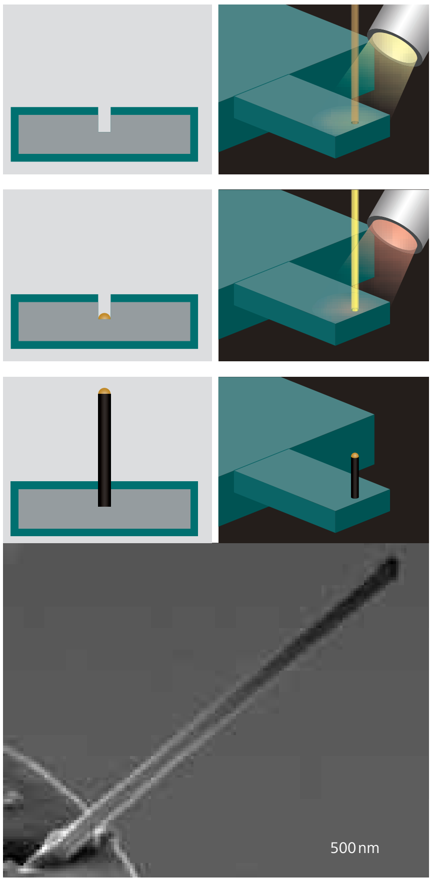


1,2
The principle of the local deposition process which is induced with a focussed electron beam (in short, FEBIP): molecules from a gas-injection system are deposited on the sample surface in a reversible manner. The focussed electron beam dissociates adsorbed gas molecules. The resulting non-volatile compounds remain permanently on the sample. The result is a nanostructure – for example the lettering for Empa – which has been written by the movements of an electron beam.

3
Electron microscope photograph of a VCSEL (vertical cavity surface emitting laser) upon which a polarisation grating has been "written" with FEBIP. VCSELs are semiconductor lasers frequently used in optical data transmission.

4
A single nanowire growing on the cantilever of an atomic force microscope. To do this, three methods were combined: to start with, a focussed ion beam "drilled" a hole; then a tiny amount of catalyst was placed in the hole using FEBIP; and from this a nanowire was grown using the VLS (vapour-liquid-solid) method.

4



Focussed ion beams, in a way similar to focussed electron beams, can not only make objects visible but they can also mill structures into a surface. In contrast to FEBIP, no additional gas molecules are necessary for this process because the heavy ions can directly sputter atoms from the surface. VLS is a common method for fabricating nanowires. Here the precursor material of the wires is added in gaseous form and is dissolved in a small amount of catalyst, generally a "drop" of liquid metal such as gold. The dissolved molecules crystallise there and the wire begins to grow.

Scientists initially "milled" a hole at a suitable location with a focussed ion beam. In it, a focussed electron beam then "planted" a tiny amount of gold, which served as the VLS catalyst. In a third step, silane (a gaseous form of silicon) was added, and individual nanowires, made up of pure crystalline silicon, started to grow out of the holes. For this experiment, the final step took place in a separate growth chamber, but in theory it could also be integrated into an electron microscope with the help of a heated sample stage.

Utke is certain that chemistry with focussed electron beams has great potential. "FEBIP could soon become a true nanofabrication platform for rapid prototyping of nanostructures in a minimally invasive way, without necessitating the large investment of a clean room." //

Literature references

"Small, Minimally Invasive, Direct: Electrons Induce Local Reactions of Adsorbed Functional Molecules on the Nanoscale", I. Utke, A. Gölzhäuser, Angewandte Chemie International Edition 49 (49) 9328 (3pp)2010, DOI: 10.1002/anie.201002677
"Tunable Nanosynthesis of Composite Materials by Electron-Impact Reaction", L. Bernau, M. Gabureac, R. Erni, I. Utke, Angewandte Chemie International Edition 49(47), (2010) 8880 (5pp), 2010, DOI: 10.1002/anie.201004220
"Granular Co-C nano-Hall sensors by focused-beam-induced deposition", M. Gabureac, L. Bernau, I. Utke, G. Boero, Nanotechnology 21 (2010) 115503 (5pp), DOI: 10.1088/0957-4484/21/11/115503
"Minimally-invasive catalyst templating on pre-structured surfaces for local VLS-growth of individual silicon nanowires ", M. G. Jenke, D. Lerose, J. Michler, S. Christiansen, I. Utke, submitted to Nanoletters, 2011.
"High speed telecommunication laser polarisation stabilisation by minimally-invasive focused electron beam triggered chemistry", I. Utke, M. Jenke, C. Roeling, P. H. Thiesen, V. Iakovlev, A. Syrbu, A. Mereuta, A. Caliman, E. Kapon, Nanoscale, DOI:10.1039/C1NR10047E, 2011.

Book reference

"Nanofabrication using focused ion and electron beams: principles and applications", Editors I. Utke, S. Moshkalev, P. Russels, Oxford Series on Nanomanufacturing. N.Y., Oxford University Press (2011 forthcoming). *ISBN 9780199734214*