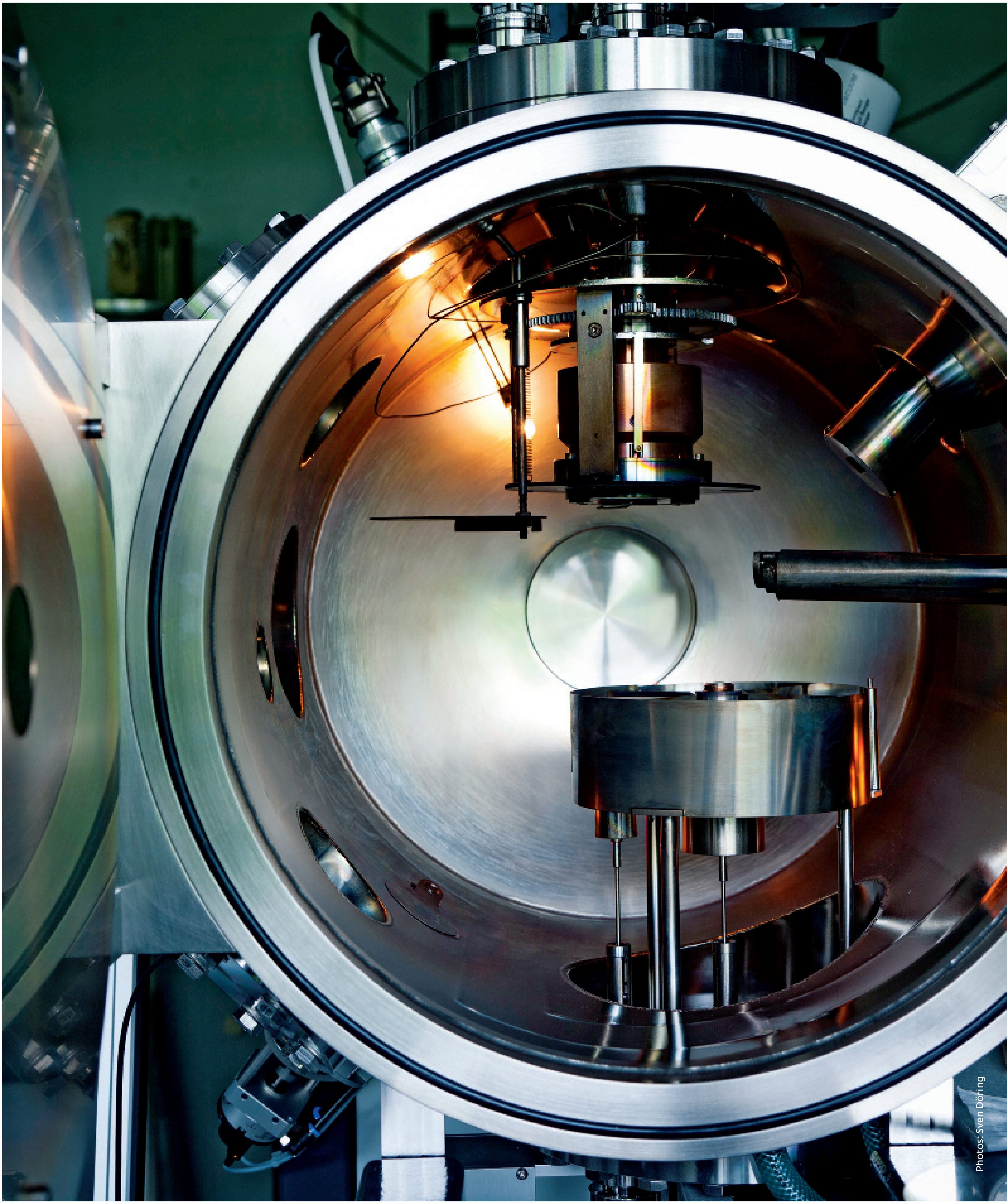
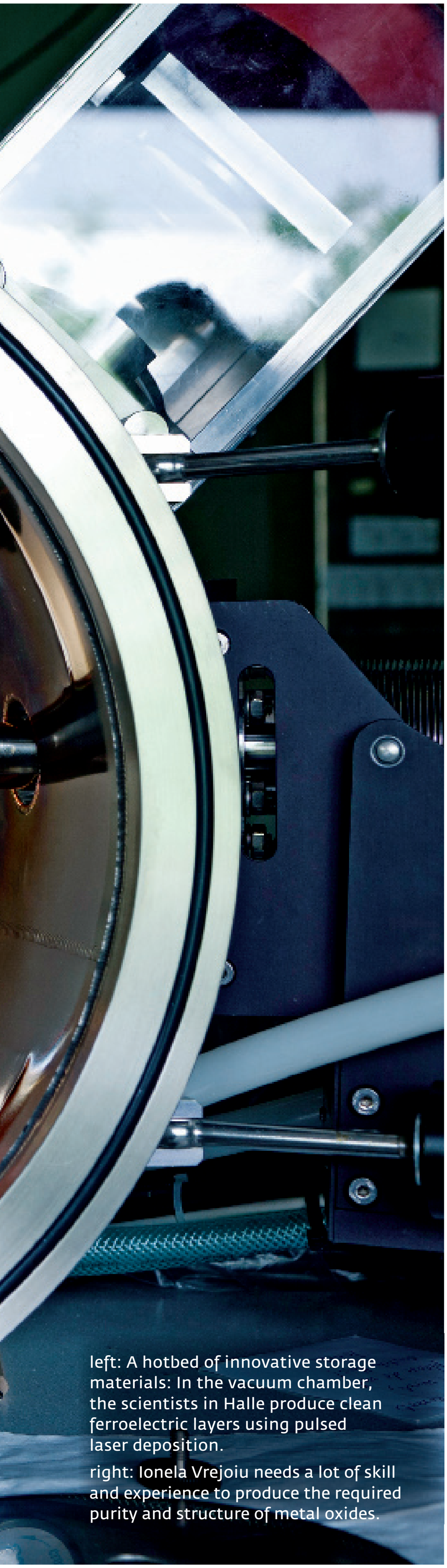


Photos: Sven Döring



left: A hotbed of innovative storage materials: In the vacuum chamber, the scientists in Halle produce clean ferroelectric layers using pulsed laser deposition.

right: Ionela Vrejoiu needs a lot of skill and experience to produce the required purity and structure of metal oxides.

Digital Memory **in Pole Position**

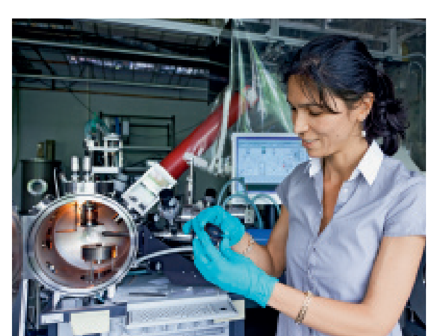
Currently, computers store data stepwise: when a computer is switched on, it first has to load from the hard disk to the internal memory. At the **Max Planck Institute of Microstructure Physics, Dietrich Hesse** and **Marin Alexe** are researching materials for computer memories that would make computer booting redundant and could compress data very densely.

TEXT **PETER HERGERSBERG**

Things got really exciting for Marin Alexe one evening when he was standing in line for a beer. Not that his day had exactly been dull. Alexe had come from Romania to Halle specifically for the Autumn School on Electron Microscopy. Scientists in various disciplines from microbiology to solid state physics had gathered here in September 1994 at the Max Planck Institute of Microstructure Physics to learn the latest on the method used to investigate metals, ceramics, viruses and protein molecules, atom by atom. Marin Alexe had previously had little to do with this in his everyday work.

"I just wanted to learn about the method," says the physicist, a cheerful man with a large, distinctive moustache. At the time, he was head of a working group at the National Institute of Material Physics in Bucharest, despite being only a recent Ph.D. himself. As he waited for his beer after attending a series of lectures, he found himself by chance standing next to Dietrich Hesse, with whom he began a discussion. This chat was to have far-reaching consequences.

The two scientists still remember every detail of their first meeting. They were sitting in Alexe's cramped office, its walls lined to the ceiling with books, and in between them, a stack of drawers with numbered specimen jars. Marin Alexe recounts how he talked with Dietrich Hesse for hours on that evening in September 1994. Some two years later, he moved from Bucharest to Halle and took up a position at the Max Planck Institute, for two years as a visiting scientist before becoming a permanent member of the institute's scientific staff. During their idle conversation, the physicists quickly realized that they were working on the same topic: ferroelectrics. >



» A memory made from a ferroelectric material can pack information very densely, and still retain it when the computer is switched off.

Globally, only a few experts are researching these materials, although they are of interest not only to physicists with an affinity for unusual effects, but also for applications in microelectronics. A computer that stores information in a ferroelectric material would have an advantage over today's computers right from the outset: instead of starting up slowly when switched on, it would come alive at the press of a button, just like a TV screen. When a computer is switched on, it loads data from the hard disk to the internal memory, from long-term to short-term memory, so to speak. Using ferroelectric memories could make this sharing redundant, since these materials combine the advantages of both hard disks and internal memories.

The hard disk stores digital information in tiny magnets whose poles go in two directions, so that the hard disk retains the information permanently. However, its data density is limited because it is written and read using a magnetic field that cannot focus down to a few nanometers. Moreover, too much heat is produced to execute the computing operations of a running software program. The internal memory does not have these problems, but it loses its data when the power is switched off. It memorizes electrically only what people need on the screen in front of them.

MERGING INTERNAL MEMORY AND HARD DISK

A memory made from a ferroelectric material can do both – compress information very densely and still retain it when the computer is switched off or a power outage occurs. In a ferroelectric material, information is stored on permanent electric dipoles. It can be called up and changed using an electrical field, a voltage that can be limited to a very narrow area.

The dipoles are created because, in ferroelectric materials, positively and negatively charged ions are slightly shifted against each other in the crystal lattice. Like magnetic dipoles, they can orient themselves in opposite directions and thus store the zero and one of the digital code. And they can do so permanently: the ions remain in the polarized positions even when the voltage used to write the zero or one is switched off, just as the magnetic moments in ferromagnets retain their orientation even without an external magnetic field. This analogy with ferromagnets is what gives ferroelectric materials their name.

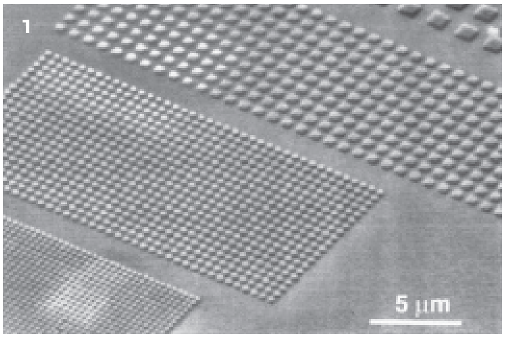
However, before these materials will make it possible to merge the internal memory and the hard disk, a few fundamental questions still need answering. To what size can ferroelectric data points shrink, and how densely can they be packed? How does polarization reversal work, exactly? Can it perhaps be speeded up? And how can transistors be efficiently produced out of this material?

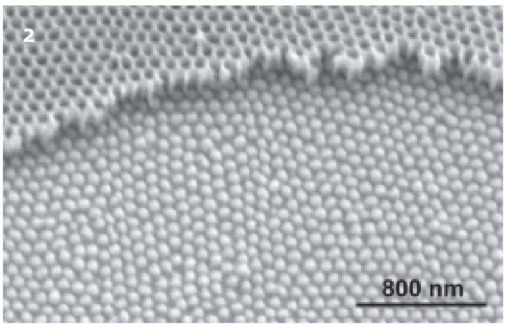
These were some of the questions that Dietrich Hesse and Marin Alexe discussed at length on that late summer evening in 1994. "I must definitely introduce you to Mr. Gösele," said Hesse to his Romanian colleague at the end of the evening, and the next morning he took him to Gösele's office. "I didn't know who Mr. Gösele was," says Alexe. "Such a nice guy, and so young – I could hardly believe he was a Director."

Ulrich Gösele, who died quite unexpectedly two years ago, had initiated the research on ferroelectrics at the Max Planck Institute of Microstructure Physics. "He always tried to solve fundamental problems with an eye to future developments in microelectronics," says Dietrich Hesse, a thoughtful, easygoing guy. And this continues to

The Halle scientists place ferroelectric substances on different sample holders for their experiments. The partially green-coated gold-colored holder in the center of the photo is used in experiments at low temperatures and in a magnetic field.

Photo: Sven Döring





1 The route to the nanodimension: Marin Alexe used an electronic beam to cut micro- and nanostructures from a metal-organic material, which he then converted into a ferroelectric material.

2 The scientists in Halle can achieve a storage density of up to one terabit per square inch, by depositing ferroelectric dots through a perforated mask.

3 The scientists etch the masks for extremely small nanostructures using a DC current in an acid bath located in can-sized containers. Cooling water at a temperature of one degree Celsius is pumped through the pipes, which are thickly wrapped for heat insulation.

define the work of the scientists in Halle today. “We clear the big boulders out of the path that leads to new electronics applications.”

One of the first boulders they encountered was the manufacture of ferroelectrics. The materials usually contain several metals, often including titanium, but also bismuth or lead, and oxygen, and have cumbersome names like bismuth titanate, lead zirconate titanate (PZT) and strontium bismuth tantalate (SBT). For these substances to adopt ferroelectrical properties, they not only have to have their ingredients combined in precisely measured ratios, but the atoms must also be arranged in a precise pattern. This is precision chemistry work, which is often too great a challenge for chemistry. The scientists therefore turn to a physics method in such cases – pulsed laser deposition. Ionela Vrejoiu is an expert in this field at the Halle-based Max Planck Institute. In the laboratory where she works, pumps hiss and hum, a cabinet of electronic control systems takes center stage, several drum shaped stainless steel chambers are supported on chest-high platforms. The apparatus to which the various instruments are attached opens on one side like a washing machine. A red plastic tube as thick as a man’s arm connects a chamber diagonally above to an ultraviolet laser.

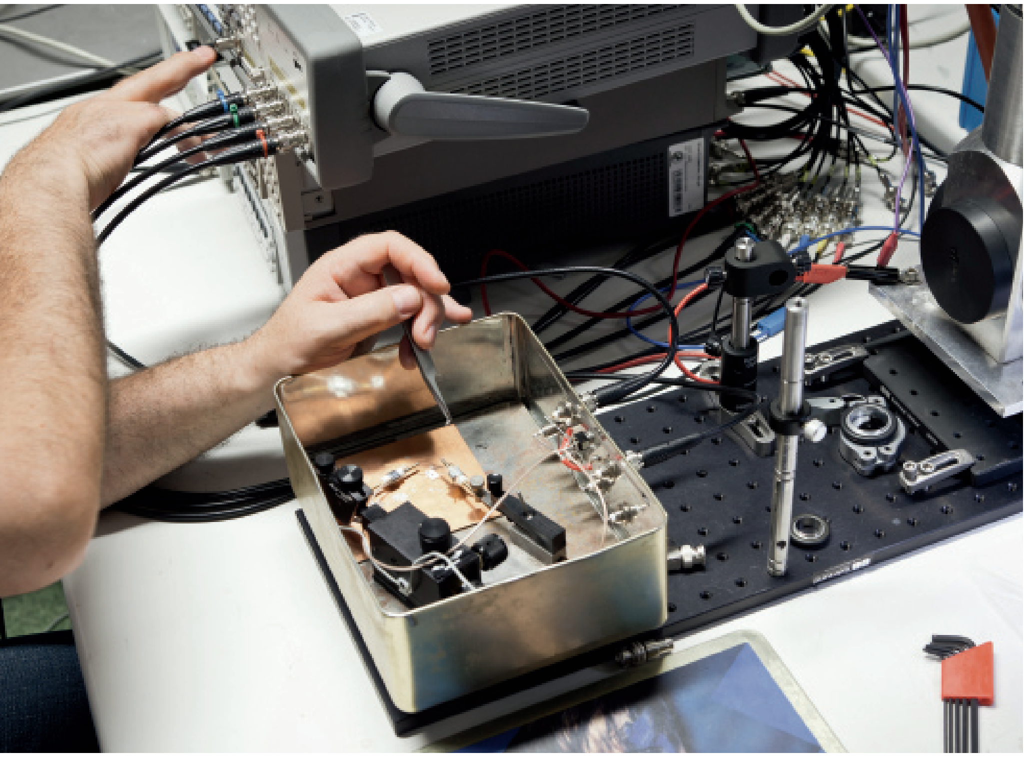
NANOSTRUCTURES FOR COMPUTER MEMORIES

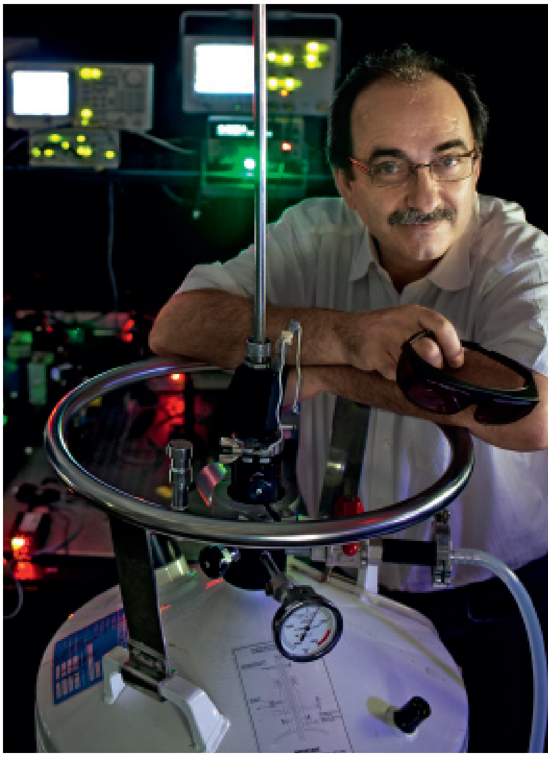
In the vacuum chamber, the laser strikes a coin-sized plate holding a metal oxide. The components of the ferroelectric material have already been mixed on this in the correct ratio, but fairly randomly. Bursts of energy from the laser vaporize the material into well-dosed plasma clouds. The ionized metal oxide gas then strikes a substrate surface attached upside down to the lid of the chamber. As the oxygen from the compounds readily vanishes on the way to the substrate, a little additional oxygen flows into the chamber. However, most of the gas particles still whizzing through the chamber are relentlessly evacuated by the pumps.

“To obtain usable samples, we have to adjust many things,” explains Ionela Vrejoiu. She can blow more or less oxygen into the chamber, cool or heat the substrate material, regulate the intensity of the laser and control the distance between the substrate and the plate holding the raw material. The physicist makes many samples until she achieves the desired result. Experience is helpful, but is not sufficient on its own. Even a slightly different composition can completely alter the behavior of a material when it comes to the muster of the atoms. “Cleaning the surface of the substrate material is also very important,” says Vrejoiu. And yet there are materials that tenaciously resist the order in accurate layers Vrejoiu and her own small research team are thus systematically investigating how difficult cases can be brought under control.

But producing perfect layers of ferroelectric materials is not enough. The scientists have to form tiny dots of uniform shape and size from them and place them regularly on a surface. “It was clear to us from the beginning that, in computers, we needed nanostructures of memory materials,” says Dietrich Hesse. Once again, he and Marin Alexe have a stroke of good fortune to thank for the breakthrough.

In 1997, James Scott arrived in Halle with a Humboldt grant. Marin Alexe speaks of him as one of the world’s





leading experts in ferroelectrics. Along with the American scientist, who is now working in Cambridge, England, they introduced the nanoworld to ferroelectric materials. "We were the ones who initiated research on nano effects in ferroelectric materials," says Dietrich Hesse.

STORAGE DENSITY OF UP TO ONE TERABIT

Accordingly, Marin Alexe and his colleagues shrank PZT and SBT data points to nano size. First they used electron beam lithography. A fine electron beam engraves intricate patterns, but only in metalo-organic layers. However, the scientists can oxidize the metalo-organic compounds, which also contain carbon in addition to metals, and transform them into crystalline ferroelectric materials using heat treatments.

Using this method, Alexe cut and burned ferroelectric nano-tiles stacked in neat rows with 100 nanometer intervals on a strontium titanate surface. The scientist then switched each tile with an electrically conductive tip of an atomic force microscope (AFM). These would be no competition for today's conventional hard disks, but it was a start. Since then, the physicists have further shrunk their ferroelectric dots by using a mask. The pattern of the mask resembles a honeycomb, but with pores having a pitch of just 100 nanometers and separated by 60-nanometer-thick walls (see box on page 39). The scientists used laser pulses to deposit lead zirconate titanate through the mask onto a platinum substrate. A platinum top lid completed the nanocapacitors, which operate as data storage points. This helped them increase the storage density to 176 gigabits per square inch. "By using this method in the laboratory, we can probably achieve one terabit per square inch," says Dietrich Hesse.

The chip industry should certainly respond and transform this into a production process for high-density ferroelectric memories. After all, pulsed laser deposition has become the method of choice for growing oxide layers flexibly in the laboratory. However, the quantities of material that can be processed in a reasonable time are too small for production on a large scale. Dietrich Hesse therefore predicts that chemical vapor deposition will be used to produce ferroelectric nanoscale memories on an industrial scale. This problem is no longer one of the big boulders that the scientists have to remove, but the physics of the ferroelectric switching process is.

A PLAYGROUND FULL OF MEASURING EQUIPMENT

Marin Alexe is investigating this problem in his laboratory one floor above his office. "This is my playground," he says as he enters the room, roughly the size of a classroom and stuffed with mysterious equipment. There is a black box as big as a washing machine next to the door, a container with liquid nitrogen stands in the room, an apparatus with a thin tube and funnel attached through which the cooling nitrogen is filtered. And of course there are lots of boxes containing control and measuring equipment.

Alexe makes his way purposefully through this high-tech inventory to the furthest corner of the laboratory and takes the most nondescript object in the room down from a shelf: a cookie box with a yellowish, badly tarnished sheen. "This is my first measuring instrument, which I built in one afternoon," explains the physicist. While left | In his early days at Halle, Marin Alexe converted a cookie box into a measuring instrument and used it to investigate how the polarization of ferroelectric materials switches under the influence of an external electrical field. The metal of the box repels external fields.

right | Marin Alexe is also studying ferroelectrics in a piece of apparatus into which he lowers specimens from above using a rod. He exposes these materials to a controlled magnetic field, which is created by a superconductive magnet cooled by liquid nitrogen.

most scientists call on the expertise and skill of colleagues in special workshops for drilling, screwing and turning operations, Alexe always worked on new instruments with his own hands. "In Romania, we built nearly everything ourselves, and there was a lot of improvisation going on."

In the modified cookie box, with cable connections inserted into its side, Alexe measured how sharply polarization increases when voltage is applied, and how long it remains stable when the voltage drops. Polarization reflects the extent to which negative and positive ions are separated in the crystal pattern, and thus provides a measure of the magnitude of the dipoles.

Most of the other equipment in Alexe's laboratory is used for similar purposes, but provides more precise measurements and gives the scientist insight into how ferroelectric materials behave at temperatures well below freezing point or in a magnetic field. Alexe still incorporates cookie boxes into some of his special high-tech apparatuses. They are made from non-magnetic metals and, unlike the stainless steel favored by equipment developers, they provide ideal protection against undesired magnetic fields.

CAN THE SWITCHING PROCESS BE SPEEDED UP?

However, the mass of equipment in Alexe's laboratory can't provide any more help with many of the problems he and Dietrich Hesse are investigating. One such problem concerns how, exactly, a ferroelectric dot switches from zero to one and vice versa. Writing information into ferroelectric memories still takes too long, because their tiny dipoles don't flip over fast enough when an external voltage is applied on them. Before they can do anything to change this, the scientists in Halle need to understand the switching process in detail.

Working with colleagues from the Oak Ridge National Laboratory in Tennessee, they discovered that the polarization reversal process always starts at one point, or more precisely at a defect, and spreads from there. The defects are small flaws in the crystal pattern, a notch on the surface of the material or a boundary where domains with differently oriented dipoles meet. In fact, these domain boundaries do not exist in a uniformly poled dot, but are an unavoidable consequence of the polarization reversal process, as the area with the new dipolar orientation expands at the expense of the other.

"We are interested in how domains grow in the nanocapacitors, and what role the boundary between two domains plays," explains Marin Alexe. The scientists have already made some progress on this, as well. As a model, they looked at a rectangle in which all dipoles extend their negative end to the top edge.

Between the top and bottom edge, the scientists apply a voltage that tries to change the orientation of the dipoles. First, the dipoles near a defect on the surface switch. The negatively charged end of the rotated dipoles then hits the positive pole of the next lower dipoles. This is energetically unfavorable. As a result, a transition zone is created in which the polarization decreases and then increases again in the reverse direction. This domain wall is relatively thick parallel to the applied voltage, because it is shielding opposite charges. It also likes to move through the material fairly rapidly in this forward direction, as this is the best way to get rid of this charge conflict.

Perpendicular to the applied voltage, the differently charged domains meet along a much narrower boundary, and it thus takes much longer for the new polarization direction to establish itself in this direction. "This observation showed us that ferroelectric nanocapacitors switch quite differently from macroscopic layers or microstructures," says Dietrich Hesse. In larger structures, a new polarization develops almost from the start over the entire width. >

MASK-MAKERS IN THE NANOWORLD

In order to process ferroelectric materials into densely packed dots, the scientists in Halle use an aluminum oxide mask perforated with nanoholes. These holes can't be drilled with a tool – an electrochemical process is used instead, aluminum electrolytic oxidation.

This is also known as the eloxal process, which gives aluminum products a protective layer and their matt sheen. The Max Planck research team's expertise with this method is such that the oxidation etches fine pores into the aluminum, each with six adjacent pores. The correct combination of temperature, acidity (pH value) and chemical composition of the electrolytes is the key. By pre-stamping the aluminum layer with a suitably studded stamp, the scientists can force the holes to arrange into a completely regular honeycomb pattern.

After figuring out this time-dependent mechanism of how polarization switches in a nanostructure, the scientists described it mathematically and later tried to track it down live. The studio where Marin Alexe and his colleagues film the polarization reversal process is in the basement. Three piezoelectric force microscopes are lined up in the laboratory. The scientists have packed one of them in a shoulder-high, cuboid metal crate to soundproof it. The equipment produces plenty of heat, but air conditioning is banned, as the airflow would disturb the measurements.

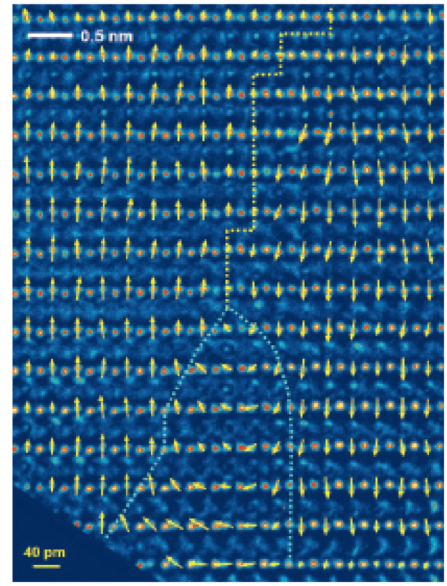
A GLANCE AT EACH DIPOLE PROVIDES AN ACCURATE PICTURE

Marin Alexe uses a setup that vaguely resembles an optical microscope without an eyepiece. He tweaks a few switches and knobs and, with a grating noise, the tip of the microscope moves close to the sample. On command, it scans the surface, which is then displayed on a screen. “A piezoelectric force microscope can determine the polarization of a sample on the nanometer scale, as well as how it changes over time,” explains the scientist. The microscopes operate in the same way as scanning force microscopes: the tip of a flexible cantilever moves over the surface of the specimen. Every bump moves the lever. How far it moves is measured by a reflection of a laser beam.

But how can the orientation of electric dipoles be established by such a sensitive finger for humps and bumps on the surface? In fact, the surface of the sample also rises or sinks when dipoles form, when they flip over or when they become distorted. Ultimately, the polarization distorts the crystal pattern. However, even a scanning force microscope does not register such height differences reliably – they get lost in the noise.

The scientists therefore apply an AC voltage to the lever and feel what pulse makes the crystal react to the voltage. Piezoelectric force microscopy is the name of the method that shows them the dipole orientation (see box below). The scientists modified the first atomic force microscope for these measurements themselves. “Getting the correct cable out of the system was difficult,” Alexe says of the modifications.

Looking through one of the three piezoelectric force microscopes is now standard procedure when Marin Alexe and his colleagues are investigating ferroelectrics. However, the scientists have not yet managed to identify everything they are interested in. More details are still needed in order to understand the switching process, the domain movement and processes at the domain walls. They have to map the polarization, plotting the direction and magnitude of the dipole in each individual simple cell, the smallest component of a crystal. For this, the scientists have to determine the position of each individual atom.



Such a detailed view can be provided only by a transmission electron microscope, and in only one version of it. This has just recently been devel-

A DELICATE TOUCH FOR ELECTRIC POLES

A scanning force microscope can be converted into a piezoelectric force microscope by applying an AC voltage to the lever used to record height differences on a surface. The voltage makes the dipoles in the ferroelectric material vibrate periodically, which rhythmically distorts the crystal. As the magnitude of the dipole changes, the crystal expands and compresses, because ions are constantly shifting around.

The key factor now is whether, when the voltage is applied, its negative pole touches the negative or the positive end of the dipolar field – in other words, how the dipoles are oriented when the measurement starts. This dictates whether the dipolar field vibrates in precise harmony with the voltage or out of phase with it. Or in terms of crystal distortion, at which time point of the AC field the crystal stretches the most and at which it contracts the most.

The scientists can now observe this, because they know the frequency of the AC voltage and thus also the rhythm of the pulsing crystal. They use a laser to observe this frequency. Since they know precisely where to look, they can recover the signal from the noise. The rise and fall of the crystal shows the changes in the dipolar field. Whether this field is vibrating in harmony or out of phase, almost syncopated, with the voltage, reveals the original orientation of the ferroelectric dipoles. This method can be used to map areas with the same polarization, so-called ferroelectric domains, in the piezoelectric force microscope.

Graphic: SCIENCE, Vol. 331, March 18, 2011

left page: A map of the dipole configuration: Together with scientists from the Jülich Research Center, the physicists in Halle have determined, from the positions of the individual ions, the orientation of all the dipoles in three ferroelectric domains. In the small domain in the lower half of the picture, the dipoles form a semicircle.

this page: Dietrich Hesse wants to find out precisely how the switching process in ferroelectric materials works, so that he can speed it up if possible. A key tool in this process is the piezoelectric force microscope, which is kept in a protective box for soundproofing purposes.

oped and is used by Knut Urban and Chun-Lin Jia at the Jülich Research Center in a highly sophisticated way. The mapping method they developed provides extremely high resolution and high-contrast images, and also displays oxygen ions, which are responsible for the negative part of the ferroelectric dipoles. Using this method, the Jülich-based scientists examined a sample of lead zirconate titanate from the Max Planck Institute in Halle, inspecting exactly a domain boundary between two opposite polarization directions.

FIRST APPLICATIONS IN ELECTRONIC RAIL TICKETS

Their eye for detail confirmed what Marin Alexe and Dietrich Hesse already suspected: dipoles don't just orient themselves up and down; in a section of the boundary where the two areas with opposite dipole orientation meet, the scientists discovered another domain. It contained only a few unit cells and their dipoles rotated minutely cell by cell, forming a semicircle with the dipoles in the two large adjacent areas. "For a long time, we didn't believe that a continuous polarization rotation was possible, because the crystal lattice will keep changing shape," says Marin Alexe. These gradual distortions were thought to be energetically unfavorable compared with the normal domain walls.

"We were also surprised, however, that, in very small domains, there was any polarization left at all," continues Dietrich Hesse. The dipoles mutually stabilize each other in their strict arrangement – if there are enough of them. In an area of just a few nanometers, there should not be enough, or so it was assumed. The fact that such small domains are also polarized is good news for memory technology. "Perhaps we'll be able to shrink ferroelectric dots to 20 or maybe even 10 nanometers," says Dietrich Hesse. Inside, the dipoles will probably orient themselves in a vortex, but this would not be a problem for the data storage. The zero and one of a bit would then be encoded by polarization in a clockwise or counter-clockwise direction.

One major computer manufacturer may have felt a tinge of regret on hearing of the extent to which ferroelectric dots can be shrunk. Its research scientists had calculated, back in the early 1970s, that a ferroelectric layer must be at least 300 nanometers thick in order to maintain the polarization. The company suspended research on these materials. Others were not so easily discouraged. "It may be a few more years yet before ferroelectric materials are used as memories in PCs, but of all the alternative storage materials, they have made the most progress so far," says Dietrich Hesse. Ferroelectric memories are, in the meantime, being manufactured industrially and are used in Japan in electronic rail tickets, for example. ◂

GLOSSARY

Ferroelectric material
A material in which positive and negative ions form permanent electric dipoles. The orientation of the dipoles is changed using an external voltage. The prefix "ferro" references the analogy with ferromagnets, whose polarity is reversed using an external magnetic field.

Polarization
The orientation of the electric dipoles in a material and the strength of the electrical field that produces the dipoles. It represents a measure of the distance between the positive and negative charges of the dipoles.

Transmission electron microscope (TEM)
An electron beam is directed through a thin sample layer. The higher the atomic number of an atom, the stronger the beam's dispersion on the atoms of the material. The crystal structure is determined from the resulting diffraction pattern. However, light atoms such as oxygen produce only very weak contrasts or none at all in a conventional TEM.