THE CNST NEWS

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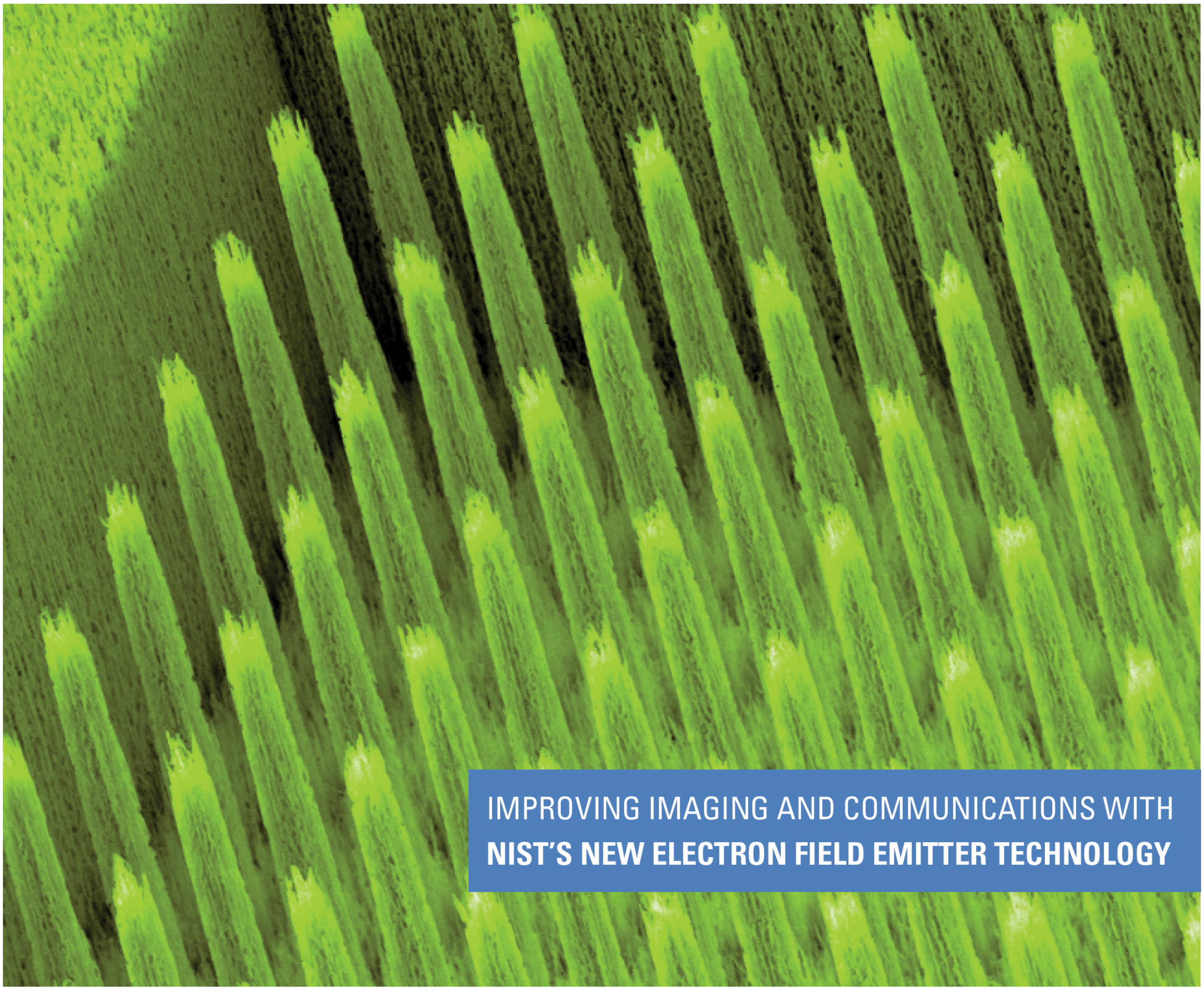

INSIDE

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

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FROM THE DIRECTOR

Because of its traditionally important contribution to the nation's economy, manufacturing is prominently in the news these days and nanomanufacturing is very much talked about as being an area of potentially strong future growth, with the capacity to revitalize the nation's high-tech industrial base. Of course, nanomanufacturing in the sense of integrated circuitry has been a mainstay of the U.S. economy for years, due mainly to the phenomenal advances in tools, processes, and design of the last fifty years that have brought us from the invention of the transistor to chips incorporating billions of transistors.

The current challenge is to turn recent nanotech discoveries into products by developing scalable nanomanufacturing techniques for relatively low-cost, low-complexity materials—e.g., nanoreinforced composites, coatings, functionalized nanoparticles, etc.—items which we may already know how to fabricate, but not manufacture. An essential difference between nanofabrication and nanomanufacturing is cost; you have to put money into nanofabrication, but expect to take money out of nanomanufacturing!

How then does a user facility, such as the CNST, help develop new nanomanufacturing industries? There are many ways. Some of our projects are aimed at prototyping simplified production methods thought amenable to scaling. Others deal with the very challenging task of developing faster, lower-cost metrologies to assess final products or even monitor production processes in real time. For example, one project aims at linking atomic-scale observation of nanotube growth with microwave measurements that are practical in the roll-to-roll production of nanotube-reinforced composite material in a manufacturing environment.

In the ideal case, a metrology linkage would be established across multiple length, time, and cost scales. It might start with nanofabrication of a device or structure on the length scale that exhibits the nanoscale phenomena at the heart of the device. For a lithium-ion battery, this might be the diffusion length of the lithium, for example. Then, measurement technology capable of providing an understanding of the operation and properties of this nanoscale object would be applied or, if necessary, developed. Once the fundamental properties and behavior of the nanostructure are well understood, the next step would be to fabricate an array of nearly identical structures on the microscale so that an ensemble measurement technique, such as optical spectroscopy, could be used to characterize the properties in a way that correlates well with the precise but time-consuming atomic-scale measurements. If this proves possible, the correlated optical technique may provide a fast, economic, and robust way to monitor, or even control, nanoscale properties in a manufacturing environment. All but the final test in a true manufacturing environment lies within the mission and combined capabilities of the CNST NanoFab and NanoLab, and demonstration projects are underway following this general design.

If you know of a technology where this approach might work well, or if you have all but one link of this metrology chain, please let us know; we just might be able to help!

Robert Celotta

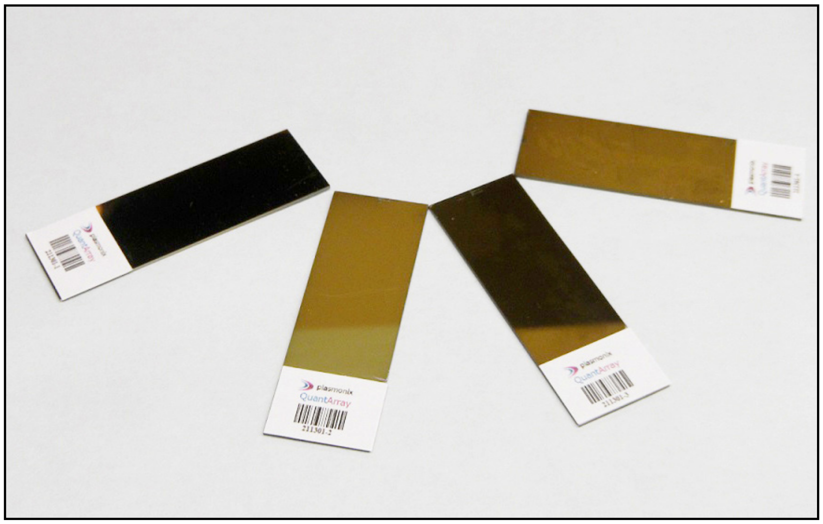
MARYLAND STARTUP IMPROVES FLUORESCENCE-BASED MICROARRAYS FOR DISEASE DETECTION

Working with CNST NanoFab engineers, researchers from Plasmonix, Inc., have built prototype plasmonic substrates for use in fluorescence-based microarrays. By allowing light to interact with metal nanoparticles, these plasmonic substrates increase the intensity of fluorophores (fluorescent molecules) by several orders of magnitude, improving the sensitivity of existing fluorescence-based protein microarray assays. Their device has the potential to expand the useful range of fluorescence for applications in clinical diagnostics and drug development without adding significant experimental time or operating costs.

Fluorescence is one of the most prevalent molecular and cellular detection technologies used today in medical research and clinical diagnostics (including immunology, pathology, cytogenetics, and microbiology). Protein microarrays, which allow parallel simultaneous detection of many disease-causing agents, use fluorescing molecules that are selectively bound to detection molecules in order to assess the state of a variety of diseases, including cancer.

Unfortunately, fluorescence signals are often too weak for detecting low abundance targets. This low signal strength has limited fluorescence's usefulness for onsite clinical diagnostic tests and for cost-effective drug development. The typical solution to this problem, when possible, has been to use complex molecular signal amplifiers that require additional time and cost.

Leveraging techniques developed at the University of Maryland, School of Medicine Center for Fluorescence Spectroscopy, the Plasmonix team, led by James Russo and Sean Higgins, has developed a device to enhance microarray fluorescence signals with only minimal increases in the background signal. The device consists of multilayered thin-films whose surface contains metal nanoparticles and is fabricated on a conventional glass or plastic microscope slide, allowing it to drop into existing commercial microarray systems. The top layers are plasmonic and excite fluorophores on the device's surface, while the lowest layer is photonic and carries light into the system.



Built on conventional microscope slides, the Plasmonix device is intended to work with existing commercial microarray systems. Designed and fabricated in the NanoFab, they enhance fluorescence by approximately a factor of a hundred over background signal.

When exposed to light of a certain wavelength, nanoparticles in the plasmonic layer excite localized surface plasmons (a type of electromagnetic field) which can interact with nearby fluorophores on the device's surface. The field makes the fluorophores brighter by altering the photo-physics of fluorophores. One key effect is that fluorophore lifetimes are decreased, reducing the time for undesired reactions to occur. Collectively, these effects contribute to increasing the fluorescence signal without increasing the background signal.

The system, which has been tested with a variety of standard fluorescence-based assays, enhances the fluorescence signal by a hundred-fold over the background signal, resulting in a corresponding improvement in assay sensitivity.

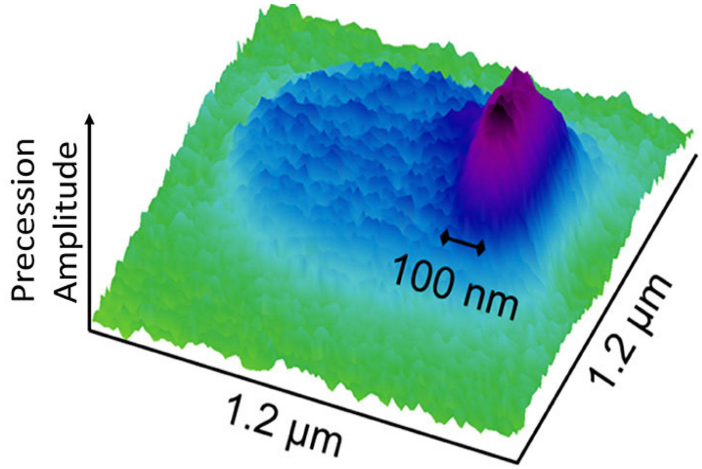
In June 2013, Plasmonix was chosen as the Maryland Incubator Company of the Year for Technology Transfer. Based in the bwtech@UMBC incubator, a research and technology park set up by the University of Maryland, Baltimore County, Plasmonix focuses on improving disease detection assays. The researchers credit their success in translating research ideas into a fabrication process to help from NanoFab staff members Vince Luciani and Gerard Henein. According to Jim Russo, "We started with a 'recipe' from an academic setting and ended up with a product that is close to commercialization. It is hard to find the type of support for developing processes that we have found at NIST in any other facility." Russo explains, "having multiple instruments, including electron beam evaporators, sputtering tools, and metrology equipment, lets us develop processes and determine the right way to build our devices without having to raise millions of dollars of investor money for process development, which would be difficult."

Based on their results, Russo believes the company has developed a practical platform that lends itself to manufacturing with product costs comparable to conventional microarray slides.

Plasmonix is now working with commercial microarray technology partners to beta-test their device in typical microarray settings. They are also scaling up the process for production. They are preparing to move the fabrication to a contract manufacturing organization that can prepare the surfaces. They have also taken cost estimates for building their own facility with their own electron beam evaporator and sputtering unit, and are investigating vendors of thin-film coatings in order to increase their capacity.

NANOSCALE EDGE VARIATIONS OBSERVED WITH RECORD-BREAKING RESOLUTION IN MAGNETIC NANODEVICES

A team of researchers from the Royal Institute of Technology, Stockholm, the University of Maryland, College Park and the CNST have measured large variations in the magnetic properties along the edge of a thin film 500 nm-diameter disk. This work represents a significant development in the measurement of magnetic thin film edge properties, which are especially important for nanodevices, such as magnetic memory cells, where the edge to area ratio is large.



Ferromagnetic resonance force microscopy image of the precession of an edge mode in a 500 nm-diameter permalloy disk. The disk appears as a blue region, and the precession of the edge mode appears as a purple peak on the right.

The researchers' technique, called ferromagnetic resonance force microscopy, detects magnetic resonance in a sample through changes in the magnetic force between the sample and a magnetic cantilever tip. Their recent measurements profiled that edge mode with a record 100 nm resolution. The technique uses an external field from a nearby microwave antenna to excite a magnetic resonance that causes the sample's magnetization to precess, wobbling like a top, billions of times per second. This precession leads to a small decrease in the time-averaged magnetization that can be detected as a change in the magnetic force on the cantilever. With an external field applied in the plane of the film, modeling predicts that an "edge mode" forms in which the precession is localized to within 30 nm of the edge. By rotating the applied field direction, the location of the edge mode is then moved along the circumference of the disk, with changes in the magnetic resonance mapping out variations in magnetic properties along the edge.

The researchers believe that continued development of ferromagnetic resonance force microscopy methods will enable measurements of individual magnetic nanodevices, providing important new information about the properties of these devices and their potential defects.

Spectroscopy and imaging of edge modes in Permalloy nanodisks, F. Guo, L. M. Belova, and R. D. McMichael, *Physical Review Letters*, **110**, 017601 (2013).

CALCULATING QUANTUM VACUUM FORCES IN NANOSTRUCTURES

One of the surprising predictions of quantum mechanics is that uncharged conductors can attract each other over small distances, even in empty space. While the resulting "Casimir force" has been accurately measured and calculated for simple flat conductors, researchers from the Department of Energy, Indiana University-Purdue University Indianapolis, and the CNST have solved the much more complicated problem of calculating this force between metal plates with complicated periodic nanoscale structures on their surfaces. This type of surface nanostructuring is currently being explored in order to control the Casimir force in microscopic mechanical sensors, actuators, and electrical relay devices.

The Casimir force has been notoriously difficult to calculate for complicated structures because an infinite number of electromagnetic quantum vacuum fluctuations have to be taken into account. Previous methods were prone to numerical errors and took weeks of computer time to carefully combine the results from numerically solving Maxwell's equations, which describe the physics of electromagnetism, thousands of times. The researchers have now analytically pre-calculated a series of eigenmodes, or exact solutions for specific cases, that can be combined much more simply to produce the force for any particular periodic nanostructure. This analytical calculation also gives simple insight into how the force behaves in various important situations.

The researchers expect the analytical techniques they have developed will have broader applications for calculating other forces induced by fluctuations, including thermal emissions and near-field heat transfer. They are now applying these techniques to understand the results of recent Casimir force experiments on nanostructured surfaces.

Quasianalytical modal approach for computing Casimir interactions in periodic nanostructures, F. Intravaia, P. S. Davids, R. S. Decca, V. A. Aksyuk, D. López, and D. A. R. Dalvit, *Physical Review A* **86**, 042101 (2012).

NEW ELECTRON FIELD EMITTER COULD IMPROVE IMAGING AND COMMUNICATIONS

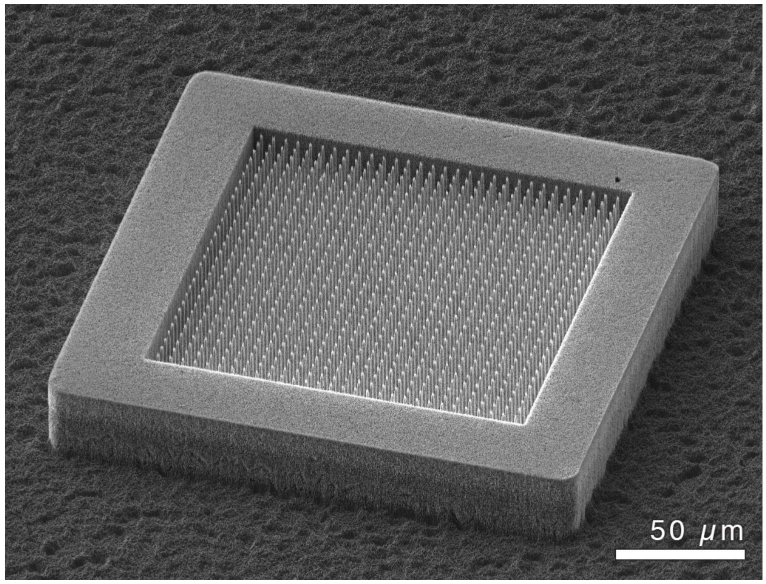
Scientists from the CNST and the University of Maryland, College Park, have built a practical, high efficiency, nanostructured electron source. This new, patent-pending technology could lead to improved microwave communications and radar, and more notably to new and improved X-ray imaging systems for security and healthcare applications.

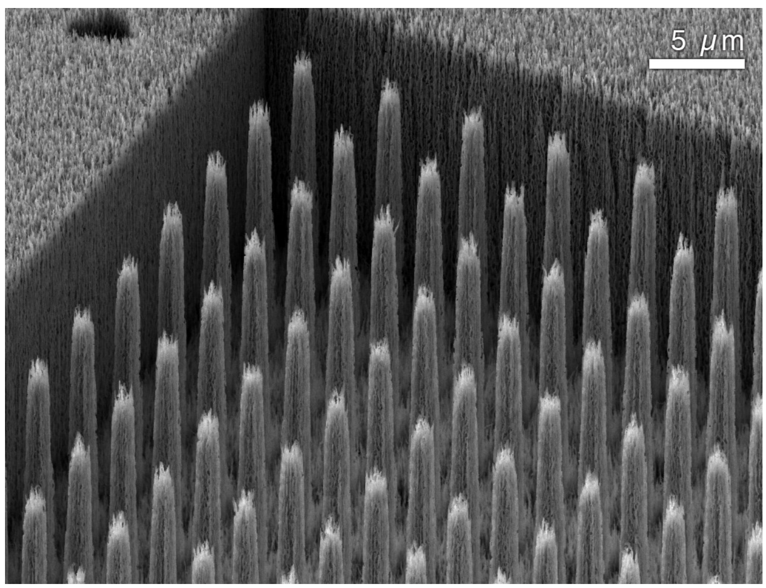
While thermionic electron sources such as the hot filaments inside cathode ray tubes have largely been replaced by LEDs and liquid crystals for display screens and televisions, they are still used to produce microwaves for radar and X-rays for medical imaging. Thermionic sources use an electric current to boil electrons off the surface of a wire filament, similar to the way an incandescent light bulb uses an electric current to heat a wire filament until it glows.

And like an incandescent light bulb, thermionic sources are generally not very energy efficient. It takes a lot of power to boil off the electrons, which spew in every direction. Those that aren't lost have to be captured and focused using a complicated system of electric and magnetic fields. Field emission electron sources require much less power and produce a much more directional and easily controllable stream of electrons.

To build their field emission source, the NIST team took a tough material—silicon carbide—and used a room temperature chemical process to make it highly porous like a sponge. They then patterned it into microscopic emitting structures in the shape of pointed rods or sharp-edged fins. When an electric field is applied, these novel field emitters can produce an electron flow comparable to a thermionic source but without all the disadvantages—and with many advantages.

According to co-inventor Fred Sharifi, the new field emitters have inherently fast response times compared with thermionic sources, and the absence of heat makes it easier to create arrays of sources. Moreover, the porous nanostructure of the emitters makes them very reliable. Even if the emitter surface wears away during use—a common problem—the newly exposed material continues to work just as well.





The silicon carbide field emitter produces a flow of electrons comparable to hot sources, but without the need for heat. By dissolving much of the material away and then using a focused ion beam system in the CNST NanoFab to etch an array of porous silicon carbide emitters with large surface areas, the scientists ensured that as an electron emission point on an individual spike wears out, another is available to take its place, making the array more durable as a whole.

Sharifi says that the NIST field emitters hold the potential to enhance the resolution and quality of X-ray images and allow for new modes of detection.

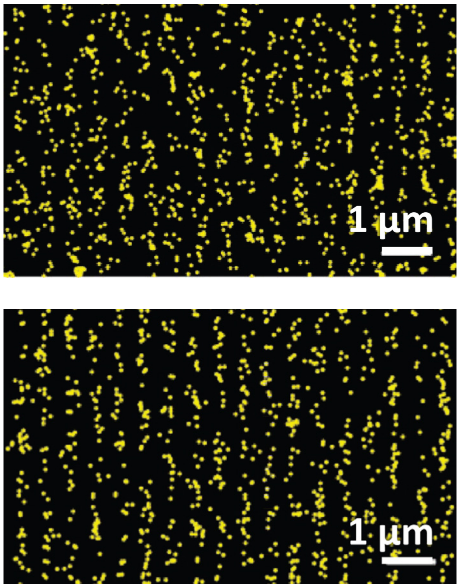
"X-ray images are based on the density of the material being examined, which limits their ability to see certain types of materials, including some types of explosives," says Sharifi. "Our field emitter will let us see not just that something is there, but, because we can build large arrays and place them at different angles, we can identify the material in question by looking at how the X-rays coming from different directions scatter from the object."

Stable field emission from nanoporous silicon carbide, M.-G. Kang, H. J. Lezec, and F. Sharifi, *Nanotechnology* **24**, 065201 (2013).

FLUORESCENCE TECHNIQUE MEASURES PHOTOACID DISTRIBUTION IN PHOTORESISTS WITH NANOSCALE RESOLUTION

A team of researchers from the CNST, the University of Maryland, College Park, and Korea University (Seoul, Korea) has measured the nanoscale distribution of photoacid molecules in photoresists using a fluorescence technique originally developed to provide images of biological structures smaller than the wavelength of light. Photoresists are light-sensitive chemicals used for manufacturing the semiconductor integrated circuits found in computers and other electronics. By measuring the chemical reactions in photoresists at a smaller length scale, this method potentially opens a path to manufacturing smaller electronic devices.

In today's photoresists, chemical amplification of light allows for the use of low-brightness short-wavelength light sources, which enable smaller feature sizes to be printed at higher throughputs. Each individual photon activates a molecule which generates a photoacid. During post-exposure baking, the photoacid diffuses, rendering a volume of the resist soluble to developer. This improves the sensitivity, or photospeed, of the resist, but at the cost of degraded image resolution: a result of the photoacid diffusion. Until now, it has only been possible to infer indirectly where the photoacid molecules are produced or how they diffuse by analyzing the resist images after the



The researchers used photoactivation localization microscopy (PALM) data from undeveloped (top) and developed (bottom) resist features. Each point represents one localized fluorophore. Fitting the fluorescent signal of each dye molecule to a two dimensional distribution allows for mapping the locations of the associated photoacid molecules with single-molecule sensitivity.

resist is fully exposed, either before or after it is developed. A more direct measurement is critically needed, however, because the distribution of the photoacid molecules within a resist film limits the minimum feature sizes that can be produced on computer chips. Precise measurements can help photoresist manufacturers understand the processes that lead to loss of image contrast and develop measures to mitigate blur induced by photoacid diffusion.

To observe the location of the photoacid molecules more directly, the research team used a novel fluorescent dye that can be switched from a dark to bright state either by exposure to ultraviolet light or by reaction with a nearby acid molecule. Over time, they fit the fluorescent signal of each dye molecule to a two-dimensional distribution, allowing them to map the locations of the associated photoacid molecules with single-molecule sensitivity. The team also developed new statistical analysis methods that enable them to extract high-resolution information even when there is a very low concentration of fluorescent molecules. This method allows them to be confident that the behavior of the system is not changed by the presence of the fluorophores.

Ultimately, the researchers believe that these techniques will be useful for measuring nanoscale transport processes in a wide variety of soft-matter systems beyond photoresists, such

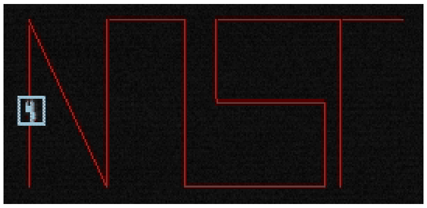
Super-resolution optical measurement of nanoscale photoacid distribution in lithographic materials, A. J. Berro, A. J. Berglund, P. T. Carmichael, J. S. Kim, and J. A. Liddle, *ACS Nano* **6**, 9496–9502 (2012).

NANOWIRE POSITION AND ORIENTATION PRECISELY CONTROLLED USING FLUID FLOW

Scientists from the CNST and the University of Maryland have used a combination of electric fields and fluid flow to precisely move and rotate nanowires, and have demonstrated that this method can be used to manipulate nanowires regardless of whether they are made from dielectric, semiconducting, or metallic materials. Since electro-osmosis, which uses an applied electrostatic potential to move liquid across a fluid channel, is equally effective at moving nanowires regardless of what they are made from, the technique has potential use in a wide variety of applications, including building structures to sense and guide electromagnetic waves, steering nanowire light sources, and guiding nanowires to precisely deliver chemicals to cells.

The researchers fabricated a 170 µm × 170 µm central control region at the intersection of four microchannels. A feedback-control system was used to generate the fluid flows needed to translate and rotate the nanowire. Based on a nanowire's position and orientation, which are observed through a microscope objective, a computer algorithm determines the quartet of voltages needed on the peripheral electrodes to create a fluid flow that will precisely move the nanowire to another specific location and orientation. The device is capable of moving nanowires with an average trapping precision of 600 nm in position and 5.4° in orientation.

Because the technique is material-independent, it can be used to manipulate any type of nanowire or other, more complex rod-shaped structures, leading the researchers to envision a variety of new measurement methods. For example, nanowires can be engineered to respond to their environment by emitting fluorescent light with an intensity related to the local optical field. Using



Micrograph showing a 10 µm × 1 µm fluorescently labeled rod being controlled using a combination of electric fields and fluid flow to travel along the "NIST" path, graphically underlaid in red. The rod is made to simultaneously rotate and align itself tangential to each of the 12 line segments by the time its center of mass reaches the end of a segment. The imaged area is 160 µm × 70 µm.

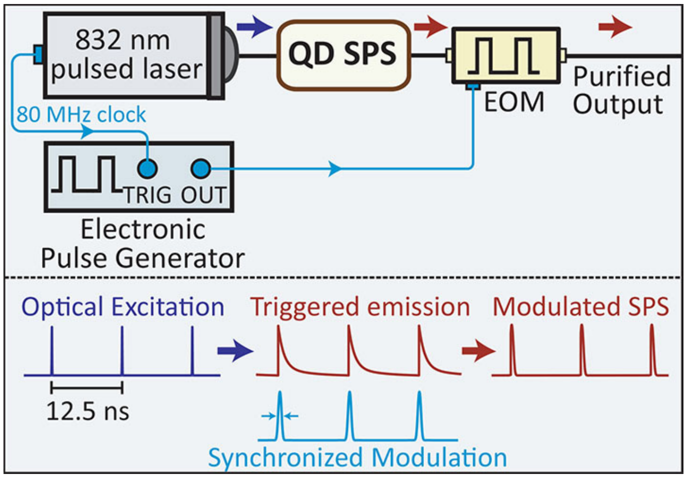
this new method, one could steer such nanowires in liquids around an object of interest, with the fluorescence intensity serving as a reporter of the local field, and thereby map those fields remotely on the nanometer scale.

Simultaneous positioning and orientation of single nano-wires using flow control, P. P. Mathai, P. T. Carmichael, B. A. Shapiro, and J. A. Liddle, *RSC Advances* **3**, 2677–2682 (2013).

NEW TEMPORAL FILTERING TECHNIQUE IMPROVES SOLID-STATE SINGLE PHOTON SOURCES

An international collaboration led by CNST researchers has demonstrated a novel temporal filtering approach that improves the performance of triggered single photon sources based on solid-state quantum emitters. The technique is compatible with a broad class of photon sources, and is expected to provide significant improvements in areas important for applications in photonic quantum information science. The team included researchers from the CNST, the University of Maryland, College Park, the University of Rochester, and Politecnico di Milano, Italy.

Solid-state quantum emitters like quantum dots have great potential to serve as bright, stable single photon sources that can be readily incorporated into systems that can be manufactured with scalable fabrication methods. However, interactions between a quantum emitter and its surrounding environment often lead to non-ideal emission. In particular, events where more than one photon is emitted at a time or where photon waveforms are non-identical are common occurrences that reduce the usefulness of these sources. Previous research has sought to overcome these obstacles by nanofabricating device geometries that make the timescale for photon emission shorter than the time over which environmental influences cause photons to become nonidentical because phase information is degraded. The CNST-led team has now demonstrated a fundamentally different approach—rather than influencing the emission process, they manipulate the emitted light after it has been generated.



Schematic showing a single photon source (SPS) that is created from a quantum dot (QD) by optically pumping it with a periodically pulsed laser. The output of the QD SPS is temporally filtered by an electro-optic modulator, which only transmits light long enough for the components of a single photon pulse that are in phase with each other to be transmitted. This temporal filtering rejects unwanted emission from the QD, producing a higher percentage of single photons and ensuring that the photons are identical to each other.

In the new technique, photons emitted from a fiber-coupled, quantum dot single photon source are directed into a commercial electro-optic modulator that acts as a temporal gate, transmitting light only at specified times and intervals. The periodically pulsed laser that excites the quantum dot also sets the timing for when the modulator is opened. The team found that by optimizing the duration over which the modulator is opened, they could improve single photon purity, rejecting the emission of photons that occur either at different times or at time-scales other than that desired for single photon emission. Furthermore, photons can be made identical to each other by allowing only the portion of the photon waveforms that are in phase with each other to be transmitted.

This temporal filtering approach is very general because it does not depend on the specifics of the source's device geometry, excitation scheme, or materials. Future work will focus on using this technique to deliver improved source performance in applications.

Improving the performance of bright quantum dot single photon sources using temporal filtering via amplitude modulation, S. Ates, I. Agha, A. Gulinatti, I. Rech, A. Badolato, and K. Srinivasan, *Scientific Reports* **3**, 1397 (2013).

A group of visiting engineers receive training on the CNST's two Oxford plasma etch systems. The systems etch a range of materials, including silicon, oxides, nitrides, polymers, III-V compounds, and metals.

CNST Center for Nanoscale Science & Technology

CENTER FOR NANOSCALE SCIENCE AND TECHNOLOGY

The CNST is a national user facility purposely designed to accelerate innovation in nanotechnology-based commerce. Its mission is to operate a national, shared resource for nanoscale fabrication and measurement and develop innovative nanoscale measurement and fabrication capabilities to support researchers from industry, academia, NIST, and other government agencies in advancing nanoscale technology from discovery to production. The Center, located in the Advanced Measurement Laboratory Complex on NIST's Gaithersburg, MD campus, disseminates new nanoscale measurement methods by incorporating them into facility operations, collaborating and partnering with others, and providing international leadership in nanotechnology.

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SUPPORTING THE DEVELOPMENT OF NANOTECHNOLOGY FROM DISCOVERY TO PRODUCTION

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CNST FEATURED ON NATIONAL PUBLIC RADIO AFFILIATE WAMU

The CNST was featured on the Friday, March 22 edition of *Metro Connection*, a weekly radio broadcast by National Public Radio affiliate WAMU that reaches Washington D.C., Maryland, and Virginia. The broadcast discussed the challenges of fabricating devices at the nanoscale and the function of the CNST as a national nanotechnology user facility, and features explanations and commentary by Robert Celotta, CNST's Director, and Vincent Luciani, the NanoFab Manager.

The broadcast, "Stepping Inside The 'NanoFab'," can be heard at: http://wamu.org/programs/metro_connection/13/03/22/stepping_inside_the_nanofab.

In April, the CNST recognized the work of its administrative staff on Administrative Professionals Day. **From top left:** Denise Rogers, Wade Hall, Amy Grafmuller, Jeff Pasternak, Luanne Mehelich, Matthew Gonzales, Teresa Figgs, and Amanda Dyson. **Not shown:** Karen Haugh, Yeehing Lam, and Jennifer Ross.

CNST HOSTS WORKSHOP ON *IN SITU* MEASUREMENTS USING TRANSMISSION ELECTRON MICROSCOPY

On April 11 and 12, 2013, the CNST hosted a workshop focused on *in situ* measurement techniques using transmission electron microscopy (TEM). The workshop, "Frontiers of *In Situ* Transmission Electron Microscopy," was jointly organized with Drexel University and Brookhaven National Laboratory, and co-sponsored by the CNST, FEI Company, and JEOL USA, Inc.

While the concept of *in situ* TEM measurements dates back to the nineteen fifties, the significance of these measurement techniques has increased dramatically during the last fifteen years as TEMs have become more versatile in order to provide the stringent metrology needed for nanotechnology. Advances in all aspects of TEM instrumentation, including application of external stimuli, high resolution spatial and temporal imaging, data capture, and camera technology now enable researchers to make nanoscale dynamic measurements in real-time during chemical reactions.

The workshop featured speakers from equipment manufacturing companies, vendors, academia, and government. The speakers addressed the current status of *in situ* TEM metrology and the need to further improve nanoscale measurement techniques in order to better understand nanofabrication processes. Breakout sessions among 50 participants stimulated lively discussions about ways of overcoming the technological barriers to adding new capabilities to TEM platforms, including ways of acquiring and processing large data sets, correcting sample drift, and more precisely measuring sample temperatures.

The outcome of these discussions will be compiled into a workshop report that will be posted at the workshop website, http://www.nist.gov/cnst/in_situ_tem_workshop.cfm, which also includes an archive of the speaker presentations.