Extracting Photons from SINGLE QUANTUM DOTS

Catalyzing Carbon Nanotube Growth with Gold
Carving Diamond into Tougher Micromachines
High Contrast Nanoplasmonic Optical Switch
Better Nanoparticles for Diagnosing Disease
Flower-Shaped Graphene Defects
Summer Students Gain Research Experience
From the Director

As you may be aware, the CNST user facility advances the development of nanotechnology in two distinct ways. While the NanoFab provides economical access to state-of-the-art commercial nanotechnology tools, our collaborative research staff are dedicated to advancing the state of the art in nanoscale measurement and fabrication. This month, I would like to highlight the wide impact of one of our collaborative research projects.

There is a world-wide search underway for devices to replace the CMOS switch that is the foundation of current nanoelectronics. Graphene electronic devices are widely considered to be among the front runners, but progress requires new ways to make and measure circuit elements based on graphene sheets that are only one atom-thick.

Following the development at Georgia Tech of methods to grow high-quality graphene on silicon carbide, Professors de Heer and First sought new ways to characterize the electronic structure of the graphene layers produced and, in particular, correlate it with atomic scale defects. They asked for the help of CNST’s Joseph Stroscio, who has built two of the world’s most advanced ultra-high vacuum scanning tunneling microscope (STM) systems. A collaboration began with a Georgia Tech graduate student bringing the graphene samples and growth technology to the CNST, and continued through multiple graduate students and postdocs who performed a highly productive series of collaborative measurements on our STM instruments.

The results of this five-year collaboration to advance graphene fabrication and measurement technologies have been manifold: three Georgia Tech students performed their doctoral research at the CNST; four postdoctoral researchers were trained; 14 papers were published, including influential publications in Science, Nature, and Nature Physics; new commercial instruments were spun off; and, most recently, a postdoc left the CNST for Intel. (You can see a highlight from his work on page 5 of this issue.)

This example is but one of dozens of collaborative projects underway with CNST researchers. These projects start when someone has a problem not addressed by current nanoscale measurement and fabrication technology. The first step in solving such a problem is to contact the most relevant CNST Project Leader (found via our website) to discuss what might be possible. If it is not clear where your solution may lie, contact me and together we will work to find the answer.

—Robert Celotta

Nanoscale Charge Transport in Bulk Heterojunction Solar Cells

Researchers in the CNST have used photoconductive atomic force microscopy (PCAFM) to characterize the nanoscale structure of organic photovoltaic (OPV) materials and have performed a careful assessment of the strengths and weaknesses of this technique. By varying the device geometry and the AFM tip material, the researchers clarified how local nanoscale experimental and material factors affect the overall OPV efficiency. OPVs consist of two types of organic molecules, electron donors and electron acceptors. When illuminated by sunlight, the photoexcited electron-hole pairs separate at the interface between the donors and acceptors. The separated charges migrate to different contacts, generating an electrical current. The most efficient OPV materials have a homogeneous mixture of donor and acceptor molecules throughout the entire structure, with charge separation occurring throughout the entire volume. Unfortunately, the photoexcited charge must pass through a highly disordered environment, which inhibits their mobility, increases recombination, decreases efficiency, and hampers the material’s ability to produce electricity. The efficiency is strongly dependent on the material morphology, making measurements that correlate nanoscale structure with performance crucial to understanding and improving OPVs. Because PCAFM is now widely used to characterize OPV materials, the CNST researchers expect their assessment of this measurement technique to be important to other researchers in the field, who must consider the technique’s strengths and pitfalls.

Nanoplasmonnic Optical Switch Has High Contrast and Low Voltage

In a recent article in Nano Letters, CNST researchers describe a new high-contrast, low operating-voltage, electrochemical optical switch that uses a volume of active dye orders of magnitude smaller than that of conventional electrochromic devices. Electrochromism refers to a reversible change in the optical absorption of a material under an applied voltage. Inorganic and organic electrochromic materials are used in displays, smart windows, and car rearview mirrors. A change in light absorption in such a material is caused by a change in the oxidation state, and requires that both ions and electrons diffuse through the material. Decreasing the material’s thickness reduces the diffusion time, making the electrochromic switch faster, but unfortunately also reduces the contrast. The NIST and University of Maryland researchers have grown crystals of the electrochromic dye Prussian Blue inside a gold nanoslit waveguide, where light propagates as a surface plasmon polariton (SPP). SPPs are collective charge oscillations coupled to an external electromagnetic field that propagate along an interface between a metal and a dielectric. The dye nanocrystals, deposited on the sidewalls of the slit by cyclic voltammetry, can be electrochemically switched to provide a transmission change of ≈ 96 % (in the red) using control voltages less than one volt. The high switching contrast is enabled by the strong spatial overlap between the SPPs and the nanocrystals confined within the slit. The contrast is also enhanced by the unexpectedly high absorption coefficient of Prussian Blue nanocrystals grown on a gold surface compared with bulk material. Even with a relatively low fill fraction of active material in the slit (≈ 25 %), the switch operates efficiently. Because the light propagates in a direction perpendicular to the direction of the charge transport, the new switch design offers significant promise for creating electrochromic devices with record-setting switching speeds.


Catalyzing Carbon Nanotube Growth? Try Some Gold

Researchers from the CNST and Arizona State University have demonstrated that the overall catalytic activity of nickel particles for the formation of carbon nanostructures is improved by the addition of a small amount of gold (below 0.2 mol fraction). In a recent Nano Letters article, the researchers evaluate Au/SiO₂, Ni/SiO₂, and Au-Ni/ SiO₂ nanoparticles as catalysts for carbon nanotube (CNT) and carbon nanofiber (CNF) formation by measuring the number of particles active during tube formation using in situ dynamic imaging in an environmental scanning transmission electron microscope (STEM). Carbon nanostructures are generally synthesized by catalytic chemical vapor deposition from carbon sources such as acetylene (C₂H₂) and nucleate from catalyst particles, including Ni. However, only some catalyst particles are active in the formation of nanostructures. This limitation affects the ultimate density and placement of the nanostructures, an important factor for nanofabrication applications.

Using high-resolution images and spectroscopy data collected during and after the synthesis, the researchers showed that most of the Au segregates to form an inactive Au-rich cap, with only a small amount of Au present in the active region of the particles. They also showed that the structure of Ni catalyst particles transforms from fcc metal to orthorhombic nickel carbide (Ni₃C). They believe that carbides form due to the dynamic equilibrium conditions present under these reaction conditions. Density functional theory calculations support the hypothesis that low levels of Au doping (0.06 mol fraction) increases the number of particles active for carbon nanostructure formation by lowering the energy barrier for the diffusion of carbon in doped Ni to 0.07 eV compared to 1.62 eV for pure Ni. The researchers are extending this technique to evaluate the role of metal carbide formation in the activity of other metal catalysts used for carbon nanotube synthesis, such as Fe and Co.

Carving Diamond for Tougher Micromachines

A new method developed by NIST semiconductor researchers for carving diamonds offers a precise way to engineer microscopic cuts in the crystal surfaces, yielding potential benefits in both the measurement and micromachine technologies fields. The team has developed a way to make precisely shaped holes in one of nature’s hardest substances, pointing the way to rapid improvement in nanometrology, and potentially leading to long-lasting micromachines.

Micro-electromechanical systems, or MEMS, are devices with moving parts that are just a few micrometers in size, but constructed with substantially the same, well established techniques as electronic chips. MEMS can detect environmental changes, including heat, pressure and acceleration, enabling them to be used as tiny sensors and actuators for a host of new devices. One way to make the moving parts last longer without breaking down is to make them from a tougher material than silicon.

“Diamond may be ideal for MEMS devices,” says NIST’s Craig McGray. “It can withstand extreme conditions, plus it’s able to vibrate at the very high frequencies that new consumer electronics demand. It’s very hard, of course, but, until now, there hasn’t been a way to engineer it very precisely at small scales. We think our method can accomplish that.”

Using a chemical etching process to create cavities in the diamond surface, the team created cavities ranging in width from 1 µm to 72 µm, each with smooth vertical sidewalls and a flat bottom. The speed of the etching process depends on the orientation of the slice, occurring at a far slower rate in the direction of the diamond crystal’s cubic “faces”. These face planes can be used as a boundary where etching can be made to stop when desired.

“We’d like to figure out how to optimize control of this process,” McGray says, “but some of the ways diamond behaved under the conditions we used were unexpected. We plan to explore some of these mysteries while we develop a prototype diamond MEMS device.”


Phase Segregation Should not Impede the Development of High Efficiency Organic Photovoltaics

Recent theoretical work conducted at the CNST explains the surprisingly small effect of macroscale phase segregation on the overall efficiency of blended organic photovoltaic (OPV) materials by showing that electrons can effectively burrow through a skin layer to get to the device’s cathode. In an OPV, light photoexcites a bound electron-hole pair. The carriers separate and migrate to different contacts, generating an electrical current. The choice of electrode material is crucial to the operation of the OPV. The cathode must preferentially collect electrons and the anode must preferentially collect holes. Recent studies of OPV materials conducted at the CNST and elsewhere revealed a donor-rich hole transporting skin layer near the cathode. This phase segregation, or high hole concentration, is due to the smaller surface energy of the donor-cathode interface relative to the acceptor-cathode interface. The fact that the electron collector has mostly holes in its vicinity would seem to be an impediment to charge collection and overall efficiency. However, the ratio of collected to excited charge is still high. By extending previously developed models to account for macroscopic phase segregation, it was theoretically determined that charges can rather easily “squeeze” through regions of reduced density. This effect explains the relatively benign influence of the skin layer on overall device performance. The work demonstrates that cathode skin layer phase segregation should not be an impediment to the development of high efficiency OPVs.

BioAssay Works Develops a More Visible Nanoparticle for Immunoassays

Researchers from BioAssay Works, based in Ijamsville, MD, have developed a new type of nanoparticle that could enable a 10-fold improvement in the detection sensitivity of lateral-flow immunoassays simply by increasing particle visibility.

In a typical gold particle-based lateral-flow immunoassay, particles functionalized with antibodies flow along a membrane in a fluid sample. If the fluid contains a target molecule of interest, such as a toxin or enzyme, then that target molecule will adhere to the antibody-coated particle. A line on the membrane is functionalized with a similar antibody, which can also adhere to the molecule of interest, binding the nanoparticle to the surface. This sandwiches the target molecule between the surface and the particle, and converts the problem of detecting a molecule into the easier problem of detecting a gold particle. As more nanoparticles accumulate, the line darkens until it can be detected.

In real-world applications, the sensitivity of the assay is limited by the visibility of the particles. Nanoscale gold is red and is difficult to see, even when it aggregates. BioAssay Works has formulated a nanoparticle using a different set of chemistries that traps light more effectively. With the help of the NanoFab’s Titan Transmission Electron Microscope (TEM), they identified the properties that increase particle visibility. The TEM allowed them to visualize down to 5 nm to 10 nm the chemical modifications that they made to the nanoparticles. This length scale turned out to be important as they tested different chemical processes, and they found that very small changes in chemistry dramatically influenced the size and shape of the particles. Lowering the sample temperature to 70 K immobilized the particles, allowing the researchers to overlay data from different tests performed on individual particles.

According to Les Kirkegaard, co-founder and head of research and development at BioAssay Works, “As a small technology company, we could not develop cutting-edge nanoparticles without the use of shared research tools. The TEM has allowed us to do a lot of things we could not do otherwise.” He was able to guide Senior Process Engineer Alline Myers as she took measurements while he looked over her shoulder, paying only an hourly rate for her time and the use of the TEM. According to Kirkegaard, “The reliability of the results we gained at NIST were important for us, because we expect our assays will eventually be used in medical applications.”

Flower-Shaped Defects in Graphene Affect a Bouquet of Properties

The pioneering graphene research team from the CNST, the Georgia Institute of Technology, and the NIST Material Measurement Laboratory (MML) have discovered a new family of grain-boundary defects in graphene. In a recent paper, the researchers describe the flower-shaped defects, only one of which has been previously observed, which can occur naturally when graphene is processed at high temperatures. The team’s modeling of graphene’s atomic structure suggests that each of these configurations should possess its own unique mechanical and electrical properties. While graphene is typically a featureless plane of carbon atoms arranged in a honeycomb lattice, according to the CNST’s Joseph Stroscio, the defects can develop due to the movement of the carbon atoms at high temperatures when producing graphene by heating silicon carbide under ultrahigh vacuum. They modify graphene’s six-member ring structure, creating pairs of five and seven member rings which conserve the number of atoms and satisfy all bonds. According to calculations by MML’s Eric Cockayne, the most energetically favorable flower pattern defect is one in which the five and seven member rings are closed-packed in a circular arrangement, forming the smallest member of the flower family. These rings are linked together to form closed loops defining an unusual rotational grain boundary in graphene’s honey comb lattice. Following up with scanning tunneling microscopy and spectroscopy measurements, the team observed this defect in graphene samples, corroborating the theoretical prediction that it should be prevalent due to its low energy. The exceedingly rigid six-member ring lattice is stronger than steel, but the defects might allow it a little flexibility, making it even more resilient to tearing or fracturing. With additional experimentation, it may be possible to correlate the appearance of defects with variations in growth conditions, in order to either avoid them entirely or produce them at will. According to Les Kirkegaard, “The reliability of the results we gained at NIST were important for us, because we expect our assays will eventually be used in medical applications.”

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Nanophotonic System Efficiently Extracts Photons from Quantum Dots

An international team of researchers led by the CNST has developed a new type of nanophotonic cavity that improves the efficiency of photon collection from individual quantum dots while enhancing the photon emission rate. Single semiconductor quantum dots grown epitaxially on a substrate could be bright and stable sources of “on demand” single photons for many applications in spectroscopy and classical and quantum information processing. However, the application of such quantum dots has been limited by the relatively small fraction of the emitted light (< 1%) that can be collected by nearby lenses because of optical effects, including total internal reflection of the light at the semiconductor-air interface. Different types of nanophotonic structures have been fabricated to enhance the emission and collection of the light, but each typically introduces other limitations, including operation over a very narrow spectral band. The team of researchers from NIST, the University of Maryland, the University of Regensburg, and the University of Rochester has developed a nanophotonic structure that increases the emission and collection of quantum dot photons while maintaining relatively broadband operation. The new device consists of a suspended 200 nm-thick GaAs membrane that contains embedded quantum dots and into which a circular dielectric grating is partially etched. The asymmetric nature of the grating leads to preferential emission of quantum dot photons out of the surface, resulting in a practical collection efficiency of ≈ 10% with simple optics — a 20-fold improvement over collection from unpatterned GaAs. In addition, the device enhances the emission rate by a factor of four and operates with ≈ 5 nm bandwidth. Simulations show that optimizing the fabrication and optics could allow > 80% collection, giving this approach great potential for creating bright, single-photon sources.


Kartik Srinivasan Receives NIST Sigma Xi Young Scientist Award

CNST researcher Kartik Srinivasan was honored with the NIST Sigma Xi Young Scientist Award for 2011. He shared this prestigious prize with Sheng Lin-Gibson of the Material Measurement Laboratory. Dr. Srinivasan was cited for his development of “innovative measurement and fabrication methods that have elucidated light-matter interactions in nanophotonic systems and enabled detailed investigation of single quantum systems, with applications in sensing and classical and quantum computations.” In presenting the award, Dr. Marilyn Jacox of the Physical Measurement Laboratory noted that Dr. Srinivasan’s work “encompassed both experiment and theory” and that, while nanoscience investigates very small aggregates of atoms and molecules, his measurements “are even more challenging because they also involve observations of these entities at very short times.” She predicted that the optomechanical system that he has recently worked on will enable development of ultra-high sensitivity, high-speed atomic force microscopy methods. The award, which acknowledges outstanding scientific achievements within 10 years of obtaining an advanced degree, was presented by the NIST Chapter of Sigma Xi at their annual banquet on June 10, 2011.

Dr. Srinivasan joined NIST in 2007, and is a Project Leader in the Nanofabrication Research Group in the CNST where he is leading projects in the field of nanophotonic measurements. He received B.S., M.S., and Ph.D. degrees in Applied Physics from the California Institute of Technology, where his graduate research was supported by a Fannie and John Hertz Foundation Fellowship. Prior to graduate school, he worked for one year at XPonent Photonics, a startup company based in Monrovia, CA. After completing his Ph.D., he continued at Caltech as a Postdoctoral Fellow at the Center for the Physics of Information. He has published over 40 peer-reviewed papers in journals such as Applied Physics Letters, Physical Review, Nature, and Science, on topics including microcavity lasers, chip-based cavity quantum electrodynamics, near-field optical probing, and the electromagnetic design and nanofabrication of photonic crystal devices.
New Tools in the NanoFab

mapping, a motorized stage, auto-location, and long scans. It will handle wafers up to 200 mm in diameter. The new tool should be available for use at the end of December. For more information, contact Gerard Henein, 301-975-5645.

Chemical Mechanical Polishing/Planarization (CMP) System – The CNST’s new CETR model CP-4 CMP system will be available for use during first quarter FY2012. The CMP removes irregular topography from samples ranging from small pieces up to 100 mm diameter wafers. It is typically used to polish copper, aluminum, tungsten, and SiO₂, and to remove excess conductors while stopping reliably at the top of an insulating layer. The CMP is located in room 215/C02-2, opposite the elevator in the basement of building 215. Users will be able to reserve time through the CORAL system. For more information, contact Gerard Henein, 301-975-5645.

Profilometer – The NanoFab has finalized the purchase of a new Bruker Dektak XT profilometer to replace the existing Dektak 6M. In addition to providing step height, surface roughness, and waviness measurements, the new profilometer will add such capabilities as 3D-
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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Announcing the Next
NanoFab Users Meeting
Friday, December 2, 2011, 2 pm to 4 pm
Building 215/C103

Current and potential NanoFab researchers and others interested in NanoFab operations are invited to the quarterly NanoFab Users meeting. Topics typically include safety, policy changes, new equipment purchases or upgrades, research highlights, and new standard processes. Every meeting also includes an open discussion to allow users to bring ideas and suggestions to our attention. Anyone wishing to have a specific item added to the agenda should contact Vincent Luciani at 301-975-2886, vincent.luciani@nist.gov.

Visit the CNST Booth at
the Maryland Entrepreneur Expo
Linthicum Heights, MD
Monday, November 14, 2011

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