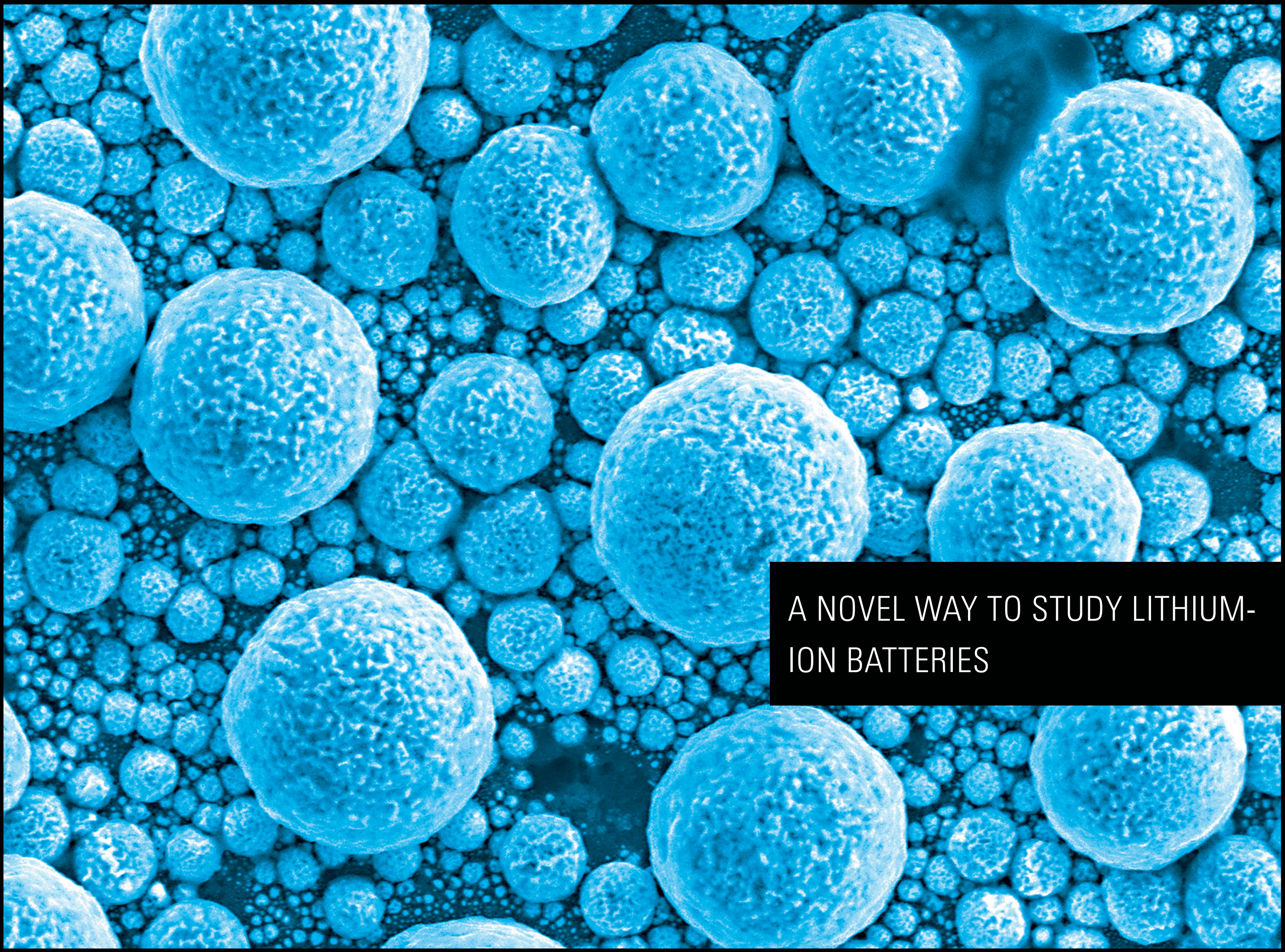
# THE CNST NEWS

SUMMER 2016



A NOVEL WAY TO STUDY LITHIUM-ION BATTERIES

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SOFTWARE OFFERS EASIER WAY TO DESIGN CURVES

TALL AND SKINNY: NEW TECHNIQUE FOR HIGH ASPECT RATIO NANOSTRUCTURES

NIST
National Institute of Standards and Technology
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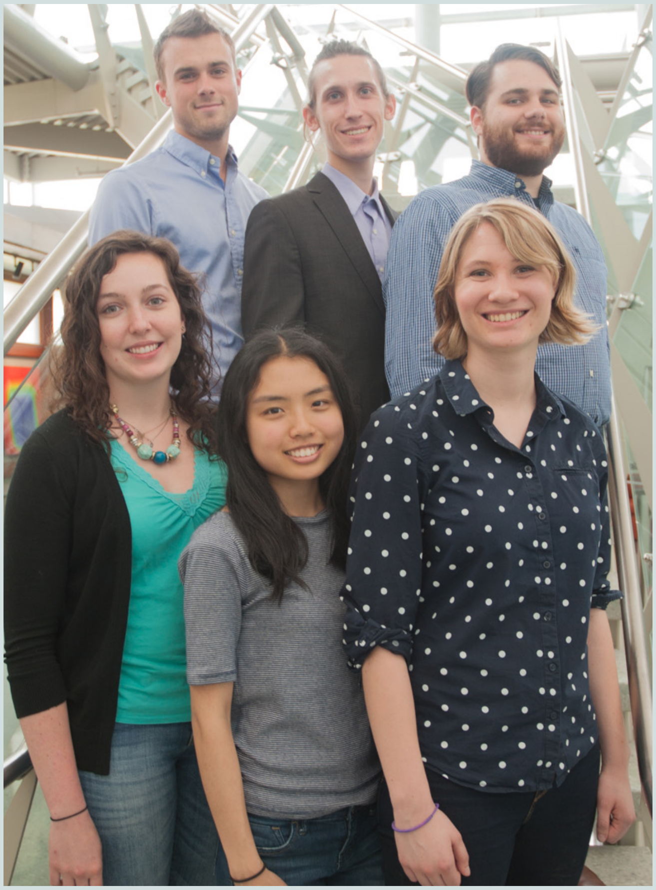
## CNST 2016 SURF STUDENTS



CNST 2016 SURF Students: **Back Row:** Gillen Beck , Jack Scaletta, and Arthur Sloan. **Front Row:** Mattie Watson, Gina Wong, and Kimi Bourland.

**Cover:** Micrograph of tiny balls of tin. By inserting lithium ions into the tin balls, CNST researchers have opened a new avenue for studying the dynamics of lithium-ion batteries.

# NEW SOFTWARE GIVES SOME CURVES TO NANOSTRUCTURE

When Robert Ilic isn't digging his crampons into the side of an icy mountain or pressing his snowshoes into a 3-foot-high drift, he's helping etch some novel impressions on semiconductor chips in the NanoLab.

Ilic, a project leader in CNST's Nanofabrication Research Group and a winter sports enthusiast, has written a software package that designs difficult-to-draw nanoscale shapes, including spirals, S-bends and tapered structures. Dubbed the Nanolithography Toolbox, the software includes a library of more than 400 shapes and enables researchers to custom design curved structures of arbitrary complexity.

"For years, semiconductor computer-aided design (CAD) has suffered from the inability to accurately represent curved geometries," Ilic says.

Like other nanolithography software, the Toolbox designs a geometric pattern from which a researcher can create a mask, or master pattern, to transfer to a wafer. But the software differs from existing semiconductor design packages, which are geared towards rectilinear designs often encountered in integrated circuit architectures. These packages have limited capabilities in drawing curved geometries at nanoscale dimensions, creating a figure that looks blocky or has sharp edges instead of a smoothly varying curve.

That's a problem for many research applications. For instance, if the design serves as a waveguide, or channel, for conveying photons or electrons, some of the particles will scatter off the sharp edges instead of traveling through the channel. And because electrons tend to crowd at sharp edges, electric fields at those locations may become too strong for some experiments.

The Toolbox circumvents such issues because Ilic has written software that codes for many non-rectangular building blocks, using vector-based shapes. Vector-based designs are created from lines or curves, such as Bezier curves, defined by a mathematical equation, rather than by the dot-to-dot approach most CAD software uses.

Vectors are mathematical expressions that have both a length and direction associated with them. In vector graphics, the vectors originate at certain locations, known as control points or nodes, that connect by directed line segments or curves to other locations.

For instance, consider drawing the letter "B" using vector graphics. The process might begin by moving to the lower left corner using a "move to" command, then creating a line segment pointing upwards from that location using a "line to" command. The curved sections would be composed of several "curve to" commands. The "B" is completed when the last "curve to" command coincides with the starting point at the lower left corner.

Because vector graphics are not based on pixels, they look the same, with shapes remaining smooth instead of blocky, even as an observer zooms in to tinier and tinier scales. (In practice, the high resolution is rendered on the nanoscale or subnanoscale level as required for the fabrication process.).

For nanoscale science, "you need that smoothness at high resolution," says Ilic. "That's something we've done that nobody else has accomplished," he adds. Available for use in the CNST NanoFab, the Toolbox also plots mathematical expressions in both rectangular and polar coordinates – a feature that doesn't currently exist in modern design software and would be difficult to implement in those packages.

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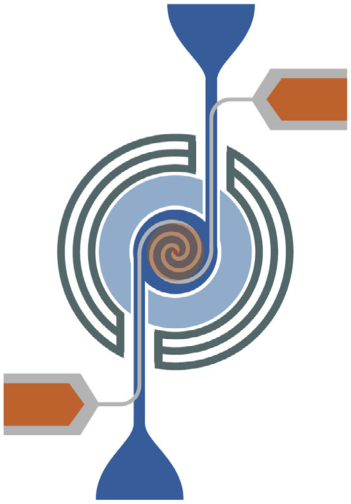
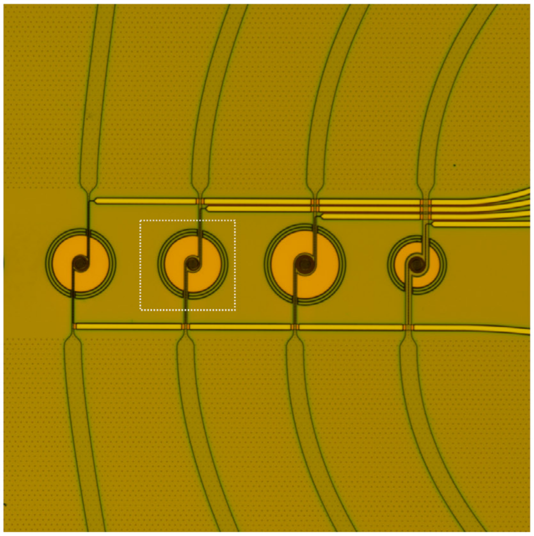
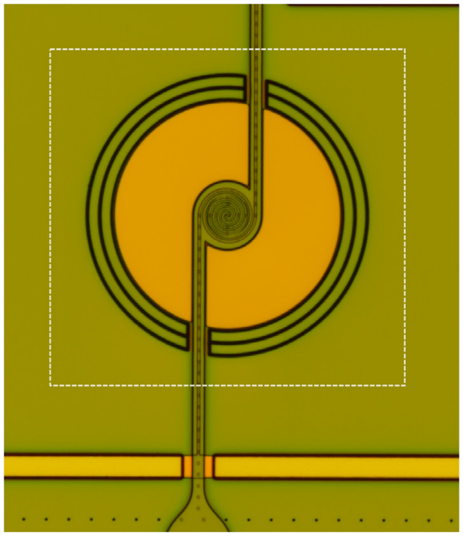




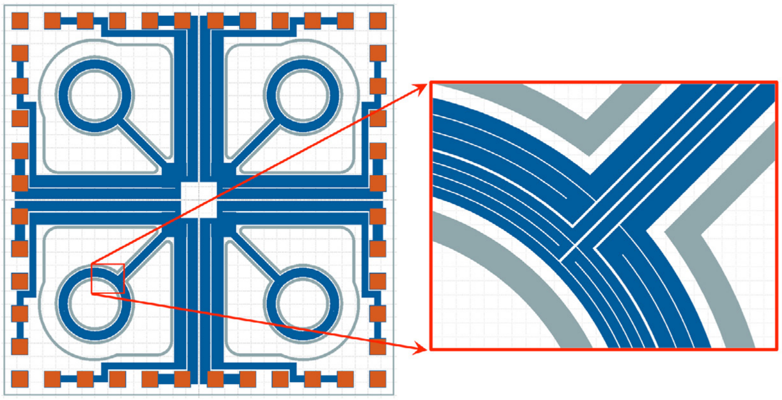


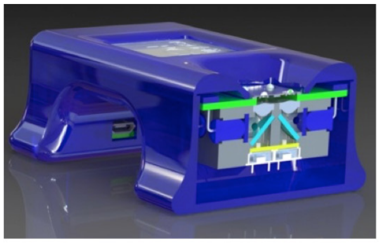
**Left:** Drawing of a spiral delay line heater element, designed with the Toolbox software. **Middle:** Several of the fabricated devices. **Right:** Close-up of one of the devices; white-dashed rectangle in this image is close-up of white-dashed rectangle in middle image. Credit: CNST/NIST

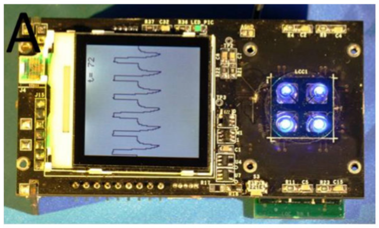
## NEW SOFTWARE (CONT'D.)

Ilic began developing the software when he learned that CNST physicist Kartik Srinivasan needed to fabricate several nanocomponents with curved geometries. "We now use the Nanolithography Toolbox for the layout of all of our nanophotonic and electro-optomechanical devices," says Srinivasan.

Ilic did much of the coding during Snowzilla, the Washington D.C. area's 2-foot snowstorm last January. With NIST closed, he worked long hours from home, taking breaks to sleep and snowshoe around his apartment complex. "It was great," says Ilic. "I had my NIST laptop and I really like snow and ice."







**Above:** Computer-aided design of a handheld polymerase chain reaction (PCR) device using the Nanolithography Toolbox software. **Right Top:** Cross-sectional illustration of the PCR device **Right Middle:** The actual PCR device, without packaging. **Right Bottom:** The packaged device.

## CNST: LIGHTS, CAMERA, ACTION .... AWARD!

A video series for middle school students featuring NIST's Center for Nanoscale Science and Technology (CNST) (http://www.nist.gov/cnst/video_collection.cfm) has won a regional Emmy award. Amy Leniart, an educational producer with the Fairfax (Va.) County Public Schools, won the honor in the Technology: Program/Special category on June 25 at the 58th annual competition held by the National Capital Chesapeake Bay Chapter of the National Academy of Television Arts and Sciences (http://www.capitalemmys.tv/).

Leniart and her crew, including a student reporter, visited the CNST last year, donning bunny suits to film process engineer Gerard Henein in the clean room explaining how scientists fabricate highly miniaturized electronic circuits, like the chips used in computers. In another video shoot, NIST fellow and CNST project leader Joseph Stroscio demonstrated how a scanning tunneling microscope works and explained how he designed the instrument, likening his role to that of a metal sculptor.

In an Emmy-award winning video for middle school children shot at NIST's Center for Nanoscale Science and Technology, NIST fellow and CNST project leader Joseph Stroscio demonstrates how a scanning tunneling microscope works. Credit: Fairfax County Public Schools

Other participants in the award-winning series, Innovation Workshop: Nanotechnology, include Lisa Friedersdorf, deputy director of the National Nanotechnology Coordination Office, and Travis Earles, a senior manager at Lockheed Martin.

The video program got its start when the state of Virginia added nanotechnology to its standards of learning for eighth grade students. A science curriculum specialist with Fairfax County Public Schools requested the show. The program provides a media resource for teachers; the YouTube link (https://www.youtube.com/playlist?list=PLGU615q8gq9znhVFriu7OIXkSuFphOEZW) is now part of the lesson plans for all eighth grade science teachers in Fairfax County Public Schools. The programming is also available for free nationally for other school systems to rebroadcast. The first broadcast reached 239 organizations, including 1,749 schools, and over a million viewers.

"I am really pleased that the fine work of Amy and her team has been recognized in this way," says CNST director Robert Celotta. "They really know how to capture the interests of students to explain and convey the excitement of nanotechnology. Their videos will reach well beyond their middle school student target audience," he adds. "The CNST staff and I thoroughly enjoyed working with them on this project."

# DNA ORIGAMI: FOLDING WITH THE MOLECULE OF LIFE

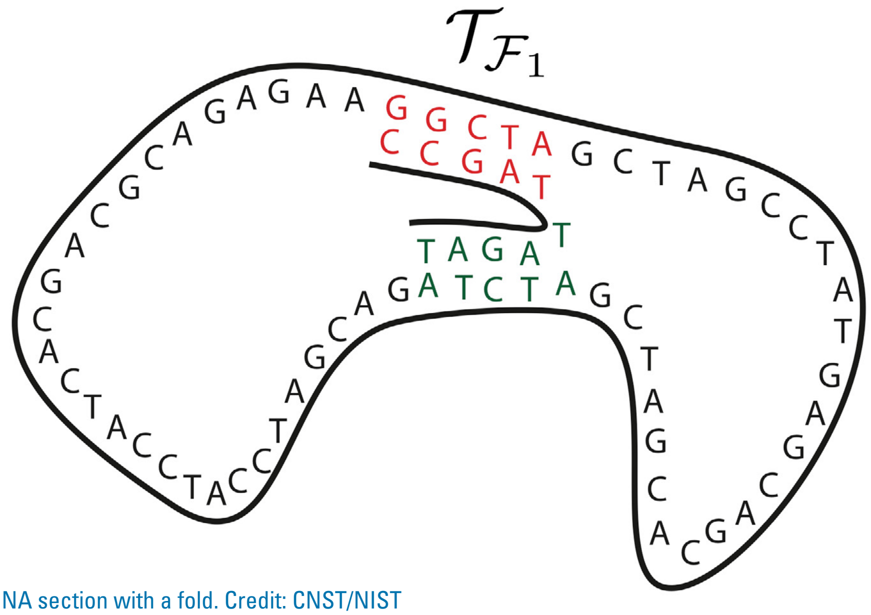
It loops, folds, sticks to itself and contorts into shapes as intricate as a miniature smiley face—all within the confines of a region one-thousandth the diameter of a human cell. DNA is the dream molecule with which nanoscientists love to sculpt.

DNA sculpting dates to the early 1980s. The technique relies on the fact that four of the molecule's building blocks, or bases, pair up. Adenine binds to thymine and cytosine binds to guanine.

But back then researches could only build structures from small bits of DNA — some 150 base-pairs long. Large structures built from these components were too floppy to maintain their shape, limiting the kinds of objects scientists could make. That changed a decade ago, when Paul Rothemund of the California Institute of Technology demonstrated that short strands of DNA could be used to staple or clip together sections of a much larger piece of DNA. He called the technique DNA origami.

With the support provided by stapling, researchers have now used origami with DNA as large as 50,000 base pairs in length. From these DNA templates, scientists have fashioned such structures as miniature containers that spring open to deliver drugs to specific parts of the body. But with the new freedom to build larger and more complex shapes comes a higher probability for error. The greater the number of folds or the more staples needed—most patterns require several hundred—the more likely that the DNA strand will fail to form the intended structure.

A high failure rate and an inability to predict the order in which folds should happen to minimize errors: Those two problems must be solved if DNA origami is to become a reliable, high-yield nanomanufacturing technique, says CNST physicist Michael Zwolak. In a new study of the thermodynamics and dynamics of folding, he has developed a formula that predicts the likelihood of error in a DNA origami folding process and suggests how to place staples in a way that minimizes or even repairs mistakes.



DNA section with a fold. Credit: CNST/NIST

"The idea is to quantify the failure modes and to calculate which folded structures will have problems and which ones won't," he says.

To understand Zwolak's formula, it's useful to consider a simpler phenomenon. Consider a chemical reaction in which two compounds, A and B, interact to produce a new compound, C. How rapidly will the combination of A + B produce C? According to the rules of chemical kinetics, the rate is proportional to the concentration of A times the concentration of B.

In the case of DNA origami, each fold occurs through a two-step process. First, the unfolded DNA and the staple interact. Then a unimolecular process follows: the DNA folds, allowing the staple to bind separated regions. Instead of inquiring how rapidly the whole process will proceed, Zwolak wants to determine the likelihood of "mishaps" during this process. To do so, he invokes what is in effect a stand-in for a second reactant during the fold. Known as the j-factor, this term includes such information as the average distance between the two sections of DNA that are to be joined and the amount of time each section would naturally spend near the other. The shorter the separating stretch of single-stranded DNA, or the more time the two regions spend together, the larger the j-factor, and the greater the likelihood that the DNA segment can be folded into the desired shape. The bottom line is that the formula can guide researchers in selecting a folding pathway that will maximize production, or yield, of the target nanostructure.

"Everybody recognizes yield as a huge problem in DNA origami," says Zwolak, "but no one had bothered to tackle it."

Zwolak's predictive formula now awaits confirmation with laboratory studies that CNST researcher Daniel Schiffels and his colleagues are now conducting. In the meantime, the development of the equation and framework remains a key step in bringing DNA origami into the manufacturing fold.

How fast—and at what temperature—does DNA origami fold? M. Zwolak, D. Schiffels and J. A. Liddle. Annual Meeting of Foundations of Nanoscience: Self Assembled Architectures and Devices, April 2016. (http://www.cs.duke.edu/FNANO16)

# READY FOR USE: NEW INSTRUMENTS IN THE NANOFAB

This summer, the NanoFab began operating a panoply of new instruments to help researchers make and measure nanostructures. The instruments range from a silane deposition tool that combines cleaning and vaporization in one instrument to a field emission scanning electron microscope with novel imaging features. Here is a quick introduction to what is new.

## Low Voltage and Imaging 200 mm Samples: New FESEM's Novel Capabilities

Imaging the structure of nanomaterials with a resolution finer than 1 nanometer and a magnification greater than a million, the NanoFab's new field emission scanning electron microscope (FESEM) offers several advantages over older tools. Because the instrument, a JEOL JSM-7800F FESEM, can operate at voltages as low as 10 volts, it can image resist-coated wafers, quartz wafers and other non-conducting samples without having to apply a conductive coating to protect the material. The microscope also has enhanced long-term beam stability along with high beam currents and can image entire wafers up to 200 mm in diameter. The instrument is located in the NanoFab cleanroom to allow easy imaging of wafers between process steps as well as imaging routine samples.

## Automated Wafer Cleaners Offer Safer and More Efficient Processing

Wafer cleaning is one of the most fundamental and critical processes in nanofabrication. The cleaning process removes particle defects, along with organic and ionic contaminants that could otherwise slow production and lead to poor performance and eventual failure of the device.

To increase the efficiency and safety of wafer cleaning, the NanoFab has installed three new automated systems. In a pre-programmed process, each system uses a high-velocity acid spray under high pressure to remove contaminants one wafer at a time without exposing researchers to harsh chemicals, while avoiding contamination between wafers. A user touches the wafer only during loading and unloading; the cleaning process is done behind the closed doors of the machine and all chemicals are confined to designated areas. Cleaning wafers as large as 200 millimeters in diameter, the automated systems limit defects to a size no bigger than 0.25 micrometers and a number no greater than 10 per wafer.

The automated devices replace the current cleaning system, in which wafers are manually immersed in an acid bath, with the user pouring the chemicals while wearing an apron, face shield and acid gloves. Although the baths are drained and washed, some of the chemicals and potential contaminants from the previous wafer may remain; the new system's spray contains only fresh chemicals that have not touched other wafers.

Two of the three automated systems are dedicated to Piranha cleaning, which uses a mixture of sulfuric acid and hydrogen peroxide. The other system uses RCA cleaning, a three-step process in which organic contaminants are first removed using ammonium hydroxide; an oxide layer and ionic contaminants introduced during the first step are then sequentially removed using several acids.

## New Rapid Thermal Annealer Provides High Ramp Rate and Greater Reliability

Heating, or annealing, is another fundamental process in a nanofabrication facility. Annealing can switch on the electrical properties of ions implanted in a semiconductor wafer, repair damage to the orderly, crystal structure of a semiconductor and remove impurities.

The CNST has installed a new rapid thermal annealing (RTA) tool, the AnnealSys AS-Master 2000 HT, which can uniformly heat wafers as large as 200 millimeters in diameter from 150 °C up to 1,500 °C. The tool can increase the temperature of samples at a rate as rapid as 200 °C /sec. The rapid heating enables diffusion processing to be highly controlled and repeatable; the high temperature allows materials with a high sublimation point, such as silicon carbide, to be treated. To limit contamination, the tool can heat samples in the inert environment of argon or nitrogen gas or in vacuum. Available in the clean room, the device also promises to open up new areas of high-temperature research in the NanoFab.

## Acid Wet Bench Offers Increased Capacity and Efficiency

The NanoFab's new acid wet bench allows three researchers to work side by side. Each

New Acid Web Bench. Credit: CNST/NIST

position on the bench is equipped with an electronic timer, a time-controlled integrated stirring hot plate, a sink, glove rinse, a nitrogen gun, an aspirator and a deionized water spray. A tapered design provides a better view of the experiment while the mesh-covered bench top allows for improved drainage.

### Upgrades to FIB Microscope Enhance Imaging and Deposition Capabilities

Upgrades to one of the pair of the NanoFab's focused ion beam microscopes have endowed the instrument with two new capabilities. As an imager, the microscope can now detect the subtle differences between materials that have highly similar composition, including composites.

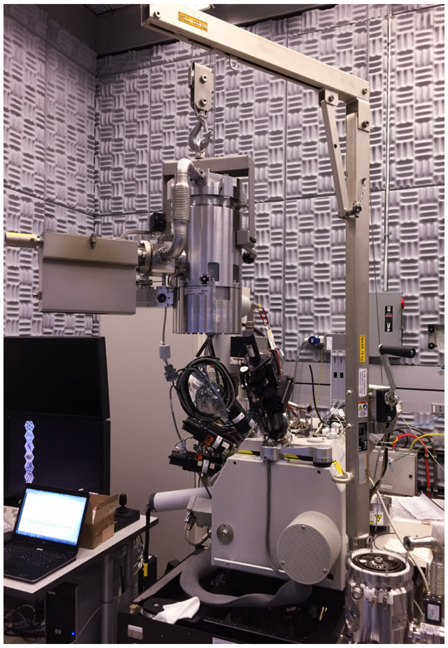
Two new electron detectors, perched high above the imaged sample, make it possible for the Helios 660 DualBeam microscope to differentiate materials with nearly identical structures. These detectors record electrons from the microscope's beam that bounce elastically off of atoms in the sample, resulting in little or no loss of electron energy. Larger atoms have a greater probability of producing elastic collisions, resulting in a greater number of these so-called low-loss and no-loss backscatter electrons. Thus, the number of electrons recorded by the new detectors is a sensitive indicator of atomic composition.

The detectors can be used in concert with the microscope's existing electron detectors, which provide topographic information by recording the secondary electrons generated when the microscope's beam ionizes the sample.

A similar upgrade to the NanoFab's other Helios DualBeam microscope is expected by the end of the summer.

### One Instrument, Two Processes: Silane Tool Combines Cleaning and Vaporization

Creating a nonstick surface, silane deposition occupies a small but crucial step in soft lithography, the process in which an elastic material—typically polydimethylsiloxane (PDMS)—is used to fabricate flexible stamps and molds. To make these flexible components, researchers begin with a patterned silicon wafer, which acts as a rigid master mold.



Assembly of FIB Miscroscope.
Credit: CNST/NIST

Before liquid PDMS is poured over that mold to make a flexible casting, the wafer is coated with a thin layer of silane, a silicone-based material. The silane coating prevents the PDMS from adhering to the wafer, making the clear, pliable material easy to peel off after hardening.

The new deposition instrument combines in one tool two processes –cleaning and vaporization—that had previously required separate instruments.

Under the old system, a researcher first cleaned the imprinted wafer with a solution, followed by exposure to a plasma, or highly ionized gas, which acts like a sandblaster to scrub away impurities. Then the user transferred the wafer, along with a container of liquid silane, to a desiccator, which vaporized the silane solution under vacuum. Vaporized silane molecules settle down on the surface of the wafer to form a monolayer coating.

The new stand-alone tool—the first of its kind at NIST—automatically accomplishes baking, plasma cleaning and silane deposition in one run, all without exposing researchers to silane-based chemicals. This will not only increase the CNST's capability to serve more users, but also provide improved process performance and productivity for nanofabrication.

### PDMS Tool Provides Thoroughly Modern Mixing

The NanoFab has a new spin on the silicone polymer known as polydimethylsiloxane (PDMS)—a staple in any soft lithography lab for fabricating flexible molds of minute, highly detailed patterns. A new tool thoroughly mixes PDMS components at precise speeds by simultaneously rotating the clear liquid in two different planes. The mixer enables trained users to produce polymer films whose thickness, composition and other properties are highly reproducible. Such uniformity enhances a key trait of PDMS—its ability, when pored over a patterned silicon wafer, to transfer patterns, such as microfluidic channels, less than a micrometer in diameter.

### PDMS Instrument Features Precision Punching with Three Needle Sizes

The NanoFab has purchased a PDMS puncher for the soft lithography laboratory. Featuring three needle sizes—500, 600 and 700 micrometers in diameter—the puncher is used in tandem with a microscope and screen, enabling researchers to home in on the precise location to punch holes in hardened PDMS. The tool is especially useful for fabricating multilayer microchannels, miniature troughs that control the flow of fluids. The small diameter of the holes allows for tighter packing of the microchannels on a chip.

# CNST: FROM INTERNSHIP TO JOB

A year ago, Alex Galli graduated from the University of Kansas with an interest in nanotechnology but no experience in the field. Now he's employed in a nanotech clean room at one of the foremost aerospace firms in the nation.

Critical to getting that job, Galli says, was a 4-month internship that he recently completed at the CNST. Co-sponsored by the Northeast Education and Technology Education Center (NEATEC) (http://neatec.org/), the internship gave Galli, now 23, hands-on experience with electron microscopes, vapor deposition tools and other nanotech instruments. (Galli's internship followed a summer workshop on nanotechnology at Penn State.) At the NanoFab, Galli applied the computer skills he acquired as a physics major at the U of Kansas to implement and configure new quality control software.

During a four-month internship in the NanoFab, Alex Galli applied his computer skills to implement and configure new quality control software. He began a full-time job at a major aerospace corporation the week after his internship ended. Credit: CNST/NIST

The software, based on a technique known as Statistical Process Control, is critical for quickly determining whether a NanoFab machine or process is meeting operating standards. For instance, the software revealed that something had gone awry in an electron beam vapor deposition process. In that operation, an electron beam heats and vaporizes a solid metal target in order to lay down a metal film of a specified thickness. Although the process should be repeatable thousands of times with virtually identical results, the software indicated that it had begun producing films about 20 nanometers thinner than desired.

Galli helped trace the problem to a cracked crucible holding the heated metal. The crack prevented the crucible from cooling properly, resulting in an anomalously thin layer.

It took time, he says, to understand the idiosyncrasies of the software and figure out the best format in which to input data collected from the NanoFab instruments. But by the end of Galli's internship, the software was monitoring some 100 processes on some 30 instruments in the NanoFab. Weekly to monthly, he also operated and recorded data from some of the instruments.

One of the best parts of the internship, he says, was simply "being part of NIST," Galli says. "There was so much going on all the time; there would be a seminar every week or so. I loved attending those because the research is so exciting."

By this fall, nine students will have completed the CNST-NEATEC internship program, which began in 2014. An intern from 2015, Paul Barrett, was hired by the CNST as a part-time lab assistant just after he finished the program.

"For someone who is still in school and just wants nanofabrication experience, or a recent graduate who's interested in the field but who may not have been exposed to it during their undergrad, it's a great opportunity," says Galli.

Always looking toward the future, Galli had applied for a job at Northrup Grumman even before he began his CNST internship. The interview took place while he was at the NanoFab. His work experience there "definitely set me apart from everyone else," Galli says. He finished the internship on Friday, April 29, and joined the company, at its Linthicum, Md., location, the following Monday.

# NANOFAB PIONEERS NEW PROCESS TO FABRICATE HIGH ASPECT RATIO NANOGRATINGS

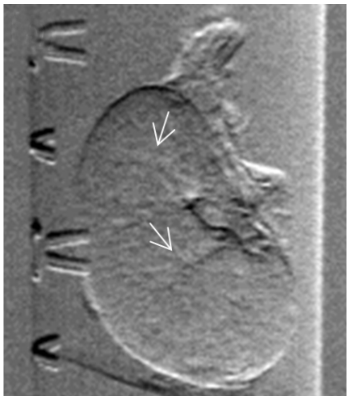
Researchers using the CNST NanoFab have developed a new method to construct nanogratings that have a high aspect ratio—structures characterized by a large ratio of height to width. Resembling the teeth of a comb shrunk to the nanoscale, the gratings have deep but narrow trenches separated by high walls. High-aspect-ratio nanogratings play a critical role in X-ray imaging, enabling medical researchers to image human tissue with a much lower X-ray dose than would otherwise be required.

However, the narrow, finely-spaced gratings are challenging to make. Fabricating the structure over a large area can be costly. In addition, etching a series of perfectly straight, high-walled silicon trenches has proven difficult because the thin walls can be easily damaged or collapse if they are not completely perpendicular to the trough. It's also been tricky to ensure that the metal coating—platinum in this case—is evenly deposited on the sidewalls and reaches to the very bottom of the trenches.

To address these issues, researchers from the National Institutes of Health working with NanoFab process engineer Lei Chen used a low cost, high-fidelity nanoimprint lithography technology to fabricate the nanogratings over a large area. They also developed several processes for etching the grating structure into a silicon wafer.

The scientists determined that using a master pattern to replicate nanogratings would be the most reliable and cost-effective method. The researchers then experimented with different plasma conditions, gas combinations and masking materials to transfer the surface pattern into high-aspect-ratio nanogratings.

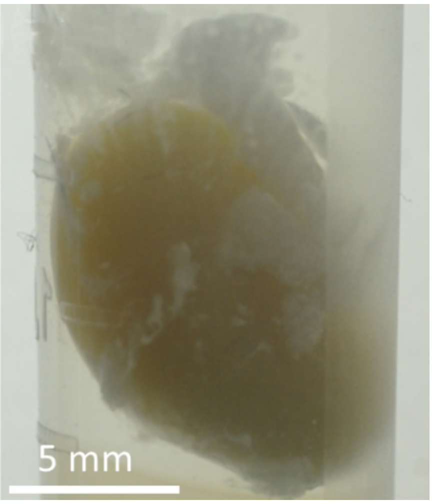
To ensure that the platinum fully covered the surface of the grating, the researchers modified the atomic vapor deposition method of applying the coating. In that method, a so-called precursor vapor reacts with the etched silicon surface, producing a single layer of platinum atoms to coat the structure. The team explored the effect of varying the time for the precursor vapor to diffuse onto the silicon surface, as well as variations in the silicon surface chemistry.



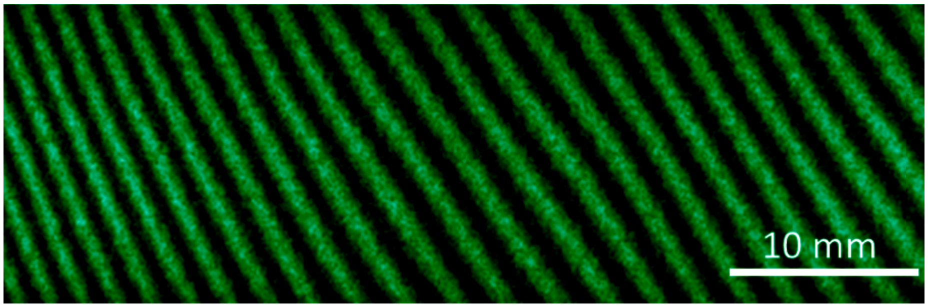
X-ray phase image using the nanograting shows the outline and internal blood vessels (white arrows) of a mouse kidney. Credit: CNST/NIST

While studying the platinum deposition process, the team found that a protective layer that had been applied to the silicon walls during etching interfered with the reaction between the gas and the surface, preventing the platinum atoms from uniformly coating the grating. The team found that by using an oxidizing agent to strip the protective layer or by covering the layer with aluminum oxide, platinum could be deposited evenly and reach the bottom of each trough.

The thin platinum coating served as a foundation upon which the researchers filled the trench with gold. The team succeeded in producing nanogratings with a height-to-width-ratio of 30:1, with little or no undercut. At NIH, scientists have now used these nanogratings in an X-ray phase imaging project. The researchers reported their findings in the April 25 *Nature Physics*.



Visible-light photograph of a mouse kidney, suspended in water, that was imaged with the X-ray nanograting. Credit: CNST/NIST



Moiré fringes, a type of interference pattern, obtained with an X-ray interferometer constructed with three nanogratings produced in the NanoFab. This picture was taken without the kidney specimen depicted in the other images.Credit: CNST/NIST

A universal moiré effect and application in X-ray phase-contrast imaging. H. Miao, A. Panna, A.A. Gomella, E.E. Bennett, S. Znati, L. Chen and H. Wen. *Nature Physics* , April 25, 2016, doi:10.1038/nphys3734

# CNST POWERS UP NEW STUDY TO MAKE A BETTER BATTERY

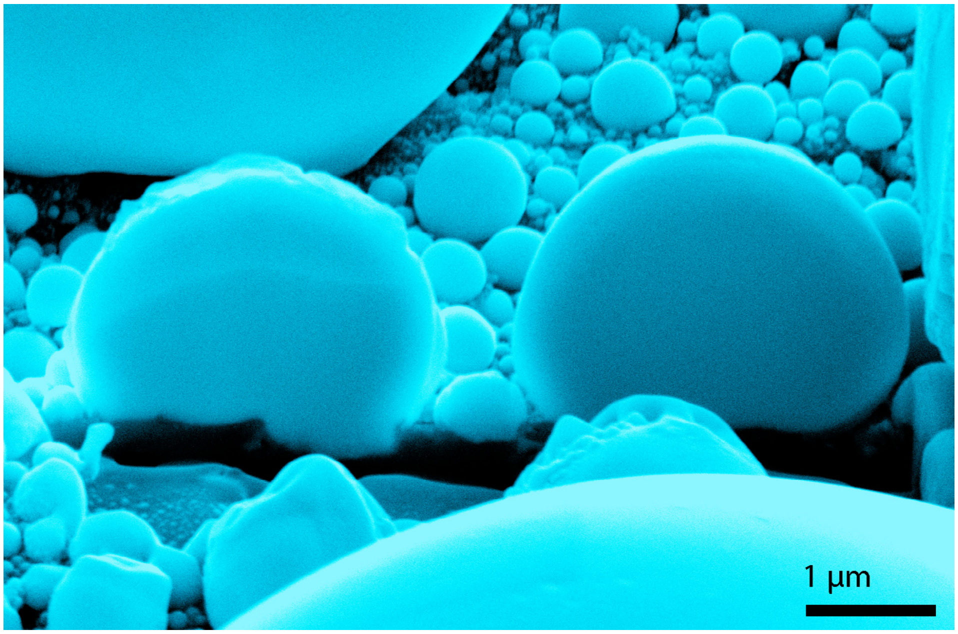
It would be hard to imagine the modern world without lithium-ion batteries. These powerhouses provide the energy for nearly all portable electronic devices—smartphones, laptop computers, music players, along with such high-tech gizmos as drones, hoverboards and electric cars.

Lithium, the lightest metal in the periodic table, can help batteries hold a charge much better than batteries made of heavier materials, such as lead, nickel and cadmium. And unlike other devices, lithium-ion batteries don't suffer from the "memory effect," which prevents batteries from holding a full charge unless they are drained completely before recharging. But even as these batteries have grown lighter and more efficient, giving rise to slimmer laptops and smartphones, they still don't meet the increasing energy demands of all the new technology being developed.

Although durable, lithium batteries lose their ability to hold a charge after about 3 years. Their ability to store power is also limited, requiring phones to be plugged in every night and capping the range of electric cars to a barely tolerable few hundred kilometers. In addition, lithium is highly flammable—millions of laptop batteries have been recalled because they have the potential to short circuit and explode, and the FAA has banned the transport of the batteries after multiple reports of cargo airplane fires.

To to make a better lithium-ion battery or find innovative alternatives, researchers must overcome a knowledge gap, says Jabez McClelland, group leader of the CNST Electron Physics Group. Although lithium-ion has been the battery of choice for two decades, scientists still lack a detailed picture of the atomic and molecular processes that govern the operation—and ultimately limit the usefulness—of these devices.

"To understand what makes a better battery or a worse battery, you have to look at the nanostructure," McClelland says. But research at this level has been lacking.



Scanning electron micrograph of a tin sphere penetrated by lithium ions. Credit: CNST/NIST

That's about to change. In collaboration with NIST's Material Measurement and Physical Measurement Laboratories, McClelland and his CNST colleagues have begun a major study of how lithium batteries behave on the nanoscale. Using instruments that resolve structures only a few tens of atoms in size, the researchers are tracking the flow of lithium ions between the two terminals of a battery—anode and cathode—and how the ions alter the materials in which they move.

"There is a whole new area of research in developing tools to study how lithium moves in materials on the microscopic scale," says McClelland.

To explore the nanoworld of lithium-ion batteries, McClelland's tool of choice is an instrument he and his colleagues developed in 2011, a focused ion beam (FIB) microscope that uses lithium ions as the probe. Using a laser to cool the lithium ions down to a few ten-thousandths of a degree above absolute zero, the researchers have honed the lithium ion beam so that it is only 30 nanometers in diameter.

The narrow beam provides high resolution when the FIB is used to image nanostructures. But in this case, the thinness of the beam is critical for a different reason. The scientists are primarily using the FIB not to image, but as an injector, inserting lithium ions into battery materials. The pencil-like beam makes it possible to inject the lithium ions at specific locations with exquisite precision.

Once the ions are inserted, the scientists watch as the ions diffuse through the materials.

Right off the bat, however, McClelland had a concern. With the lithium ion beam, "we're really smacking the lithium ions in there with an energy of 4,000 electron volts, whereas the lithium ions in a battery have just a few electron volts of energy," he notes. "So there's a big question—is what we're doing in the laboratory really relevant to the way an actual battery operates?"

To find out, he and his collaborators used the lithium ion beam to implant some 100 billion lithium ions into tiny spheres of tin, a battery anode material. They then placed identical spheres of tin in an electrochemical cell, gently injecting the spheres with lithium ions (at low energy) in just the same way as would happen in a battery.

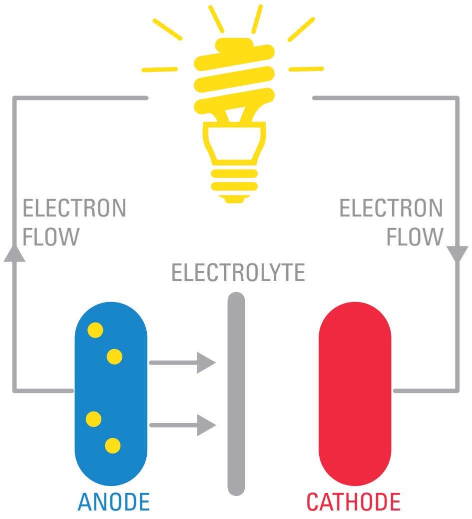
Slicing in half the tin spheres from each experiment with a gallium ion beam and examining them with an electron microscope, the researchers found the same result. In both experiments, the lithium ions had diffused in a similar pattern through the tin. "It's qualitative at this point, but this is an indication that the lithium FIB really is going to be a good tool" to study the movement of lithium in actual batteries, McClelland says. His team reported the findings earlier this year in the *Journal of the Electrochemical Society*.

Ultimately, the researchers want to continue their studies by combining the lithium FIB with an electron microscope and an atomic force microscope—all in the same instrument. This will allow the team to map the nanoscale changes directly as the lithium ions are injected into materials. One area of particular interest is the swelling that lithium ions produce in some materials, a problem that can cause anodes to deteriorate and batteries to fail.

It will take at least a year to finish outfitting a new commercial focused ion beam/electron microscope/atomic force microscope instrument with the researchers' own lithium ion source. But in the meantime, McClelland's team has several other studies they're about to begin with the lithium FIB already in the laboratory.

Over the next few months, McClelland plans to study silicon, a highly desirable anode material that has some drawbacks. Swelling is a particular problem with silicon—as lithium ions move back and forth in the silicon during charging and discharging of a battery, the silicon repeatedly swells and contracts until it crumbles.

One strategy to deal with the swelling is to construct the silicon anode in such a way that it has a Swiss-cheese structure, with microscopic holes between spherical groupings of the silicon particles. That way, when the silicon balls swell, they'll simply expand into empty space rather than bump into other silicon balls, preventing crumbling.



Lithium-Ion Battery Schematic. Yellow dots are lithium ions.

At least that's the hope. A close examination of lithium-implanted silicon at the CNST may reveal new strategies for constructing durable silicon anodes.

In preparation for this study, researchers at the CNST's NanoFab have constructed a layered silicon structure. A thin sheet of silicon, imprinted with a nanostructure, lies on top of wafers coated with silicon dioxide. After implanting lithium ions in the sample, the team plans to apply a voltage across the silicon nanostructures and watch the movement of the ions with the scanning electron microscope and/or the atomic force microscope.

"Given a certain voltage, how easy is it for the ions to move?" asks McClelland. "This will give us a really nice measurement of the mobility of the lithium ions," he adds.

"We're coming up with totally new ways of making measurements using nanotechnology," says McClelland. "We've built this lithium FIB tool knowing the field of battery research is important; now people are starting to send us samples and want to collaborate with us because there's no other focused lithium ion beam microscope like this in the world."

## THE WORKINGS OF A LITHIUM-ION BATTERY

Like all batteries, lithium-ion batteries have three components: two electrodes, known as the cathode and the anode, and an electrolyte solution that lies in between. The electrolyte solution for lithium-ion batteries allows the passage of lithium ions, but not electrons.

Lithium ions migrate back and forth between the two electrodes depending on whether the battery is powering a device or recharging. The entire process is driven by the conversion of chemical energy into electrical energy. For instance, when the battery is fully recharged, chemical energy is stored by forcing lithium into the anode. (The lithium would prefer to be in a lower energy state, when it's in the cathode.)

When the battery is connected to an electric circuit—powering a lamp, for instance—a chemical reaction prompts neutral lithium atoms in the anode to give up an electron. Stripped of their electrons, the atoms become positively charged lithium ions, which migrate from the anode to the cathode.

At the same time, the stripped electrons also leave the anode. Since the electrons cannot travel through the electrolyte, they are forced to exit the battery, moving through wires connected to the lamp, which lights up due to the flow of electric current. The electrons in the wires then re-enter the battery via the cathode, where they recombine with the lithium ions that have migrated there, turning them back into neutral atoms.

When the battery is recharging, an external voltage forces lithium back into the anode. Electrons stripped from the lithium atoms in the cathode travel through the wires back to the anode. There they rejoin the lithium ions that have traveled through the electrolyte.

Communication—Comparison of Nanoscale Focused Ion Beam and Electrochemical Lithiation in β-Sn Microspheres. S. Takeuchi, W.R. McGehee, J.L. Schaefer, T.M. Wilson, K.A. Twedt, E.H. Chang, C.L. Soles, V.P. Oleshko and J.J. McClelland. *Journal of the Electrochemical Society*, 163(6), A 1010-A1012 (2016)

CNST Center for Nanoscale Science & Technology

## CENTER FOR NANOSCALE SCIENCE AND TECHNOLOGY

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## SUPPORTING THE DEVELOPMENT OF NANOTECHNOLOGY FROM DISCOVERY TO PRODUCTION

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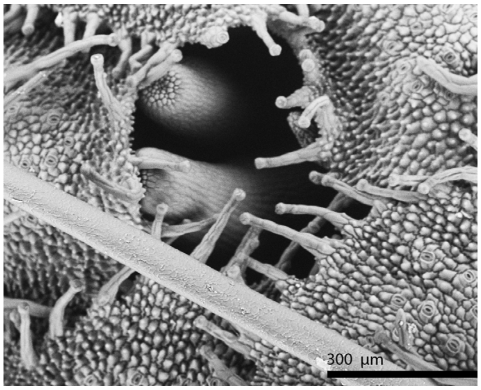
## CNST'S NANO-FARE DRAWS A CROWD AT THE MAKER FAIRE

At the June National Maker Faire in Washington, D.C. (http://www.udc.edu/wp/test/national-maker-faire), tech-savvy tinkerers, crafters and educators gave the public the chance to interact with a smorgasbord of 3D printers, homemade robots, Arduino circuit boards and assorted crafts. Among the participants: CNST electrical engineer Daron Westly, who wowed children and adults with images taken with a tabletop scanning electron microscope brought from the NanoFab.

In between imaging people's hair—juxtaposed for scale with plant parts or bugs that he or others found at the outdoor festival—Westly explained nanotechnology and the CNST's role in the field. "I also brought a real sample from Vladimir Aksyuk's lab—thanks to Thomas Michels—and put a hair on it for reference to discuss an actual ongoing photonics project," says Westly. "For some reason discussing photonics becomes more interesting to the average person when there is a hair laying right across the device."



Micrograph taken at the Maker Faire shows relative scale of a strand of hair and flower bud. Credit: Daron Westly/CNST

CNST electrical engineer Daron Westly demonstrates a tabletop electron microscope at the Maker Faire. Credit: Heather Evans/NIST

Some people who heard Westly talk on Saturday came back the next day to ask follow-up questions; one girl asked him to image an ant crawling on her finger. "For me, the heart of it is the joy of sharing," Westly says.

At the festival, Westly also showed off his personal project, a CubeSat built with the help of high school students in Puerto Rico, that is designed to fly on a high-altitude glider. Designed in collaboration with his wife and another scientist, the miniature device is outfitted with detectors to find out if fungal spores can survive in the stratosphere.