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IRON OXIDES ON THE ATOMIC SCALE
DEVICE MEASURES NANOSCALE MOVEMENT
NANOFABULOUS: A TALE OF THREE COMPANIES
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Cover: X-rays illuminate a graphene-capped array of liquids, prompting molecules in solution to emit electrons. The graphene caps allows the electrons to pass freely, carrying information on the chemical state of the molecules, but prevent water from leaking out, ensuring that the liquid samples do not dry out. Credit: A. Strelcov/CNST

POSTER PRESENTATIONS

Two CNST postdocs had winning posters in the 24th annual Postdoctoral Poster Presentation, sponsored by the NIST chapter of Sigma Xi. Left: Brian Roxworthy (in blue shirt), who placed first in the electronic and magnetic materials and engineering category, ponders a question from CNST researchers Rob Ilic and Bob de Alba. Right: Qing Li, who won first place in the computer modeling & simulation and physics category, explains his poster. Credit: S. Orski/NIST
By capping liquids with an ultrathin layer of graphene, CNST researchers and their colleagues have revitalized and extended a powerful technique to image surfaces. The graphene lids provide researchers with the first capability to easily and inexpensively image and analyze liquid interfaces and the surface of nanoscale objects immersed in liquids.

In the imaging technique, known as photoemission electron microscopy (PEEM), ultraviolet light or X-rays bombard a sample, stimulating the material to emit electrons from a region at or just beneath its surface. Electric fields act as lenses, focusing the emitted electrons to create an image.

Researchers have used the method for decades to discern such fine-scale features as chemical reaction patterns on the surface of materials, the magnetic structure of thin films and the molecular architecture of biological compounds. But PEEM has typically been restricted to samples that are under high vacuum, drastically limiting the ability to study liquids and gasses at ordinary pressures. A liquid sample, for instance, would evaporate if directly exposed to a high vacuum.

In the past, scientists have overcome the vacuum problem by using differential pumping, which bridges the gap between the high pressure of the sample and the essentially zero pressure of the microscope. But such instrumentation can cost millions and are not widely accessible for routine use, notes Andrei Kolmakov, a project leader in the CNST Energy Research Group.

Instead, he and his colleagues from CNST, the University of Maryland, NIST’s Material Measurement Laboratory, the University of Saskatchewan, the Canadian Light Source and Oregon State University developed an inexpensive and easy-to-implement alternative. Sealing a liquid or gaseous sample with an atomically-thin layer of graphene keeps the liquid or gas at atmospheric pressure while allowing the system to be placed under vacuum.

In the Jan. 25 Nano Letters, the scientists report that the graphene microcaps enabled electrons emitted by the test liquids to pass nearly unimpeded to the detector, yet kept the liquids from escaping into the vacuum of the PEEM.

“This very simple solution, adding a layer of graphene” allows researchers to use PEEM in its standard configuration, without the need for extra and expensive equipment, says Kolmakov.

“The concept of extending the use of PEEM to probe liquids is in a way revolutionary,” comments physicist Andrea Locatelli of Synchrotron Radiation Laboratory Elettra in Trieste, Italy, who was not part of the research team. “Countless applications can indeed be foreseen,” he adds.
Roche Sequencing Solutions engineer Juraj Topolancik was looking for a way to decode DNA from cancer patients in a matter of minutes.

Rajesh Krishnamurthy, a researcher with the start-up company 3i Diagnostics, needed help in fabricating a key component of a device that rapidly identifies infection-causing bacteria.

Ranbir Singh, an engineer with GeneSiC Semiconductor Inc., in Dulles, Va., sought to construct and analyze a semiconductor chip that transmits voltages large enough to power electric cars and spacecraft.

These researchers all credit the NanoFab, which provides cutting-edge nanotechnology capabilities for NIST scientists that is also accessible to outside users, with supplying the state-of-art tools, know-how and dependability to realize their goals.

When Krishnamurthy, whose company is based in Germantown, Md., needed an infrared filter for the bacteria-identifying chip, proximity was but one factor in reaching out to the NanoFab.

“Even more important was the level of expertise you have here,” he says. “The attention to detail and the trust we have in the staff is so important—we didn’t have to worry if they would do a good job, which gives us tremendous peace of mind,” Krishnamurthy notes.

The NanoFab also aided his project in another, unexpected way. Krishnamurthy had initially thought that the design for his company’s device would require a costly, highly customized silicon chip. But in reviewing design plans with engineers at the NanoFab, “they came up with a very creative way” to use a more standard, less expensive silicon wafer that would achieve the same goals, he notes.

“The impact in the short term is that we didn’t have to pay as much [to build and test] the device at the NanoFab, which matters quite a bit because we’re a start-up company,” says Krishnamurthy. “In the long run, this will be a huge factor in [enabling us to mass produce] the device, keeping our costs low because, thanks to the input from the NanoFab, the source material is not a custom material.”

Singh came to the NanoFab with a different mission. His company is developing a gallium nitride semiconductor device durable enough to transmit hundreds to thousands of volts without deteriorating. He relies on the NanoFab’s metal deposition tools and high-resolution lithography instruments to finish building and assess the properties of the device.

“Not only is there a wide diversity of tools, but within each task there are multiple technologies,” Singh adds.

For instance, he notes, technologies offered at the NanoFab for depositing exquisitely thin and highly uniform layers of metal—which Singh found crucial for making reliable electrical contacts—include both evaporation and sputtering, he says.

The wide range of metals available for deposition at the NanoFab, uncommon at other nanotech facilities, was another draw. “We needed different metals compared to those commonly used on silicon wafers and the NanoFab provided those materials,” notes Singh.
Topolancik, the Roche Sequencing Solutions engineer, needed high precision etching and deposition tools to fabricate a device that may ultimately improve cancer treatment. His company’s plan to rapidly sequence DNA from cancer patients could quickly determine if potential anti-cancer drugs and those already in use are producing the genetic mutations necessary to fight cancer.

“We want to know if the drug is working, and if not, to stop using it and change the treatment,” says Topolancik.

In the standard method to sequence the double-stranded DNA molecule, a strand is peeled off and resynthesized, base by base, with each base—cytosine, adenine, guanine and thymine—tagged with a different fluorescent label. “It’s a very accurate but slow method,” says Topolancik.

Instead of peeling apart the molecule, Topolancik is devising a method to read DNA directly, a much faster process. Borrowing a technique from the magnetic recording industry, he sandwiches the DNA between two electrodes separated by a gap just nanometers in width.

According to quantum theory, if the gap is small enough, electrons will spontaneously “tunnel” from one electrode to the other. In Topolancik’s setup, the tunneling electrons must pass through the DNA in order to reach the other electrode.

The strength of the tunneling current identifies the bases of the DNA trapped between the electrodes. It’s an extremely rapid process, but for the technique to work reliably, the electrodes and the gap between them must be fabricated with extraordinarily high precision.

That’s where the NanoFab comes in. To deposit layers of different metals just nanometers in thickness on a wafer, Topolancik relies on the NanoFab’s ion beam deposition tool. And to etch a pattern in those ultrathin, supersmooth layers without disturbing them—a final step in fabricating the electrodes—requires the NanoFab’s ion etching instrument.

“These are specialty tools that are not usually accessible in academic facilities, but here [at the NanoFab] you have full, 24/7 access to them,” says Topolancik. “And if a tool goes down, it gets fixed right away,” he adds. “People here care about you, they want you to succeed because that’s the mission of the NanoFab.” As a result, he notes, “I can get done here in two weeks what would take half a year any place else.”
Scientists at the CNST have developed a new device that measures the motion of super-tiny particles traversing distances nearly unimaginably small—shorter than the diameter of a hydrogen atom, or less than one-millionth the width of a human hair. Not only can the handheld device sense the atomic-scale motion of its tiny parts with unprecedented precision, but the researchers have devised a method to mass produce the highly sensitive measuring tool.

It’s relatively easy to measure small movements of large objects but much more difficult when the moving parts are on the scale of nanometers, or billionths of a meter. The ability to accurately measure tiny displacements of microscopic bodies has applications in sensing trace amounts of hazardous biological or chemical agents, perfecting the movement of miniature robots, accurately deploying airbags and detecting extremely weak sound waves traveling through thin films.

CNST physicists Brian Roxworthy and Vladimir Aksyuk described their work in the Dec. 6, 2016, *Nature Communications*. The researchers measured subatomic-scale motion in a gold nanoparticle. They did this by engineering a small air gap, about 15 nanometers in width, between the gold nanoparticle and a gold sheet. This gap is so small that laser light cannot penetrate it.

However, the light energized surface plasmons—the collective, wave-like motion of groups of electrons confined to travel along the boundary between the gold surface and the air.

While measuring the motion of the plasmons, the researchers noted that the laser light wavelength, the distance between successive peaks of the light wave. With the right choice of wavelength, or equivalently, its frequency, the laser light causes plasmons of a particular frequency to oscillate back and forth, or resonate, along the gap, like the reverberations of a plucked guitar string.

Meanwhile, as the nanoparticle moves, it changes the width of the gap and, like tuning a guitar string, changes the frequency at which the plasmons resonate.

The interaction between the laser light and the plasmons is critical for sensing tiny displacements from nanoscale particles,
notes Aksyuk. Light can’t easily detect the location or motion of an object smaller than the wavelength of the laser, but converting the light to plasmons overcomes this limitation. Because the plasmons are confined to the tiny gap, they are more sensitive than light is for sensing the motion of small objects like the gold nanoparticle.

The amount of laser light reflected back from the plasmon device reveals the width of the gap and the motion of the nanoparticle. Suppose, for example, that the gap changes—due to the motion of the nanoparticle—in such a way that the natural frequency, or resonance, of the plasmons more closely matches the frequency of the laser light. In that case, the plasmons are able to absorb more energy from the laser light, and less light is reflected.

To use this motion-sensing technique in a practical device, Aksyuk and Roxworthy embedded the gold nanoparticle in a microscopic-scale mechanical structure—a vibrating cantilever, sort of a miniature diving board—that was a few micrometers long, made of silicon nitride.

Even when they’re not set in motion, such devices never sit perfectly still, but vibrate at high frequency, jostled by the random motion of their molecules at room temperature. Even though the amplitude of the vibration was tiny—moving subatomic distances—it was easy to detect with the new plasmonic technique.

Similar, though typically larger, mechanical structures are commonly used for both scientific measurements and practical sensors; for example, detecting motion and orientation in cars and smartphones. The scientists hope their new way of measuring motion at the nanoscale will help to further miniaturize and improve performance of many such micromechanical systems.

“This architecture paves the way for advances in nanomechanical sensing,” the researchers write. “We can detect tiny motion more locally and precisely with these plasmonic resonators than any other way of doing it,” said Aksyuk.

The team’s fabrication approach allows production of some 25,000 of the devices on a computer chip, with each device tailored to detect motion according to the needs of the manufacturer.
In work that could help make possible a faster, longer-lasting, and lower-energy method of data storage for consumers and businesses, researchers have developed a technique for imaging and studying a promising class of magnetic devices with 10 times more detail than optical microscopes.

Magnetic materials have attracted a growing number of researchers in the quest to more rapidly store and read bits of digital information. In a magnetic system, data is encoded by the direction of the magnetization: A bar magnet with its north pole pointing up can represent the binary code “0,” while the same magnet with its north pole pointing down can represent a “1.” Unlike the standard semiconductor computer chip, magnetic memory devices can retain information even if the power is turned off.

By controlling when and how quickly the magnetization can be flipped without expending significant electrical power, scientists hope to develop an existing technology called Magnetic Random Access Memory, or MRAM, into a leading tool for reading, writing and storing information.

To realize the promise of MRAM, researchers are probing the nanoscale magnetic structure of thin metal films that have the potential to serve as memory devices. At the CNST, Ian Gilbert and his colleagues from NIST’s Material Science and Engineering Division and the University of Maryland have used a high-resolution electron-imaging technique, developed by CNST physicist John Unguris, to examine the nanostructure of magnetic films before and after their magnetization is reversed.

The technique, scanning electron microscopy with polarization analysis (SEMPA), uses a beam of electrons scattered off a thin film to reveal the nanoscale topography, replete with miniature hills and valleys, of the film’s surface. Electrons ejected from the surface by the incoming electron beam are also detected and separated according to the direction of their spin—a quantum property that endows the charged particles with an intrinsic angular momentum and tiny magnetic field. The direction of the ejected electrons’ spins reveals variations in the sample’s magnetic structure on a scale about 10 times smaller than seen with an optical microscope.

SEMPA’s ability to discern tiny magnetic structures is critical as engineers fabricate smaller and smaller magnetic memory devices, notes Gilbert. With SEMPA, “we can see these really fine textures in the magnetization,” he says.

Gilbert and his collaborators also used electron spin to flip the magnetization in their thin-film sample, an alloy of cobalt, iron and boron. By passing a small current through an underlying strip of a nonmagnetic metal film such as platinum, the team created a stream of electrons whose spins all point in the same direction. When this stream of electrons, known as a spin current, passed through the magnetic thin film, their spin exerted a small twisting force, or torque, on the magnetic regions of the film. The torque was large enough to rotate and flip the magnetization.

The SEMPA images taken before a current was applied revealed that the direction of the magnetization varied, on the nanoscale,
across the thin-film sample. Each small region of the sample has its own preferred axis along which the magnetization points, says Gilbert. The team reported its findings in the Sept. 23, 2016 Physical Review B.

Such nanoscale variations of the magnetization could become crucial to document, says Gilbert, for engineers trying to optimize the performance of a magnetic memory device. The variation in magnetization direction could also affect the ability of electron spin to flip the magnetization.

“Instead of flipping magnetization up or down, the spin current flips the magnetization along whatever its preferred local axis happens to be,” notes Gilbert. The variation in magnetization direction suggests that materials used for magnetic memory devices may need to be gently heated, a process that aligns nanoscale magnetic domains.

In separate work, CNST scientists Mark Stiles and Vivek Amin, who has a joint appointment with the University of Maryland, focus on the theory describing the torque measured in the same SEMPA experiment. There, a stream of polarized electrons generated in a nonmagnetic metal strip interacts with the magnetization of an overlying material. In particular, the team has developed a model that may help determine which group of polarized electrons plays the more important role in reversing the direction of magnetization in the overlying material—those electrons originating at the surface of the nonmagnetic material or those from the interior.

The answer could guide the fabrication of more efficient magnetic memory devices. For instance, determining which group of electrons are the dominant actors could suggest ways to minimize the current needed to flip the magnetization, Stiles says.

“Right now, we’re in the process of publicizing the model to experimentalists, trying to get them to use it to better understand their data,” he notes.


NEW TOOLS IN THE NANOFAB

A new Scanning Electron Microscope (SEM) is now available in the NanoFab cleanroom, allowing easy imaging of wafers between process steps. The SEM is a JEOL JSM 7800F FESEM, which operates at voltages from 10 to 30,000 volts. Imaging entire wafers up to 200 mm in diameter, the SEM can examine a full range of samples, including metals, semiconductors and insulating materials. The instrument’s low operating voltage is especially suited for imaging non-conducting materials such as quartz wafers, polymers and ceramics. Key features of the SEM include:

• Edge-to-edge Inspection of 200-mm wafers
• Imaging many photoresists without a conductive coating
• Improved depth of focus
• Saving imaging settings for easy recall

The NanoFab Soft Lithography Lab has a new microfluidic test station, allowing researchers to test microfluidic devices at a constant flow rate and pressure without damaging or altering the devices. The system, a CorSolutions Microfluidic Digital Microscope Work Station, includes a digital microscope with zoom range of 25X-200X, motorized z-axis unit and 4x6-inch glass plate X/Y stage with top and bottom LED illumination. A PneuWave pneumatic closed-loop 2-channel pump delivers gas or liquid used for testing through fluidic indexing connectors with ports sized for common tubing diameters.

For additional information visit the NanoFab tool page or contact Robert Newby 301-975-6070, robert.newby@nist.gov.
Among the most abundant minerals on Earth, iron oxides play a leading role in magnetic data storage, the coloring of paint and drug delivery. These materials, commonly known as rust, also serve as a catalyst for several types of chemical reactions, including the production of ammonia for fertilizer.

To fine-tune and attain the desired properties of these minerals, scientists work with nano-sized particles of the oxides. But to do so, researchers need a detailed, atomic-scale understanding of reduction, a key chemical reaction that iron oxides undergo. That knowledge, however, is often lacking because reduction—a process that is essentially the opposite of rusting—proceeds too rapidly for many types of probes to explore at such a fine level.

In a new effort to study the microscopic details of metal oxide reduction, CNST researchers and their collaborators used a specially adapted transmission electron microscope (TEM) in the NanoLab to document the step-by-step transformation of nanocrystals of the iron oxide hematite ($\text{Fe}_2\text{O}_3$) to the iron oxide magnetite ($\text{Fe}_3\text{O}_4$), and finally to iron metal.

“Even though people have studied iron oxides for many years, there have been no studies at the atomic scale,” says Wenhui Zhu of the State University of New York at Binghamton, who worked on her doctorate in the NanoLab in 2015 and 2016. “We are seeing what’s actually happening during the entire reduction process instead of studying just the initial steps.”

That’s critical, adds Renu Sharma of the CNST, “if you want to control the composition or properties of iron oxides and understand the relationships between them.”

By lowering the temperature of the reaction and decreasing the pressure of the hydrogen gas that acted as a reducing agent, the scientists slowed down the reduction process so that it could be captured with an environmental TEM. The instrument enables researchers to perform atomic-resolution imaging of a sample under real-life conditions—the gaseous environment necessary for iron oxides to undergo reduction—rather than under the vacuum needed in ordinary TEMs.

“This is the most powerful tool I’ve used in my research and one of the very few in the United States,” says Zhu. She, Sharma and their colleagues described their findings in the December 13, 2016 *ACS Nano*.

The team examined the reduction process in a bicrystal of iron oxide, consisting of two identical iron oxide crystals rotated at 21.8 degrees with respect to each other. The bicrystal structure also served to slow down the reduction process, making it easier to image with the environmental TEM.

In studying the reduction reaction, the researchers identified a previously unknown intermediate state in the transformation from magnetite to hematite. In the middle stage, the iron oxide retained its original chemical structure, $\text{Fe}_2\text{O}_4$, but changed the crystallographic arrangement of its atoms from rhombohedral to cubic.

This intermediate state featured a defect in which oxygen atoms fail to populate some of the sites in the crystal that it normally would. This so-called oxygen vacancy defect is not uncommon and is known to strongly influence the electrical and other properties of oxides. But the researchers were surprised to find that the defect occurred in an ordered pattern, which had never been found before in the reduction of $\text{Fe}_2\text{O}_3$ to $\text{Fe}_3\text{O}_4$, Sharma says.

The significance of the intermediate state remains under study but it may be important for controlling the reduction rate and other properties of the reduction process, she adds. “The more we understand, the better we can manipulate the microstructure of these oxides,” says Zhu.

When Brandon Canedy graduated last year from the Rochester Institute of Technology, he knew he wanted to pursue a career in nanotechnology but had taken only a few courses in the subject. That all changed during a recent 4-month internship at the NanoFab, co-sponsored by the Northeast Education and Technology Education Center (NEATEC) (http://neatec.org/).

He became adept at a key task in the quality control of films etched in the NanoFab—making sure that the microscopic trenches etched in the films had the proper depth. To perform the necessary measurements, Canedy learned to operate a profilometer, a device whose stylus resembles that of a phonograph needle. The instrument measures depth variations as a sample is moved relative to the contact point of the stylus.

If the variations were too large, Canedy alerted the equipment team to determine if further investigation was needed. He also charted the measurements to determine how variations in depth fluctuated from week to week and month to month. If fluctuations increased significantly over time, it might indicate an etching tool needed to be serviced. One problem emerged after an etching tool had been repaired, says Canedy, revealing that the instrument required a further adjustment.

Working with process engineer Lei Chen, Canedy also gained expertise in an experimental technique for making nanostructures with conventional photolithography and plasma etching.

In one standard technique, engineers employ an electron beam to inscribe custom-designed shapes on a surface covered with an electron-sensitive film. The electron beam chemically alters the solubility of those regions of the film that it impinges. As a result, when the film is immersed in a special solution, only the chemically altered regions are washed away, leaving behind a transparent pattern. However, the method is relatively slow and costly.

Under the tutelage of Chen, Canedy tried a different, less expensive method to fabricate nanostructures. Working with a resist material made of a polymer, he blasted the sample with oxygen plasma, which slowly erodes exposed sections of the polymer. Using a test pattern of polymer dots larger than a micrometer in diameter, Canedy and his colleague showed that the oxygen plasma could whittle the dots down to a diameter of less than 100 nanometers. The result suggests that the oxygen plasma technique can reduce the size of inscribed shapes in a controlled manner.

Using an atomic force microscope to study the nanostructures “was challenging at first—everything from properly placing the tip of the microscope to getting an image,” says Canedy. Many of the pictures Canedy took were fuzzy until Chen diagnosed the problem as surface charge that was obscuring the sample during the electron-imaging process.

What was the coolest part of the internship? “Everything,” says Canedy. “It gives you a solid laboratory experience and exposure to working with statistical process control,” he notes. “You really understand the reason why you’re doing [a procedure] and you’re working with a really fantastic group of engineers.”

Canedy’s time in the NanoFab appears to have had an added bonus. Shortly after his internship ended in January, Globalfoundries, a semiconductor manufacturing company in Albany, N.Y., hired him as a process technician.

In applying for the job, “It definitely helped to have this exposure to a clean-room environment and operating tools and working with this dynamic and diverse group of experts,” he says.
A NEW EXPERT ARRIVES AT THE NANOFAB

The NanoFab is about to get a new Pro—an expert available 24/7.

Dubbed the NanoPro, this online resource, set to debut by the end of March, features a reservoir of knowledge about NanoFab processes, tool description and performance, training videos and instruction manuals for all instruments.

The new knowledge base will improve accessibility to detailed documents and other information about the NanoFab and encourage information sharing among users, notes assistant NanoFab manager Jessie Zhang. She and NanoFab manager Vincent Luciani, with help from NIST software specialist Michael Shaw, assembled the system over the past 15 months.

In addition to users of the NanoFab, NanoPro will be available to everyone on the NIST campus, and upon request to the general public by contacting NOG_NanoPro@nist.gov.